U.S. Army Environmental Center

# FINAL REPORT ON THE DEMONSTRATION RESULTS FOR THE PHYTOEXTRACTION OF LEAD-CONTAMINATED SOIL AT THE TWIN CITIES ARMY AMMUNITION PLANT, ARDEN HILLS, MINNESOTA

*Prepared for*

**U.S. ARMY ENVIRONMENTAL CENTER**

*Aberdeen Proving Ground, Maryland*

*Funded Through*

*Prepared by*

**Tennessee Valley Authority**

*Muscle Shoals, Alabama*

**JULY 2000**

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*Prepared for*

**U.S. Army Environmental Center**
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**This report describes the results of a two-year field demonstration conducted to determine if phytoextraction is a viable and feasible technology for remediation of metals (specifically lead) in soil. The project goal was to demonstrate the effectiveness of phytoextraction techniques for removing ionic lead from contaminated soils. The report also provides implementation guidance describing additional improvements needed prior to implementing this technology based on the field results. During the demonstration, soil acidifiers and a chelating agent were used to increase the water solubility of lead and the availability of lead to plants. The demonstration was conducted at the Twin Cities Army Ammunition Plant in Arden Hills, Minnesota. The report indicates that, overall, phytoextraction methods did not perform to expectations. An economic analysis indicates that the *in situ* phytoextraction as a sole use technology would not be economically viable at a highly contaminated site, even if performed under optimum conditions. Conditions that would improve performance would be uniform, agronomically viable soils that are not conducive to movement of lead out of the rooting zone, and in which soil lead is present in ionic forms.**

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# Executive Summary

This project was executed under a partnering agreement between the:

- U.S. Army Environmental Center (USAEC)
- Tennessee Valley Authority (TVA)
- Twin Cities Army Ammunition Plant (TCAAP) and their operating contractor, Alliant Techsystems Inc.(ATK)

The Environmental Security Technology Certification Program (ESTCP) funded this project as part of the Department of Defense (DoD) program to conduct field demonstrations of remediation technologies for removing heavy metals from contaminated soils. The project was funded from January 1998 through May 2000 as reported herein. The emphasis was on lead, due to its inherent toxicity and the quantity discharged. Lead may be present in soil either in particulate (e.g., bullet fragments) or ionic (i.e., compound lead) forms. The remediation technology tested in this project to remove lead from contaminated soil was phytoextraction.

Phytoextraction is an *in situ* remediation method in which plants are used to remove ionic (non-particulate) lead or other ionic metals from contaminated soils. Particulate metals (i.e., bullets) cannot be remediated by this process. Ordinarily, lead is very insoluble in soil, and thus plants cannot remove it from the soil through their roots and shoots (i.e., plant uptake). However, in the phytoextraction process, a chelate (in this case, potassium EDTA) and a soil acidifier (acetic acid) were used to convert soil lead into a water-soluble form that plants can take up and remove from the soil. Lead is translocated from the roots into the plant tops, and the tops are harvested and smelted or otherwise disposed of, thereby removing lead from the soil.

The objective of this project was to determine if phytoextraction could be practically and economically utilized *in situ* to remove lead contamination from soils under the heterogeneous soil and diverse waste conditions found at military sites, such as ammunition plant disposal sites, open burn/open detonation sites, and other areas contaminated with ionic lead. The field design consisted of a 6x6 grid pattern (thirty-six 15-foot-square grids). The field demonstration was conducted for two years (1998, 1999) at TCAAP on a small portion (0.2 acre) of Site C (total area - 16.4 acres) and on a 0.2-acre portion of Site 129-3 (total area - 1.5 acres). The whole of both Site C and Site 129-3 were designated CERCLA sites which were scheduled for remediation at the end of the two-year demonstration, including the demonstration plots. For convenience, the small demonstration plots will hereafter be referred to as Site C and Site 129-3.

Preliminary soil sampling to map lead contamination within the demonstration plots was done in November 1997. Crops were grown in 1998 and 1999 to test the technology. No crops were grown in 2000, but groundwater, surface water, and deep core soil sampling was conducted in April 2000 (mainly at Site C) to determine environmental effects of the technology. Lead and EDTA was observed in groundwater, and additional groundwater and surface water sampling was

conducted in April and May 2000. No further phytoremediation was done. Extensive plant and soil sampling was conducted throughout the demonstration to measure the effectiveness of the technology in removing lead from the soil.

In 1998, the demonstration areas were planted with grain corn followed by white mustard. The lead uptake for the corn crop was 0.65% (6,500 mg/kg) lead in the biomass which was promising. These results met expected levels based on results of previous greenhouse studies and information in the literature. However, the relatively poor agronomic properties of the sites and the presence of toxic contaminants other than lead in the soil, particularly at Site C, made growing the crop difficult. Therefore, biomass yields were less than anticipated. The level of lead uptake in the white mustard was less than anticipated due to adverse weather and a slow application rate of EDTA which damaged the plants before sufficient lead uptake occurred.

Based on lessons learned in the 1998 demonstration, several modifications and refinements were made to improve the demonstration approach in 1999. The grain corn variety was replaced with a deeper rooting silage corn variety in an attempt to improve yields and also to improve root scavenging of soil lead. The hose applicator system that was used to apply soil amendments to corn was changed to a drip delivery system for mustard in 1998. However, the delivery rate proved to be too slow, and the system was replaced in 1999 with one having triple the number of delivery tubes. The amount of EDTA that was applied to soil in 1999 was calculated based on the frequency of occurrence of a given lead concentration across the plot rather than on the average total soil lead concentration as in 1998. This reduced the amount of EDTA applied by one-third.

Planting of the 1999 silage corn was delayed by excessive rainfall early in the season. Heavy rainfall and cool temperatures shortly after planting caused poor stand establishment, and extensive bird damage required several replantings, resulting in a stand of various growth stages. Due to insufficient growth of the corn that resulted in bare areas in the plots, only selected areas were designated to receive soil amendments of acetic acid and EDTA. Only these areas were used for pre- and post-amendment plant and soil sampling, which reduced the amount of data collected.

The lead concentration in the 1999 corn plants at Site C after amendment additions averaged tenfold less than obtained in corn treated in 1998. Excess rain and toxic contaminants in the soil that limited root growth to the top 6- to 8-inch soil layer, and the varied growth stages drastically reduced yields and uptake of lead. Only two grids were sampled at Site 129-3, and evaluation of treatment effectiveness was not possible because of insufficient data.

Since weather and other factors severely limited the amount of data that was collected in 1998 and 1999, a third-year demonstration was planned for 2000 which would incorporate lessons learned from 1998 and 1999. Before beginning the year 2000 demonstration, however, groundwater samples were taken at Site C in the spring to assess movement of lead and EDTA in the soil. Both lead and EDTA were found in shallow groundwater in the immediate vicinity of the plot, although neither had moved very far from the demonstration plot. However, there is no historical groundwater data at this particular area of Site C. Historical data exists for the northern areas of Site C, i.e., Area C-1, but not the southern area where the demonstration plot is located.

At that time, all demonstration activities were halted, and additional groundwater and surface water samples were collected to determine the extent of lead and EDTA movement. Analysis showed that the major part of EDTA and lead was localized beneath and in the close vicinity of the demonstration plot, and that movement away from the plot was occurring very slowly in keeping with the slow rate of groundwater flow.

Lead was not moving in the groundwater in soluble form to any great extent in association with EDTA. Instead, lead was being displaced from the EDTA complex by innocuous cations (e.g., calcium, iron, and magnesium) and re-precipitated in the soil as insoluble lead. EDTA combines with lead on a one-to-one molar basis. If the EDTA:lead ratio is greater than 1:1, this means that lead had been displaced from the EDTA by another cation. A high EDTA:lead ratio observed for groundwater samples and the relatively high concentrations of Ca, Mg, and Fe in the water indicated that much of the lead had been displaced from the EDTA complex.

The decreasing EDTA concentrations with distance from the plot indicated that: (1) EDTA was being adsorbed in the soil and (2) degradation of EDTA was likely occurring, with subsequent displacement of lead from the complex into insoluble forms. The results for lead were below detection limits in surface water samples taken from a drainage ditch located near the plot.

Lead and EDTA in the groundwater likely was due in large part to the presence of a fluctuating shallow groundwater table underneath the demonstration plot. The fluctuating groundwater may have moved up into the EDTA-treated rooting zone and periodically “washed” the soil of adsorbed EDTA/lead. Iron oxide deposition was common in 4-ft deep soil samples as were manganese sulfide concretions (usually a representation of alternating aerobic and anaerobic zones in the soil profile, likely caused by a fluctuating water table).

The large amount of debris and extreme variation in soil type and texture within the plot exacerbated the movement of the EDTA-lead complex. The soils at site C were found to be much more heterogeneous than was originally anticipated. Seven soil types, ranging from sand to clay, were identified in deep soil cores which is contrary to the single soil type identified in the RI/FS. Clay and sand lenses were common throughout the soil, and a considerable amount of burned and unburned wood was found. Debris consisting of glass, metal, wire, concrete, bullets, and brass shell casings was found throughout the plot.

Since Site C is located in the middle of a CERCLA area already scheduled for remediation, the environmental impact of solubilized lead and EDTA in the slow-moving groundwater stream should be minimal. Given the alkaline pH of the system and the mineralogy of the soil and aquifer, the indications are that lead already in the groundwater will continue to be displaced from the EDTA complex and become insoluble, and that the scheduled excavation of the soil from the plot will remove the source of additional lead and EDTA.

From an environmental perspective, EDTA is a non-regulated chemical; many thousand tons are released into the environment annually. For example, annual amounts of EDTA released into the Ruhr River, Germany, in 1984 were about 60 tons, and over 1,080 tons were released annually into the Rhine River, Germany, from 1985 to 1987. In this demonstration, EDTA was used to

complex lead into a water-soluble form which was taken up into plants. The EDTA-lead complex not taken up by the plants was transformed by chemical and microbial processes. In soil, the processes of competition, exchange, adsorption, and precipitation attenuated lead complexed in soluble form with EDTA. Degradation of EDTA and dissolution of the EDTA-lead complex with re-sorption of lead in the soil further diminishes any environmental risks. The 2000 sampling results showed that the EDTA previously applied to soil did not degrade as rapidly as expected, possibly due to the anaerobic environment in the groundwater and other toxic contaminants in the soil which were not favorable to a population of EDTA-degrading microorganisms. The data indicated that degradation was occurring, although at a slower rate than normally seen in soils.

Throughout the demonstration, the considerable spatial variability in soil lead concentrations across the plot due to the large amount of particulate lead deposited in the site made analysis and interpretation of the data very difficult. The variability made the application of modern statistical techniques (i.e., parametrics, geostatistics, kriging) to the results ineffective in measuring a change in soil lead concentrations. The only indicator of lead removal that could be utilized with confidence was the amount of lead in the harvested crops.

In addition, the considerable debris (e.g., rail ties, metal scrap, concrete, burned materials) buried at Site C made soil tilling, sampling, and characterization difficult and contributed to vertical movement of lead and EDTA. The natural soil structure was destroyed, which prevented a uniform hydraulic conductivity and resulted in erratic water movement in the soil. The extreme conditions were not apparent when the demonstration began. Deep core soil sampling in 2000 revealed that seven different soil types, ranging from coarse sand to clay, were present within the plot area, likely because soils from other areas of TCAAP were introduced at Site C when waste and scrap were deposited in the area. Soil tends to be variable even under normal circumstances, and these extremes in physical characteristics allowed vertical movement of solubilized lead and EDTA. Such vertical movement was mostly likely due to preferential flow and channeling in the soil/debris mix rather than to actual leaching through the soil.

In order to estimate the costs for *in situ* phytoextraction, it was assumed that a phytoextraction project would be conducted in an environment suitable for good growth of agricultural crops and with moderate levels of lead contamination. Under these circumstances it was assumed that:

- The growing season would allow growth of 2 crops per year.
- Two crops of silage corn could be grown per year.
- Soil conditions would be optimal for plant growth.
- The total lead content of the soil was 1,000 - 2,000 ppm.
- Potentially plant-available lead concentration would be 55% of the total concentration.
- Modern production agriculture practices and equipment would be used on-site.
- Site preparation was complete and soil was ready for treatment.

The cost for phytoextraction of one acre to a depth of one foot is estimated to be $42,145 per crop, assuming:

- The starting lead concentration is 1500 mg/kg.
- The clean-up goal is 1000 mg/kg.
- Plant-available lead is 55% of the total lead.
- The biomass production is 8 tons per acre.
- The concentration of lead in the biomass is 0.5%.
- Two crops per year are grown at the site.

The cost is equivalent to $26.13 per cubic yard per crop. This remediation would require 27 crops over a period of 14 years, for a total cost of $706 per cubic yard.

All other assumptions remaining constant, if the initial soil lead concentration were 1200 mg/kg, the remediation would require 11 crops over a six year period, at an approximate cost of $287 per cubic yard. Based on these costs, *in situ* phytoextraction as a sole technology would be economical only when the initial lead concentration is close to the clean-up goal. Reagent costs (EDTA, acetic acid, other soil amendments) account for a significant portion of total costs. Costs for site preparation, i.e., clearing and removal of trees, removal of buildings and debris, etc., would be site-specific and would be in addition to the above cost.

Formulas for calculating the time required for phytoremediation of lead-contaminated soil for any project were developed. These calculations provide a direct measure of total soil lead reduction over time. Variables (i.e., lead concentration in soil, number of crops, lead concentration in crop, etc.) may be changed to fit a specific site. For a soil with even a moderate concentration (e.g., 2,000 ppm) of lead, the time required for remediation by phytoextraction is unrealistically long and far greater than anticipated when phytoextraction began to be seriously considered and tested as an *in situ* soil remediation method.

The overall results of the phytoremediation technology during the demonstration were less than hoped for with respect to crop growth, plant lead uptake, and removal of lead from the soil. In order for this technology to be effective, greater uptake of lead by plants from the soil will have to be realized. This cannot be achieved in the site conditions that exist at TCAAP, particularly at Site C. The poor chemical and physical condition of the soil and the extreme heterogeneity of both the concentration and the form of lead in the soil made growing conditions very poor which resulted in low yields for the site and low plant uptake of lead.

Based on the findings from this project, phytoextraction does not appear suitable as a technology for *in situ* application under the highly heterogeneous, highly contaminated conditions typically found at open burn/open detonation disposal areas. Considering the fact that, on average, only about half of the lead in the soil can be extracted using this technology, phytoextraction does not appear viable as a *sole use* technology for areas where open burn and open detonation have been used, due to the resultant contamination with a variety of solid debris, other toxic contaminants, and particulate lead. However, combining this technology with appropriate screening and separation processes to remove extraneous materials and particulate contaminants, and with confinement and collection measures to allay environmental impacts, could produce a useful remediation package.

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# ABBREVIATIONS

| | |
|---|---|
| 2,4-D | -2,4-Dichlorophenoxy Acetic Acid |
| AA | -Atomic Absorption |
| AAP | -Army Ammunition Plant |
| ACM | -Asbestos Containing Material |
| AEC | -U.S. Army Environmental Center (officially USAEC) |
| AET | -American Engineering and Testing, Inc. |
| AERTA | -Army Environmental Requirements and Technology Assessments |
| ANOVA | -Analysis of Variance |
| Al | -Aluminum |
| ARARs | -Applicable or Relevant and Appropriate Requirements |
| As | -Arsenic |
| ATK | -Alliant Techsystems Inc. |
| Be | -Beryllium |
| Ca | -Calcium |
| Cd | -Cadmium |
| CEC | -Cation Exchange Capacity |
| CERCLA | -Comprehensive Environmental Response, Compensation, and Liability Act |
| CFR | -Code of Federal Regulations |
| cm | -Centimeter |
| $CO_2$ | -Carbon Dioxide |
| COC | -Contaminants of Concern |
| CRZ | -Contamination Reduction Zone |
| CSP | -Concentrated Super Phosphate |
| Cu | -Copper |
| DERA | -Department of Defense Environmental Restoration Accounts |
| DERP | -Department of Defense Environmental Restoration Program |
| dL | -Deciliter |
| DoD | -Department of Defense |
| DOE | -Department of Energy |
| DSERTS | -Defense Site Environmental Restoration Tracking System |
| DTPA | -Diethylene-trinitrilo-pentaacetic Acid |
| EA | -Environmental Assessment |
| ED3A | -Ethylenediaminetriacetic Acid |
| EDDA | -Ethylenediaminediacetic Acid |
| EDMA | -Ethylenediaminemonoacetic Acid |
| EDTA | -Ethylenedinitrilo-tetraacetic Acid |
| ESTCP | -Environmental Security Technology Certification Program |
| EQ | -Environmental Quality |
| EZ | -Exclusion Zone |
| Fe | -Iron |
| FIA | -Flow Injection Analyzer |
| ft | -Foot |
| GC | -Gas Chromatography |

## ABBREVIATIONS (Continued)

| | |
|---|---|
| HAP | -Hazardous Air Pollutant |
| HASP | -Health and Safety Plan |
| HAZWOPER | -Hazardous Waste Operations and Emergency Response |
| HCl | -Hydrochloric Acid |
| HDPE | -High Density Polyethylene |
| HEPA | -High Efficiency Particulate |
| HPLC | -High Performance Liquid Chromatography |
| ICP | -Inductively Coupled Plasma |
| IDA | -Imidodiacetic Acid |
| IEUBK | -Integrated Exposure Uptake Biokinetic |
| IRP | -Installation Restoration Program |
| K | -Potassium |
| kg | -Kilogram |
| L | -Liter |
| lb | -Pound |
| $m^3$ | -Cubic Meter |
| MCES | -Metropolitan Council Environmental Services |
| MDH | -Minnesota Department of Health |
| MDL | -Method Detection Limit |
| Mg | -Magnesium |
| mg | -Milligram |
| mg/kg | -Milligram per Kilogram |
| mg/L | -Milligram per Liter |
| mL | -Milliliter |
| Mn | -Manganese |
| MPCA | -Minnesota Pollution Control Agency |
| N | -Nitrogen |
| NAAQS | -National Ambient Air Quality Standards |
| NEPA | -National Environmental Policy Act |
| NIOSH | -National Institute for Occupational Safety and Health |
| NTA | -Nitrilotriacetic Acid |
| O.M. | -Organic Matter |
| OSHA | -Occupational Safety and Health Administration |
| OSC | -Operations Support Command |
| P | -Phosphorus |
| Pb | -Lead |
| $Pb^{2+}$ | -Ionic Lead |
| PCB | -Polychlorinated Biphenyl |
| $PO_4$ | -Orthophosphate |
| $PO_4$-P | -Orthophosphate-Phosphorus |
| PPE | -Personal Protective Equipment |
| ppm | -Parts Per Million |

## ABBREVIATIONS (Continued)

| | |
|---|---|
| PTO | -Power Takeoff |
| PVC | -Polyvinyl Chloride |
| QA | -Quality Assurance |
| QAPP | -Quality Assurance Project Plan |
| QC | -Quality Control |
| R&D | -Research and Development |
| RAB | -Restoration Advisory Board |
| RCRA | -Resource Conservation and Recovery Act |
| RfD | -Reference Dose Threshold Value |
| ROD | -Record of Decision |
| SARA | -Superfund Amendments and Reauthorization Act |
| SAS | -Statistical Analysis Systems |
| Sb | -Antimony |
| SDWA | -Safe Drinking Water Act |
| SZ | -Support Zone |
| TCAAP | -Twin Cities Army Ammunition Plant |
| TCE | -Trichloroethylene |
| TCLP | -Toxicity Characteristic Leaching Procedure |
| TKN | -Total Kjeldahl Nitrogen |
| Tl | -Thallium |
| TOC | -Total Organic Carbon |
| TSP | -Triple Super Phosphate |
| TVA | -Tennessee Valley Authority |
| µg | -Microgram |
| $\mu g/m^3$ | -Micrograms per cubic meter |
| µg/dL | -Micrograms per deciliter |
| U.S. | -United States |
| USAEC | -United States Army Environmental Center |
| USC | -United States Code |
| USEPA | -United States Environmental Protection Agency |
| USGS | -United States Geologic Survey |
| VAAP | -Volunteer Army Ammunition Plant |
| VOA | -Volatile Organic Analyte |
| VOC | -Volatile Organic Compounds |
| WZ | -Work Zone |
| Zn | -Zinc |
| ZPC | -Zero Point of Change |

# Section 1.0
# Introduction

## 1.1 Background Information

A number of Department of Defense (DoD) installations have heavy metal-contaminated soils requiring remediation, in part because the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) has identified heavy metals, lead (Pb) in particular, as a priority concern. Particulate-type heavy metals (bullet fragments, etc.) were often deposited as the result of firing range use. In addition, ionic forms of metals were commonly deposited when metal-bearing propellants, ammunitions, and powders were burned at explosive disposal sites or when particulates dissolved. The DoD is currently emphasizing lead removal due to the inherent toxicity of lead and the quantity discharged to the environment. Hence, a need for cost-effective procedures for removing lead from contaminated soils has emerged. This project was funded from January 1998 through May 2000 as discussed in this report.

The phytoremediation technique that was demonstrated, phytoextraction, uses selected plant species in combination with soil amendments to extract lead. The technology can be implemented to extract other heavy metals, but the focus of this project was on lead. The heavy metals are subsequently stored in the plant shoot tissues. After the plants died, due to excessive lead uptake, the shoots were harvested and the plants smelted using a standard smelting technique.

The expected benefit of the technology was to provide an economical, effective *in situ* phytoremediation technique for extracting ionic heavy metals, specifically lead, from contaminated soils. The Environmental Security Technology Certification Program (ESTCP) funded this project as part of a DoD program to evaluate treatment technologies under field conditions and to transfer technical and economic performance information to the DoD user communities. Several procedures for remediating metals-contaminated soil sites are currently available. These include traditional and proven *ex situ* methods, as well as emerging, state-of-the-art *in situ* technologies. Conventional *ex situ* methodologies include:

- Landfilling of contaminated soil
- Soil washing (separation) - excavation of soil followed by soil washing, return of clean soil to the site, and landfilling of soil which is still contaminated
- Incineration - excavation and incineration, with the remaining mineral fraction returned to the original site, or landfilling if decontamination is not complete
- Solidification - excavation and *ex situ* solidification with pozzolanic agents and landfilling of the stabilized material

These methods are effective, however, they usually involve long-term monitoring and permanent and sometimes drastic alterations to the original site.

*In situ* methods include:

- *In situ* soil flushing - in-place washing of soil using acid or chelate solutions followed by pumping of contaminated soil solution to the surface for treatment

- Solidification/stabilization - similar to *ex situ* but involves proprietary reagent delivery and mixing systems and may be less costly for large soil volumes and depths greater than 10 feet

- Containment - placing an impermeable cap on the contaminated site to eliminate water infiltration into the contaminated soil

- Electrokinetics - use of low intensity direct current fields between electrodes in soil to mobilize and capture contaminants at the electrodes for removal

- Phytoremediation - a broad term for the use of plants to remediate contaminated soil and water

The *in situ* technologies, except containment and flushing, provide a clean site and normally avoid future liability and restrictions to site use. Depending on site conditions, phytoremediation may have the potential to be among the lower cost options. Site conditions, including the nature and depth of contamination, presence of debris and other contaminants in the soil, the depth to groundwater, and soil type will influence the applicability and economics of the technology, to where phytoremediation may not be suitable for certain sites.

**1.2 Official DoD Requirement Statement**

The DoD requirement statements that were addressed, as stipulated in the 1994 Tri-Service Environmental Quality Strategic Plan (EQ Strat Plan) Report, are as follows:

1.4.d - Lead Contamination - Army
1.3.e - Soil Inorganic - Army
1.4.c - Heavy Metals - Army
1.2010 - Heavy Metals in Excavated Soil Treatment - Air Force
1.I.4.J - Improved Isolation and Treatment of Heavy Metals in Soil - Navy

The Army has provided updated information in the Army Environmental Requirements and Technology Assessments (AERTA) that addresses the specific problems and needs for the following requirements that are addressed by:

1.3.e. - Innovative and In-Situ and/or Onsite Ex-Situ Treatment Technologies for Soils Contaminated with Inorganics
1.4.c. - Remediation of Heavy Metal Contamination of Facilities
1.4.d. - Lead Contamination

### 1.2.1 How Requirements Were Addressed

The overall plan for addressing environmental problems at military sites is described in the 1994 Tri-Service Environmental Quality Strategic Plan (EQ Strat Plan), also known as the Green Book.[Ref 1] Four pillars are described for managing environmental problems. The cleanup pillar which this project addressed has three objectives:

- Improving technologies for site characterization and monitoring
- Developing less costly remediation technologies
- Generating user-based risk assessment methodologies

This project was aimed at the second objective. The demonstration of phytoremediation offered a cleanup option with the potential to be less costly than existing *ex situ* remediation technologies. Phytoremediation addressed the AERTA needs identified above since the technology is applicable to treatment of lead and heavy metal contamination and could potentially be conducted under *in situ* conditions. The technology would also be applicable for excavated soils at Army, Navy, and Air Force sites.

The DoD requirement statements mentioned in Section 1.2.1 are all addressed in Cleanup Program Thrust 1.N. The problem statement for 1.N is:

**DOD PILLAR 1:** Cleanup

**PROGRAM THRUST 1.N:** Inorganic-Contaminated Soils

**USER PROBLEM:** Currently, few techniques exist for the treatment of inorganic-contaminated soils and sludges. Those which do exist do not remove inorganic or heavy metals from contaminated soils and sludges.

**TECHNOLOGY OBJECTIVE:** To develop cost-effective technologies for the remediation of inorganic- and heavy metal-contaminated soils and sludges.

**TRI-SERVICE REQUIREMENTS**

**REQUIREMENT SUMMARY:** Inorganic and heavy metal treatment technologies are required to reduce the volume of material requiring ultimate disposal and to reduce treatment cost for inorganic- and metal-contaminated soils and sludges.

**PROBLEM SCOPE AND MAGNITUDE:** As of 1999, inorganic and heavy metal contamination was reported at over 940 military sites in soils and sludges. Typical military activities resulting in heavy metal contamination include plating operations, firing ranges, motor pool activities, metal finishing, incineration activities, cooling water treatment, and burning pits. Few technologies currently exist for the *in situ* treatment of metal-contaminated soils. This program was implemented to develop such technologies.

This project was directly aimed at providing a cost-effective method for treating lead contamination in soil. The purpose of the project was to provide a means of removing lead from the soil, not just isolating the contamination. If the technology could be applied under suitable conditions, it should benefit installations and organizations responsible for the design and execution of military restoration activities involving lead contamination in soil.

### 1.3 Objectives of the Demonstration

The primary objective of this environmental technology demonstration was to provide a technically and economically feasible means of reducing lead contamination in soils through the utilization of plant species in conjunction with soil amendments.

The demonstration was conducted in two 0.2-acre (90-ft by 90-ft) plots. The two plots had different concentrations of lead contamination in the soil, representing use of phytoremediation in two different stages of site cleanup. The demonstration took place at the Twin Cities Army Ammunition Plant (TCAAP) in Arden Hills, Minnesota. The project was executed under a cooperative arrangement among the:

- U.S. Army Environmental Center (USAEC)
- Tennessee Valley Authority (TVA)
- TCAAP and its operating contractor Alliant Techsystems Inc. (ATK)

The U.S. Army Operations Support Command (OSC) assisted the USAEC by providing sites containing lead-contaminated soil at TCAAP. TVA provided scientific expertise, research, and technology demonstration. In particular for this project, TVA provided technical expertise in agronomy, soil fertilization, plant physiology, plant botany, heavy metals chemistry in soil and plants, and application of soil amendments. ATK, the operating contractor at TCAAP, conducted day-to-day field demonstration site operations.

The project was executed in seven phases, these being:

- Site Screening, Soil Collection, and Metal Analysis (Phase 1) - During this phase, contaminated soil from three TCAAP sites being considered for use was collected and analyzed for pH and heavy metals. The data collected were used to select two demonstration sites.

- Technology Demonstration Plan Development (Phase 2) - During this phase, the Technology Demonstration Plan was developed, written, reviewed, and approved by the Army, ESTCP, and the Minnesota Pollution Control Agency (MPCA).

- Site Preparation (Phase 3) - During this phase, the selected sites were prepared for use. Tasks conducted during this phase included: delineating site locations, delineating contamination reduction zones, erecting fences, eradicating existing vegetation, installing soil solution monitoring systems, installing irrigation systems, preparing the soil, and pre-operational inspection of these subsystems.

- 1998 Field Demonstration (Phase 4) - This phase consisted of a demonstration of the use of two crops in a growing season: a warm season crop and a cool season crop. An interim results report with preliminary implementation guidance was issued at the end of this phase to document results and provide planning for future implementation.

- 1999 Field Demonstration (Phase 5) - This phase consisted of a second demonstration of the use of a warm season crop.

- 2000 Post-Demonstration Sampling (Phase 6) - The original plans for this phase were to demonstrate phytoextraction only at Site 129-3. After observation of lead and EDTA in groundwater, the activities were modified to consist of soil, surface water, and groundwater sampling and analyses to assess the impact of soil amendments used in phytoremediation on these parameters.

- Final Report Writing (Phase 7) - During this phase, the final results document was written using the preliminary implementation guidance document developed in Phase 4 and the Final Report was reviewed, approved, and published. The final implementation guidance document (Section 8.0) outlines the applicability and restrictions to the use of this technology and the conditions under which it can be applied in the field.

This project began on October 7, 1997, when TVA initiated site selection procedures (Phase 1). During Phase 1, lead-contaminated soil samples were collected from two sites located within TCAAP (November 1997). Soil samples from these sites were taken to TVA's facility in Muscle Shoals, Alabama, for analysis. Upon completion of the analysis, a preliminary assessment was made of the local conditions and an approach was developed upon which the Technology Demonstration Plan could be devised. Development of the Technology Demonstration Plan was initiated on December 15, 1997 (Phase 2).

Upon approval of the Technology Demonstration Plan, two CERCLA sites were prepared for demonstration (Phase 3). These sites were prepared by installing phytoextraction process subsystems including: fences, decontamination areas, soil solution monitoring systems, and plant irrigation systems. Tasks such as clearing the site of vegetation also occurred at this time. Phytoextraction subsystems were installed at two sites at TCAAP. The first site was located within Site C and the second site within Site 129-3. Based on initial soil analysis, the soil at Site C contained lead concentrations in the range of 1,300-8,000 mg/kg (parts per million - ppm). The demonstration conducted within Site C was intended to illustrate the effectiveness of phytoextraction methods on moderately contaminated sites during the early stages of a multi-year remediation program.

In contrast, the demonstration within the second site, Site 129-3, was intended to illustrate the effectiveness of phytoextraction methods near the conclusion of a remediation program, or for situations in which the level of contamination is low and the use of a "polishing treatment" is desirable. Lead concentrations ranged from 23 to 740 ppm at the site. Demonstrating remediation at low-end concentrations was considered to be important because the effectiveness of a phytoextraction technique can vary with soil lead concentration. Consequently, it was

important to identify any problems that may be encountered at low lead concentrations which are not observable at high concentrations.

The demonstrations at Sites C and 129-3 were conducted over a two-year period, with assessment of the impact of the technology on soil and groundwater conditions conducted in the third year. These periods are referred to as the 1998 Demonstration (Phase 4), the 1999 Demonstration (Phase 5), and the 2000 Post-Demonstration Sampling (Phase 6). Two crops were planted in the first year of the demonstration: a warm season crop (field corn) and a cool season crop (white mustard). For the second demonstration year, only one crop, a silage corn variety, was planted. An interim results document, with preliminary implementation guidance, was issued as part of the 1998 Demonstration (Phase 4). Phase 7 consisted of writing the final results document, including the final implementation guidance.

### 1.4 Regulatory Issues

The FY92 Defense Authorization Act required the Director of Defense Research and Engineering to develop a strategic investment plan for Environmental Quality Research and Development. A report called the Tri-Service Environmental Quality R&D Strategic Plan was published in 1993 and revised in 1994. It provided a 5-year plan for environmental activities at U.S. military sites.

The Department of Defense established the Defense Environmental Restoration Program (DERP) in 1984 to promote and coordinate efforts for evaluation and remediation of contamination at DoD facilities. Congress established the Defense Environmental Restoration Account (DERA) in 1986 as Title 10, United States Code (USC) 2701-2707 and 2810, as a part of the Superfund Amendments and Reauthorization Act (SARA). Section 11 of SARA, as amended in November 1993, requires an annual report to Congress on progress made with environmental restoration at military installations. SARA establishes Applicable or Relevant and Appropriate Requirements (ARARs) levels for cleanup for specific chemicals, as discussed below for lead.

Lead contamination is commonly seen at DoD installations. Typical military activities that result in lead contamination include production and handling of ammunition, plating operations, firing ranges, motor pool activities, metal finishing, incineration activities, and burning pits. Lead is frequently identified as a Contaminant of Concern.

Lead has attracted the attention of regulators for many years. Although the health effects of lead have been studied in great detail, there is still a lack of knowledge in determining the levels of lead that correspond to specific health effects or risk levels.

The carcinogenicity of lead salts administered to rats orally or by injection has been demonstrated, and the United States Environmental Protection Agency (USEPA) has classified these compounds in Group B2 (probable human carcinogen). But because occupational exposure to lead has not resulted in corresponding blood lead levels, USEPA has not developed a cancer slope factor and has focused on the non-carcinogenic effects.

The major adverse non-carcinogenic health effects of lead include changes in the hematopoietic (blood-forming organs) and nervous systems. The health effects of lead are most closely related to the total amount of lead contained in the body, with the concentration of lead in whole blood being the most widely used index of total lead exposure. Some health effects of lead have been shown to occur at almost undetectable levels which have prevented the development of a reference dose (RfD) threshold value.

USEPA's alternative approach to the use of cancer slope factors and RfDs to evaluate lead exposure is to consider the effect of exposure on the total body burden, i.e., blood lead levels. USEPA currently has determined that 10 μg/dL should be the level of concern based on the most sensitive effects on the most sensitive population, that being neurological effects on small children. This blood lead level is the basis for determining cleanup levels in drinking water and soil at CERCLA sites.

For lead in soil, USEPA has developed a preliminary remediation goal of 400 mg/kg using the Integrated Exposure Uptake Biokinetic (IEUBK) model (USEPA, 1994a). This model is designed to evaluate exposure from lead in air, water, soil, dust, diet, paint, and other sources, and predict blood lead levels in children 6 months to 7 years old. It is important to remember that the remediation goal of 400 mg/kg is based on residential (daily) exposure to small children and may not be applicable at all sites.

Lead-containing soils are regulated under the Resource Conservation and Recovery Act (RCRA). Limits have been established by USEPA for the toxicity of lead and these limits are published in the Code of Federal Regulations (CFR). The 40 CFR, Section 261.24, identifies lead in solids as a hazardous waste due to toxicity at 5.0 mg/L. This value is established using the Toxicity Characteristic Leaching Procedure (TCLP) developed by USEPA. Thus, the concentration of lead may be higher than 5.0 ppm in the soil, but the leachability of the lead cannot exceed the 5 mg/L level. The Safe Drinking Water Act (SDWA) establishes ARARs for cleanup. The 40 CFR, Section 268.40, establishes 5.0 mg/L as the standard for lead contamination in wastewaters and non-wastewaters.

Lead concentrations in air are regulated by the Clean Air Act of 1970, as amended in 1977 and 1990. Lead is included in the National Ambient Air Quality Standards (NAAQS) as a criteria pollutant. The primary standard for lead is 1.5 $\mu g/m^3$ as an arithmetic mean averaged quarterly. Lead is regulated as a hazardous air pollutant (HAP). Lead in soil can become airborne during activities that create dust at sites with lead soil contamination.

### 1.5 Previous Testing of the Technology

In the mid-1990s, the USAEC became interested in phytoremediation methods after private sector laboratory studies and field trials suggested that the technique might become a cost-efficient means of remediating metals-contaminated soils (see Tables 1-1 and 1-2).

In 1996, the USAEC funded a greenhouse study at TVA to determine whether the effectiveness of phytoextraction techniques could be increased. The primary goal of that project was to determine whether enhancing the water solubility of soil-borne lead would be a practical method

for improving the phytoextraction of lead-contaminated soils. The greenhouse study was conducted by TVA using soil from the Sunflower Army Ammunition Plant (SFAAP) located at Desoto, Kansas. TVA provided technical expertise and conducted the greenhouse study at the TVA greenhouse and environmental growth chamber facilities in Muscle Shoals, Alabama. The results of this study can be found in the report "*Results of a Greenhouse Study Investigating the Phytoextraction of Lead From Contaminated Soils Obtained From the Sunflower Army Ammunition Plant, Desoto, Kansas*," USAEC Report No. SFIM-AEC-ET-CR-98036. [Ref. 2]

Specific findings of the greenhouse study[Ref. 2] were:

- Amending the soil with chelates for white mustard, or chelates in conjunction with soil acidification to a pH of 5.5 for corn, increased lead concentrations in the plants up to 1,000-fold over unamended soils.

- When using soil amendments to stimulate lead uptake, the lead concentrations in the plant shoots were up to 1% in corn and sorghum-sudan grass, 1.2% in alfalfa, 2% in Indian mustard, and 2.4% in white mustard.

- Translocation of lead from root to shoot occurred within 24 hours of chelate application (in agreement with Huang *et al*.[Ref. 3]).

- The plants most efficient at accumulating lead in shoots also produced the largest amount of shoot biomass. Shoot biomass is essential for maximum lead removal.

- A lead concentration of up to 2.4% in white mustard was achieved using a chelate alone, suggesting that soil acidification was not necessary when this species was used. Accumulation of lead in corn and white mustard was a function of the lead concentration in the soil (higher soil lead = greater plant lead). Blaylock *et al.*[Ref. 12] reported similar findings in EDTA produced much higher lead concentrations in white mustard coincident with the increase in the total concentration of lead in the soil.

- A planted soil column study, which was designed to determine the persistence and movement of EDTA in the soil, showed an average 55% recovery of applied chelate, with the highest concentrations found in the top 15 cm of the soil. Blaylock *et al.*[Ref. 12] reported similar findings in a field study.

The results of the greenhouse study were sufficiently encouraging to warrant a field demonstration of the phytoextraction technique, as funded by ESTCP and reported in this document.

**Table 1-1**

**List of Promising Research With Synopsis of Findings**

- In greenhouse pot tests, translocation of lead from roots to shoots in corn plants increased 120-fold within 24 hours of a soil application of 1,000 mg/kg ethylenedinitrilo-tetraacetic acid (EDTA).[Ref. 3]
- In laboratory pot trials with addition of chelators to soil, shoot lead concentrations have reached 1% lead in corn and peas.[Ref. 4]
- Corn exposed to low lead concentrations (4 ppm) in hydroponic solutions accumulated 0.2% lead in shoots.[Ref. 5]
- Cultivars of Indian mustard selected for lead uptake using hydroponic solutions or sand/perlite mixtures for growth and lead application accumulated up to 3.5% Pb in shoots.[Ref. 6]

**Table 1-2**

**List of Known Phytoremediation Field Trials With Synopsis of Findings**

- Bayonne, New Jersey, site: Soil at a Texaco Oil site contaminated with 1,000 ppm lead was remediated using the plant species Indian mustard, with soil amendments of the chelator EDTA alone and EDTA in combination with acetic acid to lower soil pH. Lead concentrations in plant shoots have attained 0.4%. Remediation is estimated to require two to three years. [No published data - discussion by Dr. I. Raskin at Phytoremediation Conference, Alabama A&M Univ.[Ref. 7]]

- Palmerton, Pennsylvania, site: A Superfund site contaminated with 2,000 to 50,000 ppm zinc and 38 to 1,020 ppm cadmium has been used to assess the effectiveness of the species Alpine pennycrest (*Thlaspi caerulescens*), in conjunction with soil amendments to acidify the soil, to remove soil contaminants.[Ref. 8] Zinc (Zn) concentrations in Alpine pennycrest shoots from the field site were 0.6% to 1.0%.[Ref. 9] In greenhouse studies using soil from the Palmerton site, Alpine pennycrest accumulated 1.8% Zn and 0.1% cadmium (Cd) in the shoots without yield reduction associated with metals toxicity.[Ref. 10]

- Liberty Park, New Jersey, site: Soil contaminated with chromium was remediated by planting with Indian mustard.[Ref. 11]

- Trenton, New Jersey, site: A Brownfield industrial site, formerly used for the manufacture of Magic Marker pens and batteries, had soil contaminated with 927 ppm lead and was remediated with chelating agents and a crop of Indian mustard. Cleanup was almost complete in one summer and sampling of the plot down to 45 cm six months after application of 3,000 mg/kg EDTA indicated no significant leaching of the chelate below 15 cm.[Ref. 12]

- Butte, Montana, site: The Department of Energy (DOE) began large plot field tests in 1997 to determine uptake capacity of several *Brassica* varieties (Indian mustard, rape, turnip) and grasses for cadmium, zinc, and radioactive cesium and strontium.[Ref. 13]

- Superfund Innovative Technology Evaluation Program site in Ohio: A field demonstration is in progress on soil at a former metal plating facility to evaluate phytoextraction of cadmium, lead, and hexavalent chromium by Indian mustard. The demonstration was initiated in 1996 and includes monitoring the soil, groundwater, and plant material until at least 1999. To date, there has been no downward movement of lead through the soil profile.[Ref. 14]

**Table 1-2 (Continued)**

**List of Known Phytoremediation Field Trials With Synopsis of Findings**

- A field study investigated the potential of red root pigweed, Indian mustard, and tepary bean for phytoextraction of radioactive $^{137}$cesium from contaminated soil. Pigweed showed much higher potential for removing cesium from the soil than mustard and bean (40-fold more), with approximately 3% of the total $^{137}$cesium being removed from the top 15 cm of soil. The project is continuing to investigate the effect of inorganic and organic soil amendments on potential for leaching of $^{137}$cesium.[Ref. 15]

- A field study is ongoing at a site in Chernobyl, Ukraine, using sixteen high biomass cultivars of amaranthus, amaranthus x Jerusalem artichoke hybrid, sunflower x Jerusalem artichoke hybrid, corn, peas, sunflower, and Indian mustard in combination with 20 different soil amendments to remediate soil contaminated with radioactive $^{137}$cesium. Soil amendments included chelates, surfactants, organic and inorganic acids, and salts. Amaranthus showed the highest bioaccumulation coefficients for cesium and the highest yields, with significant variation within cultivars. Indian mustard was intermediate in cesium bioaccumulation, but lowest in yields; sunflower showed a low bioaccumulation coefficient and low yields. Of the soil amendments, only ammonium salts were effective in increasing extraction of $^{137}$cesium from the soil by the plants. Cropping resulted in only a small decrease in $^{137}$cesium activity in the soil.[Ref. 16]

# Section 2.0
# Technology Description

## 2.1 Description

### 2.1.1 Waste and Media Application

Phytoextraction is an *in situ* remediation method which uses plants to remove ionic metals (e.g., lead) from contaminated soils. Ionic metals are commonly produced when metal-bearing propellants, ammunitions, and powders are burned on the soil surface or particulate lead dissolves. Ionic lead contamination may also occur when leaded chemicals or fuels are spilled. Particulate elemental lead, bullet fragments for example, cannot be treated by this process. Phytoextraction methods may practically be used to remediate soils contaminated with lead in the 100 to 2,000 ppm range. For the technology to work, at least 50% of the total soil lead should be in a form amenable to extraction by plants. Expectations for reduction in soil lead concentrations are in the range of 100 to 200 mg lead/kg soil per year. Treatment at higher soil lead concentrations is technically feasible; however, the time required to achieve complete remediation will be excessive and unrealistic.

### 2.1.2 Description of Technology

In phytoextraction, heavy metals are taken up in plant tissues in sufficient concentrations to cause plant death. After the plants die, the plant shoots are harvested and can either be processed for metals recovery or disposed of as a hazardous waste. In contrast to some other remediation methods, phytoextraction techniques allow for the extraction and recovery of metals *in situ*; mechanical removal of the soil should not be necessary.

The extraction of ionic lead by plants is the primary focus of this technology. However, lead is not easily taken up by plants and removed from soil. Lead is considered the least soluble, the least mobile, and the least plant-available of the heavy metals in soils. Ionic lead ($Pb^{2+}$) is usually present in soil in various insoluble solid phases (i.e., lead carbonate - $Pb_3(CO_3)_2(OH)_2$, lead cerrusite - $PbCO_3$, lead phosphates, etc.) which do not readily release lead into the soil solution; thus, plant availability of lead is generally low. Lead also tends to accumulate within the root structures of most plants rather than moving to the aerial shoots. Before being taken up by a plant, lead in solid phases must be dissolved and released into the soil solution as ionic lead. The lead then is absorbed into the plant roots and translocated from the roots to the plant shoots.

In phytoextraction, plant uptake of lead may be increased by adding soil amendments to increase lead solubility. Solubilization makes lead more available for plant uptake. The soluble forms of lead easily move into the plant roots and are translocated to and accumulate in the aboveground shoots of certain plant species at much higher concentrations than would otherwise occur. The use of these amendments with selected plant species allows lead accumulation of up to 2% in the aboveground portion of the plant.

Soil amendments currently used for phytoextraction are soil acidifiers and chelates. Soil acidifiers, such as acetic acid, temporarily increase soil acidity which solubilizes lead out of soil

solid phases and into the solution phase of the soil (the soil solution). Chelates, such as EDTA, enhance solid phase solubilization by chelating the lead that is in solution and shifting the equilibrium toward further dissolution (i.e., lead ions combine with the chelating agent, thereby, removing ionic lead from the liquid phase and promoting additional release of the solid phase lead into the liquid phase). Chelation may be viewed as the multiple bonding of a metal to coordinating groups (or ligands) of an organic compound to form a stable charge transfer structure which protects the metal ion from reacting with the soil to form insoluble compounds.

There are several components of a phytoextraction scheme. The "processing unit" of a lead phytoextraction system consists of a plowed field of the contaminated soil, a crop, an irrigation system, a fence, the necessary farm equipment, decontamination equipment, and a decontamination area. The decontamination area is used for decontamination of personnel and farm equipment leaving the contaminated area. The addition of soil amendments greatly enhances lead uptake by the plants; however, plant species vary considerably in ability to take up lead, even when it is in a soluble form. Plant species that have suitable characteristics for lead remediation are corn, alfalfa, Indian mustard, and white mustard.

To "operate" the field, a crop, which is chosen for good growth in the climate of the area, is planted and grown to full vegetative biomass maturity (i.e., to a stage just before fruit or grain production) using common farm practices. After the plants have matured, the amendments are added to the soil to solubilize lead into a plant-available form. Within a few days, the plants begin to senesce (die) due to uptake of large amounts of lead and chelate. After plant death, the shoots are harvested, either by use of common farming techniques or by hand. The harvested crop is then either disposed of as a hazardous waste or processed (smelted) for metals recovery. The number of extraction crops that can be grown to full vegetative biomass depends on the type of plant and local climate and may range from one to four crops per year. When possible, a cover crop may be grown in the winter season to control wind and water erosion. The cover crop is tilled back into the soil prior to planting the spring crop. Examples of common cover crops are wheat, barley, and annual and perennial ryegrass.

### 2.2 Strengths, Advantages, and Weaknesses

Several strengths and advantages have been attributed to phytoremediation. However, this demonstration showed that in this particular case, the weaknesses outweighed the advantages. The feasibility of implementing a phytoextraction program at a particular site is influenced by the following factors:

- The lead content of the soil
- The underlying geology
- The potential for phosphorus deficiencies in the soil
- Local weather conditions
- Plant selection
- Chelator cost
- Size of area to remediate
- Time limitations for remediation
- Regulatory requirements within a state

Sites with lead concentrations within 200 - 300 mg ionic lead/kg soil of the clean-up level are the most suitable for phytoextraction, since this type of site could be remediated within 5 years. However, the expected reduction in soil lead ranges from 50 - 100 mg lead/kg soil per year, so the time required to successfully conclude a remediation program may become unrealistic for higher concentrations.

The underlying soil geology may also be a concern. Soil amendments increase lead solubility and it is possible for lead to move out of the plant root zone into lower soil layers, adjoining areas, or groundwater. Therefore, careful attention must be paid to the nature of the underlying geology (soil texture, clay content, hydraulic conductivity, soil moisture, depth of water table, etc.), as well as the levels of soil amendment application.

Phosphorus (P)-deficient soils may complicate phytoextraction schemes. Lead-contaminated soils tend to be deficient in plant-available phosphorus because some of the applied phosphorus may precipitate with lead as insoluble lead-phosphate complexes. The symptoms of phosphorus deficiency include decreased plant growth and decreased biomass production. Phosphorus deficiency lowers remediation effectiveness by reducing total lead uptake.[Ref. 3] This can be remedied by supplying additional phosphorus to the plant, either by foliar application (i.e., spraying a water-soluble phosphate fertilizer solution directly on the plant) or by band application of phosphorus at planting (i.e., applying bands of phosphate fertilizer below the soil surface and to the side of the plant or seed row). However, this can easily be done only with crops that are planted in rows, such as corn. This may not be practical for crops that are broadcast-seeded, such as mustard.

Local weather conditions affect the length of the growing seasons, the type of crop to be grown, and crop sequence. In turn, the types of plants to be grown at a site are subject to evaluation for a number of considerations including: the length of the growing season, the availability of rainfall and rainfall accumulations, adaptability to local conditions, soil fertility, and ability to take up lead. Corn (*Zea mays*) appears to be the most suitable warm season crop, while white mustard (*Sinapis alba*), Indian mustard (*Brassica juncea* L.), and alfalfa (*Medicago sativa* L.) appear to be suitable cool season crops.

Chelate costs are a major part of the expenses for a phytoextraction project and fluctuations in prices may significantly impact projected budgets. If feasible, long-term contracts with the vendor to supply the required amount of chelate over the life of the project at a pre-set cost would be very desirable.

The size of the area to be remediated directly affects both the level and type of labor and equipment required, which in turn affect cost. A practical area size limit for completion using manual practices (i.e., soil core sampling, hand tilling, planting, and harvesting) would be half an acre. Larger areas will require the use of mechanized equipment. Manual labor is initially cheaper, but there will be a point where this cost savings will quickly be offset by the time and effort required to accomplish each task. At that point, mechanized equipment becomes more practical.

The time required to phytoextract an area is a function of the potentially extractable and plant-available lead concentration in the soil and the cleanup level (residential or industrial standard) to be achieved. In most cases, phytoextraction is slower than other methods. The ultimate use of the area dictates the maximum time that can be allotted for remediation. For example, simple economics dictate that an area designated for general construction will require a more expedient method than phytoremediation for cleanup. However, if there are no immediate plans for use of the area, and all that is required is that the area be cleaned up, then phytoextraction will be entirely suitable.

Additional aspects of phytoextraction relative to other remediation technologies include:

- Low remediation costs, ranging from $25 to $127 per cubic yard.[Refs.17,18]
- Heavy metals removal by plant harvesting minimizes site disturbance and limits the dispersal of contaminants.
- Heavy metals recycling is possible via the processing (smelting) of the harvested plant tissues.
- If the heavy metals are recycled, the cost and long-term liability associated with maintaining a landfilled hazardous waste is substantially reduced or eliminated.
- Operating space requirements are limited to the field being treated.
- The technology is relatively simple and easy to implement.

Relative to other technologies, phytoremediation also has a number of weaknesses:

- Can require several years for remediation.
- Only applies to limited situations (lead concentrations, site conditions, soil type).
- Will be prohibitively expensive for higher soil lead concentrations.
- Technology is greatly impacted by weather and other environmental factors.
- May require liners to prevent lead leveling, which will increase costs.
- EDTA is an effective chelate for solubilizing lead, but carry-over EDTA may become toxic to plants.

## 2.3 Factors Influencing Cost and Performance

Factors which affect the cost and performance of phytoextraction technology include:

- Soil (Matrix) Properties
  - Soil type
  - Clay content and/or particle size distribution
  - Hydraulic conductivity
  - Moisture content
  - Porosity
  - pH
  - Contaminant depth

- Properties of Organics in Soil
  - Total organic carbon

- Non-Matrix (non-soil) Characteristics
  - Contaminants
  - Ambient temperatures
  - Geology and hydrogeology
  - Cleanup levels
  - Weather conditions (rainfall, drought)
  - Growing season
  - Chemical costs

The potential effects of each of these factors on cost or performance are listed in Table 2-1 and procedures for measuring these parameters are listed in Table 2-2.

Other factors which can be relevant to the performance of the technology are outlined in Table 2-3 in accordance with the guidelines given in "Guide to Documenting and Managing Cost and Performance Information for Remediation Projects:"[Ref. 19]

- The applicability of the technology to a specific situation
- Competing technologies
- The maturity of the technology

The implication of these factors are outlined in Table 2-3.

## Table 2-1

## Matrix Characteristics and Operating Parameters that Affect Phytoremediation Technology Treatment Cost or Performance

| Parameter | Potential Effects on Cost or Performance |
|---|---|
| **Matrix Characteristics** | |
| **Soil Properties** | |
| Soil Type | 1. Sand and sandy loam soil types are conducive to leaching of nutrients; consequently, natural fertility usually is low and nutrient deficiencies may develop in plants. Applied chelate and inorganic contaminants solubilized by the chelate may be subject to downward movement, which may move contaminants of interest beyond the root interception zone of remediation crop, and uptake by crop may be reduced.<br>2. Mineralogy of soil--an enriched iron oxide content will promote strong adsorption of chelate, which may reduce chelate effectiveness or may result in carryover to successive crops. |
| Clay Content and/or Particle Size Distribution | 1. Presence of clay lenses or a fine clay/sand hardpan layer increases difficulty and labor requirements of sampling.<br>2. Also results in reduced and non-uniform infiltration (areas over-saturated or under-saturated) of added soil amendments (chelate and acidifier) which may result in loss by runoff and reduced amount in root zone (treatment effectiveness compromised). |
| Hydraulic Conductivity | 1. Variable in sandy loam from slow to fast. This results in variable infiltration rates and non-uniform amendment application and placement within crop; potential for runoff increased.<br>2. Fast in sand. May result in too rapid downward movement of amendments and reduced contact time with roots--reduced treatment effectiveness.<br>3. Slow in clay. May result in restricted downward movement of amendments and prolonged contact time with roots--reduced treatment effectiveness. May result in runoff of soil amendments. |
| Moisture Content | Soil moisture should be regulated by selective irrigation so that the required amount of soil amendment may be applied in a volume which does not exceed field capacity in the top 2 feet of soil (rooting zone). |
| Porosity | Directly affects the water-holding capacity and field capacity of soils. |
| pH | 1. Must be within the tolerance range of crop to be grown for efficient nutrient utilization and maximum yield.<br>2. pH is reduced to 5.5 to facilitate solubilization of inorganic contaminants into plant-available form and to increase efficiency of chelate. |
| Contaminant Depth | Contamination in soil must be restricted to a depth accessible to plant roots (usually top 2 to 3 feet). |
| **Properties of Organics in Soil** | |
| Total Organic Carbon | This influences important soil chemical and physical properties, i.e., fertility, exchange capacity, and moisture-holding capacity. This may also affect reactions of inorganic contaminants (metals, oxyanions) both before and after solubilization by amendments. |

**Table 2-1 (Continued)**

**Matrix Characteristics and Operating Parameters that Affect Phytoremediation Technology Treatment Cost or Performance**

| Parameter | Potential Effects on Cost or Performance |
|---|---|
| **Matrix Characteristics** | |
| **Non-Matrix Characteristics** | |
| Contaminants | The primary contaminant of interest should have the greatest interaction with the soil amendments (acidifier and chelate) and the selected amendments should be tailored to the primary contaminant. Other Contaminants of Concern (COCs) should be identified and quantified and a determination made of potential adverse effects on crop growth. Crops with low tolerance to any contaminants should not be grown. |
| Ambient Temperature | Ambient temperature affects metabolic processes of plants. Lower temperatures may reduce rates of uptake and assimilation. |
| Geology and Hydrogeology | Heterogeneous material, i.e., sandy soil with gravel and cobbles, will increase sampling difficulty and will promote variable hydraulic rates. May limit usefulness of suction lysimeters as monitoring tool for solubilized metals in soil solution. A shallow or perched water table may be subject to contamination by amendments and solubilized COCs and may reduce percolation rates. Heavy clay soils may inhibit infiltration. Direction of flow should be considered to determine suitability of site for amendment application. Shallow hard pan restricts root growth and encourages shallow rooting. |
| Cleanup Levels | Technology may not be suitable for reducing all COCs to appropriate level or the desired level may not be achievable within an appropriate timeframe. There may be a wide disparity in cleanup levels among the COCs. A dual level (industrial and residential) may exist for some contaminants. |

## Table 2-2

## Measurement Procedures for Matrix Characteristics and Operating Parameters That Affect Phytoremediation Technology Treatment Cost or Performance

| Parameter | Measurement Procedures |
|---|---|
| **System Parameters** | |
| Soil Classification | Official Soil Series Descriptions, USDA-NRCS Soil Survey Division, Iowa State University |
| pH | ASA Method 12-2.6 |
| Temperature | Standard ambient temperature mercury thermometer |
| Porosity | ASA Method 8-2.3, *Water Retentivity*. |
| **Biological Activity** | |
| Nutrients/Soil Amendments | 1. Organic Carbon measured by ASA Method 29-3.5.2; nitrogen as ammonia by ASTM D 1426-89, *Test Methods for Ammonia Nitrogen in Water*; nitrogen as nitrite-nitrate by ASTM D 3867-90, *Test Method for Nitrite-Nitrate in Water*; phosphorus by ASTM D 515-88, *Test Methods for Phosphorus in Water*; aluminum, calcium and magnesium by ASA 9-3.1; extractable iron by ASA Method 17-4.3.<br><br>2. EDTA in soil and plants by Method AP-0057 and Method AP-0047. |
| Plants Per Unit Area and Plant Type | 1. Representative areas in remediation plots selected and measured, area calculated, and number of growing plants in area counted. Total plant population calculated by extrapolation to a per acre basis.<br><br>2. Amount of biomass produced determined by subsample weighing and extrapolation to total field area and by actual weight determination at disposal site, i.e., a smelter. |

## Table 2-3

## Other Factors Affecting Project Demonstration Performance

**Applicability of the Technology**

- Phytoextraction is suitable for the range of lead concentrations (100 to 2,000 mg/kg) present in demonstration sites. Sites with higher lead concentrations may be remediated without interfering with plant growth. However, the expected lead reduction in soil ranges from 50 to 100 mg/kg per year and time constraints may limit use for higher concentrations.
- Technology usefulness may be limited by the sandy soils on demonstration sites which are conducive to downward movement of solubilized metals, as well as EDTA.
- Highly stratified soil with hardpan near surface may restrict root growth, encourage shallow rooting, and reduce infiltration while promoting runoff of added soil amendments.
- Stratified soils of varying texture within the soil profile restrict use of lysimeters for monitoring potential downward movement of chelate and contaminants.
- Presence of clay lenses may result in non-uniform infiltration of amendments across the continuum of the demonstration area.
- Presence of beryllium and thallium, even at very low soluble concentrations (2 ppm) in soil, may limit plant growth and sensitive accumulator crops may be severely damaged. These elements show indication of solubility into plant-available form by application of soil amendments or into a form which may migrate through soil, causing damage to roots. Therefore, phytoextraction may not be suitable for soils which contain these elements.
- The forms of soil lead govern the potential amount of lead that may be solubilized by a chelate, and thus the amount of lead available to plants.
- Application of the technology will be severely limited in areas having a shallow and/or fluctuating groundwater table that periodically intrudes into the amendment-treated rooting zone.

**Competing Technologies**

- Phytoextraction competes with conventional established technologies such as landfilling, soil washing (separation), *in situ* soil flushing, and containment.
- Commercial-for-profit vendors are actively promoting and using phytoextraction. However, methods are proprietary and operational success is not certain at present.

**Maturity of the Technology**

- Phytoextraction is an emerging technology and the methodologies and processes of applying the technology are still being defined through demonstrations. Several problematic areas, for example, chelate application methods, application rates, and chelate persistence in soil remain to be satisfactorily addressed and resolved.
- Current technology demonstrations and contaminants being addressed are: Arden Hills, Minnesota (lead); Bayonne, New Jersey (lead; Palmerton, Pennsylvania (zinc and cadmium); Liberty Park, New Jersey (chromium); Trenton, New Jersey (lead); Butte, Montana (cadmium, zinc, and radioactive cesium and strontium); and at the Superfund Innovative Technology Evaluation (SITE) Program site in Ohio (cadmium, lead, and hexavalent chromium).

# Section 3.0
# Site/Facility Description

## 3.1 Background

### 3.1.1 Site Selection Criteria

The USAEC, in consultation with TVA, selected TCAAP as the demonstration site based on the soil and geologic conditions, the local climatic conditions, implementation cost, facility interest, and the interest of regulatory agencies in the affected state. TCAAP was selected for the following reasons:

Soil and Geologic Considerations

- TCAAP had sites with both moderate and low levels of ionic lead contamination.
- Metallic debris (i.e., bullet jackets) were present in the soil at Site C, so a demonstration at that site would provide a perspective on the impact of metallic lead particulate on remediation efforts.
- The soils at TCAAP were thought to be sandier than those used during the Sunflower greenhouse study and, therefore, would have better infiltration characteristics.
- The depth of the water tables varied considerably at the TCAAP sites, providing opportunities to examine the effect of these differences on the technology. At Site C, the water table could fluctuate between 2 to 10 feet below the surface, although there is no historical groundwater data at the area where the demonstration plot was located. However, the plot was on the highest part of Site C proper, and groundwater was not encountered beneath the plot area during lysimeter installation or during soil sampling. At Site 129-3, the water table is estimated to be 140 to 200 feet below the surface.

Climatic Considerations

- Minnesota does not have a long growing season and can have early/late frosts, snow, etc. This provided an opportunity to examine operational feasibility in a relatively difficult climate.

Cost Considerations

- Local ATK personnel could be used for demonstration activities.
- A smelter was located nearby.

Local Facility and Regulatory Considerations

- TCAAP was interested in demonstrating the use of innovative technologies.
- The State of Minnesota, in general, has a "forward" thinking approach in environmental matters.
- Regulators in the State of Minnesota are interested in the new technologies.

### 3.1.2 Facility Description

TCAAP is a 2,370-acre facility located in Arden Hills, Minnesota, approximately ten miles north of Minneapolis-St. Paul, Minnesota (Figure 3-1).

TCAAP is surrounded by four suburban towns including:

- Shoreview to the north and east
- Mounds View to the west
- New Brighton to the southwest
- Arden Hills to the south

TCAAP was established in 1941 and was used for the production and storage of small arms ammunition (.30 and .50 caliber), related materials, fuzes, and artillery shell metal parts. The facility also provided proof testing of small arms ammunition and the storage and handling of strategic and critical raw materials for other government agencies. At its peak, the facility contained 7 major production buildings and over 300 auxiliary buildings (Figure 3-2). The facility is currently inactive.

The phytoremediation demonstration was conducted on areas within Sites C and 129-3. Site C is located immediately east of Mounds View Road, just northeast of the central portion of TCAAP (Figure 3-2). Site C's northern boundary is approximately 0.5 mile south of the northern plant boundary. The site is bounded by railroad tracks to the east and by Building 190 to the south (Figure 3-3). It is about 550 feet wide in the east-west direction and 1,300 feet long in the north-south direction.

Site 129-3 lies west of Snelling Avenue, just south of the Snelling Avenue and Upper Range Road intersection near the center of TCAAP (Figure 3-2). Site 129-3 is located about 0.1 miles west of the TCAAP internal reservoir. The site is roughly shaped like a parallelogram and has approximate dimensions of 225 feet in the north-south direction by 280 feet in the east-west direction (Figure 3-4).

### 3.1.3 Facility History

#### 3.1.3.1 Current Operations at TCAAP

TCAAP is a government-owned military industrial installation under the jurisdiction of the Commanding General, Headquarters, United States Army Operations Support Command. The OSC was formed on October 1, 1995, and has its headquarters at the Rock Island Arsenal, Rock Island, Illinois. OSC is a major subordinate command of the U.S. Army Materiel Command.

From 1941 to 1976, the mission of TCAAP was to produce a wide variety of ammunition for the U.S. and its allies during World War II, the Korean conflict, and the Southeast Asian conflict. Since active production has not been required since the late 1970s, TCAAP today is in modified caretaker status. This means that there are no active Army production activities

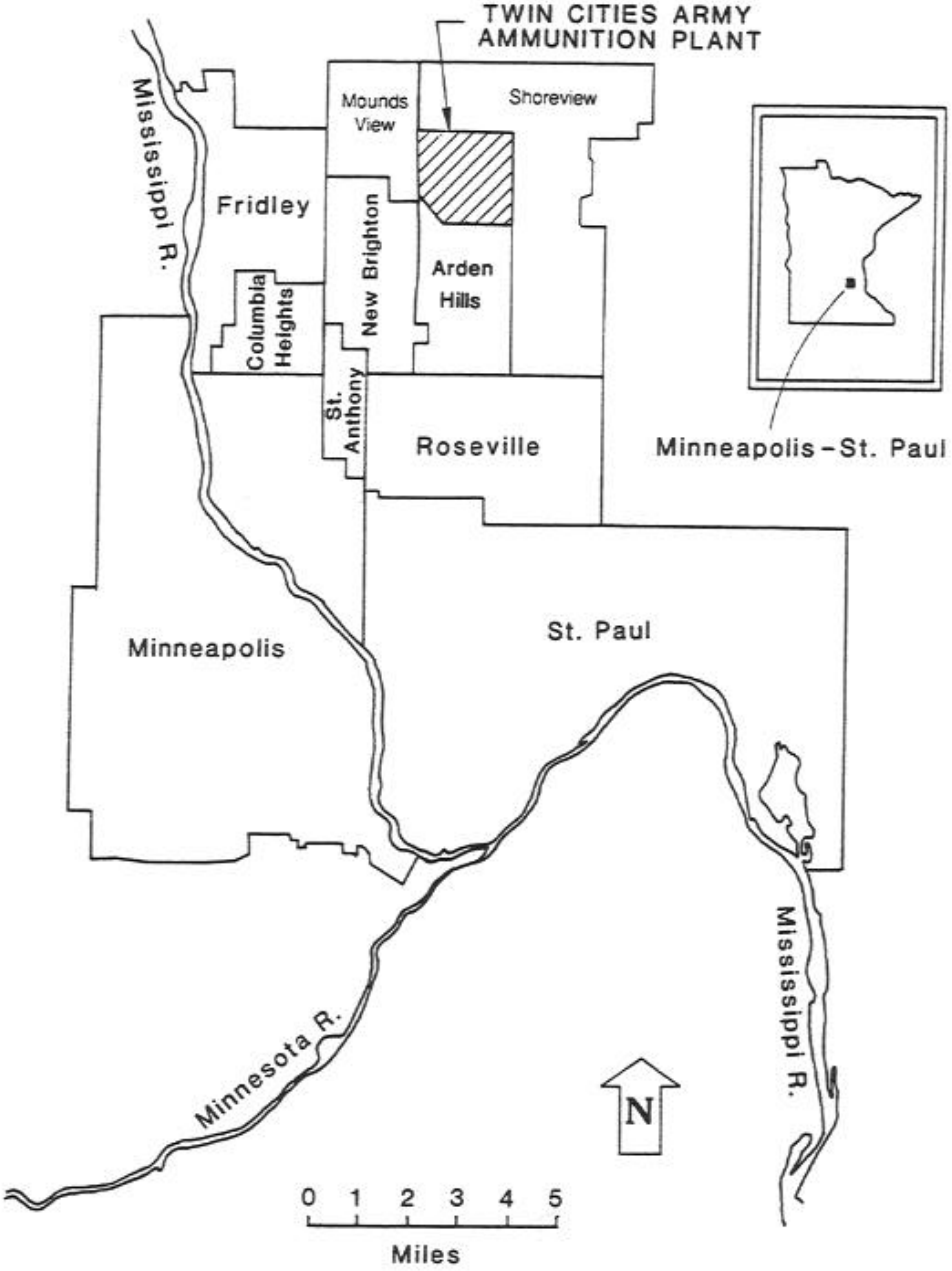



**Figure 3-1**

**Location of TCAAP in the State of Minnesota**

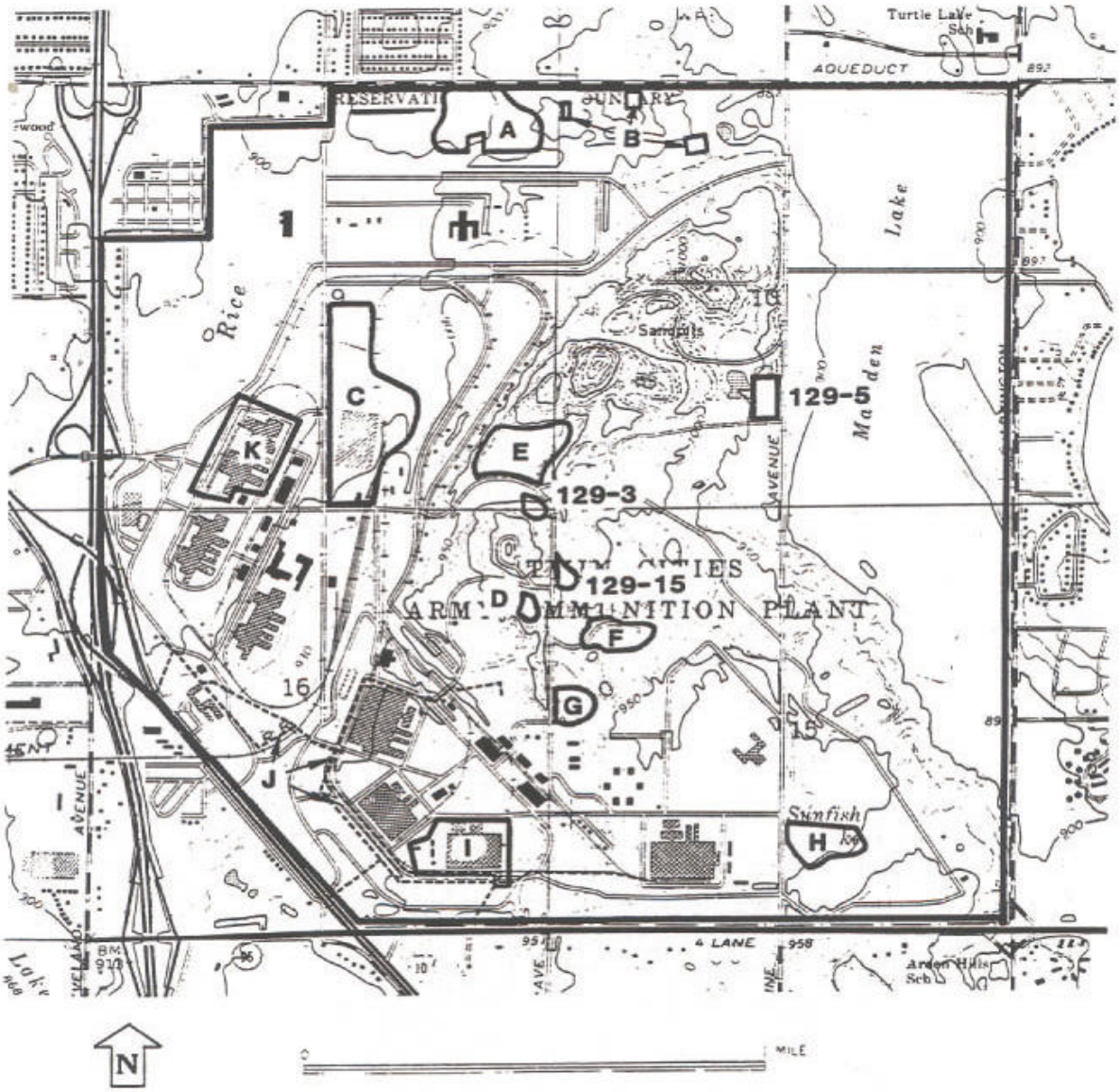



**Figure 3-2**

**TCAAP Boundaries and Potential Contaminant Sources**

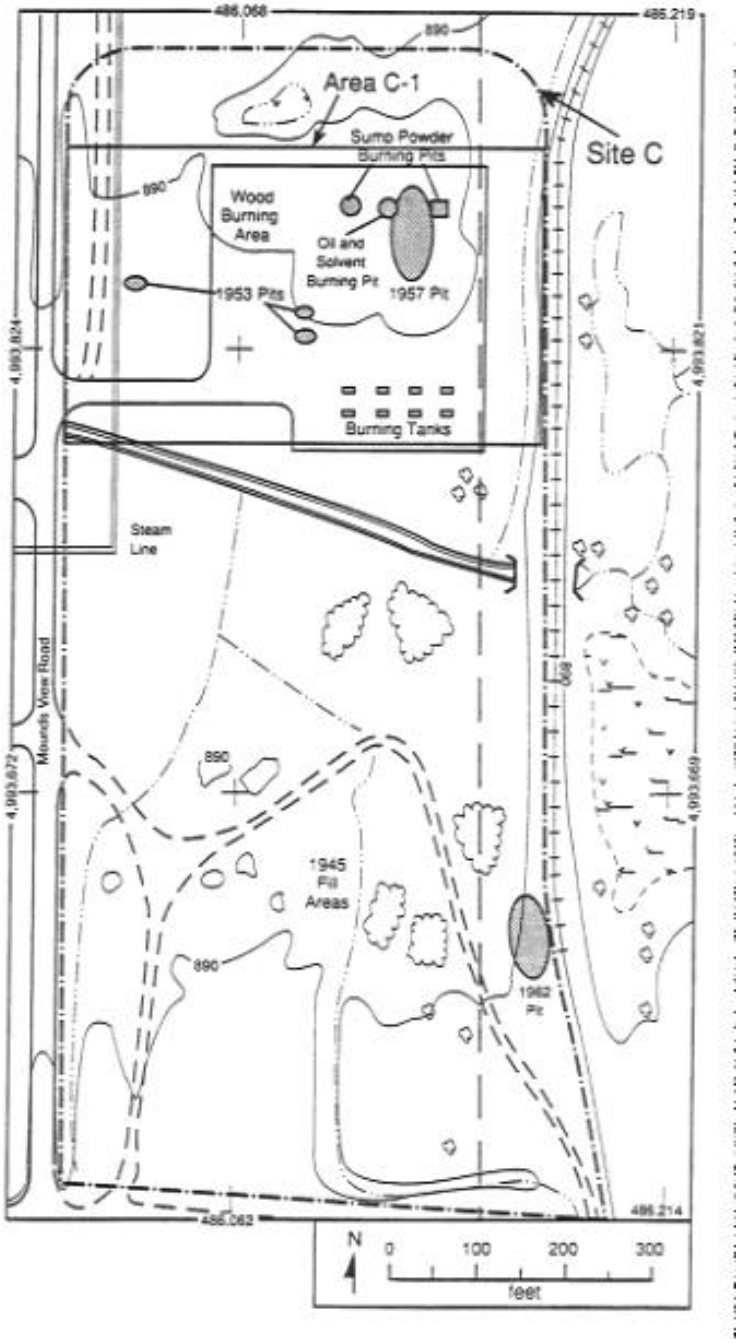



**Figure 3-3**

**Layout of Site C**

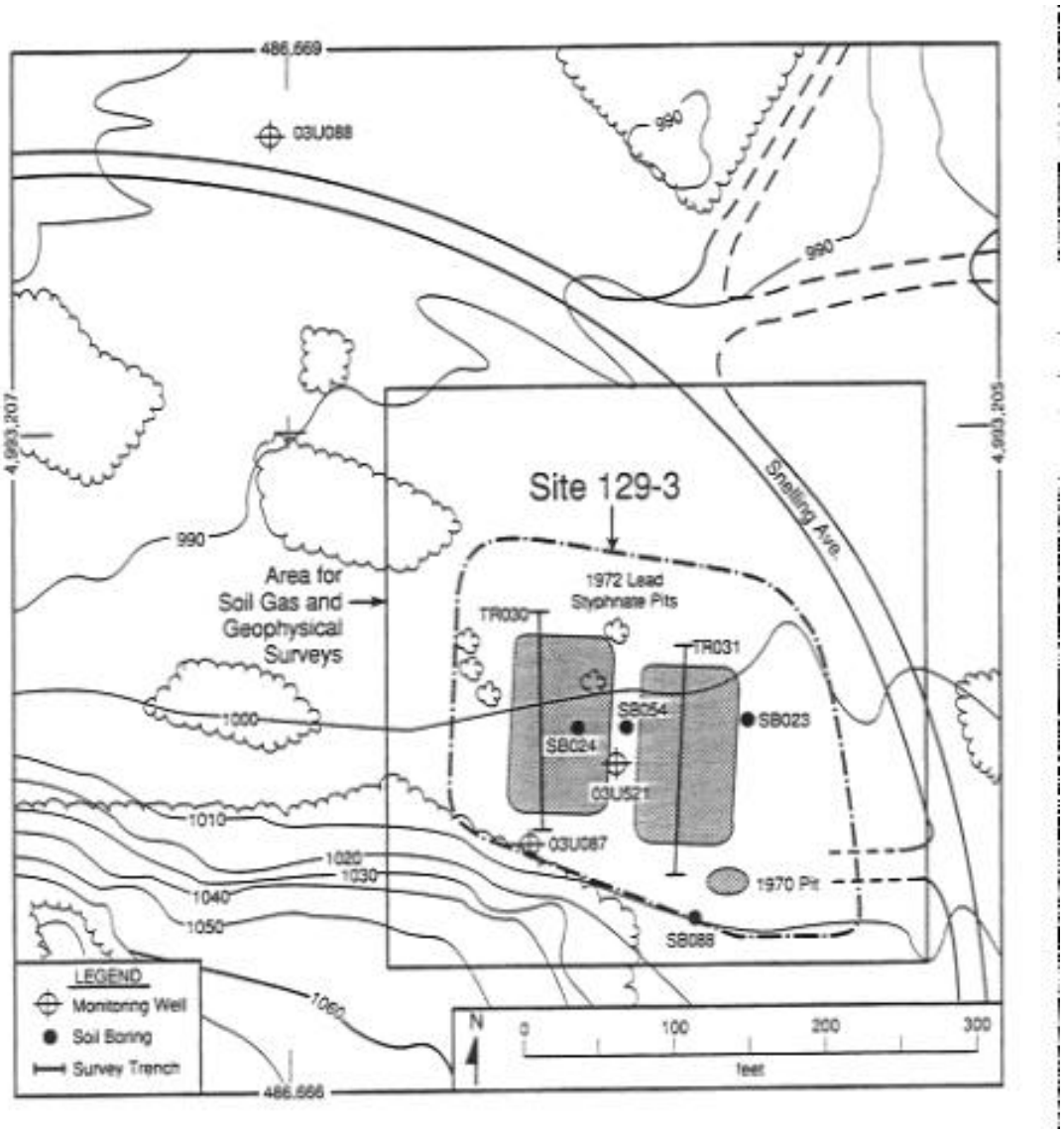



**Figure 3-4**

**Layout of Site 129-3**

except for that conducted by companies that occupy facilities on the installation under some form of contractual arrangement with the Army. DoD contractor Alliant Techsystems Inc. is such a tenant that also currently serves as the Installation Support Services contractor. In addition, TCAAP serves as host to the U.S. Army Reserves and the Minnesota National Guard. TCAAP has focused its attention on the mission of environmental cleanup and is implementing its comprehensive environmental cleanup program under CERCLA.

TCAAP's current mission is to retain control of the site until the facility has been remediated to industrial use standards. Ownership of lands is currently retained by the OSC.

TCAAP is participating in the Installation Restoration Program (IRP), a specially funded program developed by DoD in 1978 to identify, investigate, and control the migration of hazardous contaminants on military and other DoD installations.

ATK also operates production facilities on TCAAP property for DoD production contracts. The property was declared excess by OSC in 1992 due to reduction-in-force structure requirements. Remediation efforts are proceeding on the property.

#### 3.1.3.2 Past Operations at TCAAP

TCAAP was established in 1941 as part of the World War II buildup. Employment reached a historic high of near 24,000 during World War II. The installation supported both the Korean and Southeast Asian conflicts. A small-caliber ammunition modernization program was initiated in 1967, with additional prototypes in 1974. Production was completed in 1976.

In 1981, environmental studies indicated that contaminated groundwater from the TCAAP was migrating into the Minneapolis-St. Paul metropolitan groundwater supply. These studies suggested that a number of sites within TCAAP were contributing to groundwater and soil contamination. These sites included: former landfills, impoundments, burning and burial grounds, ammunition testing and disposal sites, industrial operations buildings, and sewer system discharges. The primary groundwater contaminants were volatile organic compounds (VOCs). The primary soil contaminants were ammunition-related heavy metals (copper, lead, and mercury), followed by VOCs and polychlorinated biphenyls (PCBs).

#### 3.1.3.3 Past Operations at Site C

Documentation on materials disposal or other activities at Site C is limited. The site's history has been deduced mainly on a review of aerial photographs. In 1940, Site C consisted of agricultural fields and two farmsteads. From 1947 to 1957, the site was used for burning scrap wood boxes, solvents, oils, corn cobs, and production materials. The site was also used as an open storage site from 1947 to 1982. Typically, the northern portion of Site C, commonly referred to as Site C-1 (Figure 3-3), was used as a burning ground and general waste disposal area. In May 1962, a 60-foot x 20-foot x 30-foot pit was dug in the southeast portion of Site C next to a railroad track (Figure 3-3). This pit, commonly referred to as the 1962 Pit, was used to decontaminate 64 machines from Building 103. These machines, contaminated with explosives, were subjected to open-flamed fires fed with wood and No. 2 fuel oil. The decontaminated machines were later removed and sold as scrap. The phytoremediation demonstration site is located in the approximate area of the 1962 Pit.

#### 3.1.3.4 Past Operations at Site 129-3

Documentation of some of the disposal activities at Site 129-3 is based on aerial photographs. A 1940 aerial photograph indicates that Site 129-3 was once an agricultural field. The photographic evidence suggests the site was vacant from 1945 to 1966. In 1970, aerial photographs indicated that a large rectangular pit had been installed in Site 129-3 and a pipe was extending from the southeast corner of the pit to the adjoining road. By 1972, two rectangular pits appeared (Figure 3-4). Each pit was approximately 65 feet wide x 120 feet long. The pits were separated by about 20 feet. These pits are believed to have contained contaminated wastewater from a lead styphnate production facility constructed in December 1971 during the Southeast Asian conflict.

Production of lead styphnate was carried out in Buildings 138-A, -B, -C, and -D. Contaminated wastewater from the facility was treated with steam at the facility to break down tetracene. Sodium hydroxide was then added to precipitate lead, and aluminum powder was added to neutralize the resulting basic solution. Facility records suggest that after treatment, the wastewater was transported to the lead styphnate leaching pits at Site 129-3. It is believed that wastewaters from primer explosive mixing (Building 328), primer filling (Building 135), and tetracene manufacturing operations (Building 327) were also disposed of in the leaching pits located at Site 129-3.

The material put in the pits was about 90% water and was taken to the pits by sump trucks. Liquids from the trucks were channeled into the leaching pits through pipes in the southeast corner of each pit. An estimated 1,500,000 to 2,000,000 gallons of wastewater were discharged annually into the pits. After discharge, water leached into the ground or evaporated. The pits were also flashed with scrap propellant powder. This flashing may have been done on an irregular basis, especially in winter when several months could pass between flashings because of snow.

Although it has been claimed that the pits were used until 1978, it seems likely that activity ceased in 1976. Activities associated with the Southeast Asian conflict ended at TCAAP in September 1974. A 1977 aerial photograph shows that both pits remained open with no liquid in either pit and with what appeared to be a light-toned residue in the western pit. The pits were eventually sealed, as documented in a letter dated October 25, 1977. According to operating personnel, the pits were filled with sand, capped with clay, and sloped. A 1980 aerial photograph shows that the site had revegetated, but the access road was still visible.

A small circular pit containing light-toned material was also visible in the 1970 photo, but was not evident in the 1972 photo (see 1972 Pit in Figure 3-4). This pit may have been used for the disposal of mercurous nitrate. According to operating personnel, the pit was "filled in", however, no details of this action are available. Spent mercurous nitrate solution, which was used in the quality control (QC) testing of brass cartridge cases, was discharged untreated into the pit. It has been estimated that the solution contained about 10,000 mg/L of mercury. It is not known whether this value represents the total amount of mercury disposed of or the amount

of mercury in solution for each disposal activity. The frequency of disposal between 1970 and 1972 is also unknown.

## 3.2 Site/Facility Characteristics

### 3.2.1 Local Climate

The Minneapolis-St. Paul area has a continental climate with wide variations in temperature, ample summer rainfall, and winter precipitation. In general, there exists a tendency toward extremes of almost all climatic aspects.

Regional precipitation data indicate an average total precipitation (both rainfall and snow) rate of 28.6 inches of water per year and an annual snowfall rate of 46 inches of snow per year. The maximum monthly precipitation rate (17.9 inches) was recorded in July 1987. The minimum monthly precipitation rate (a trace) was recorded in December 1943. Temperature data (1966-1996) indicate an annual average temperature of approximately 49.6$^{o}$F. Monthly highs average 83$^{o}$F in July with the highest recorded temperature being 105$^{o}$F. The area experiences an average of 15 +90$^{o}$F days per year. Monthly lows average 2$^{o}$F in December with the lowest recorded temperature being -34$^{o}$F. The area experiences an average of 158 freezing days a year, with 34 of these being below-zero days. Average relative humidity ranges from 68% to 74% year-round. Prevailing winds alternate from May to October in a south and southeasterly direction. From November to April, the prevailing winds are northeasterly.

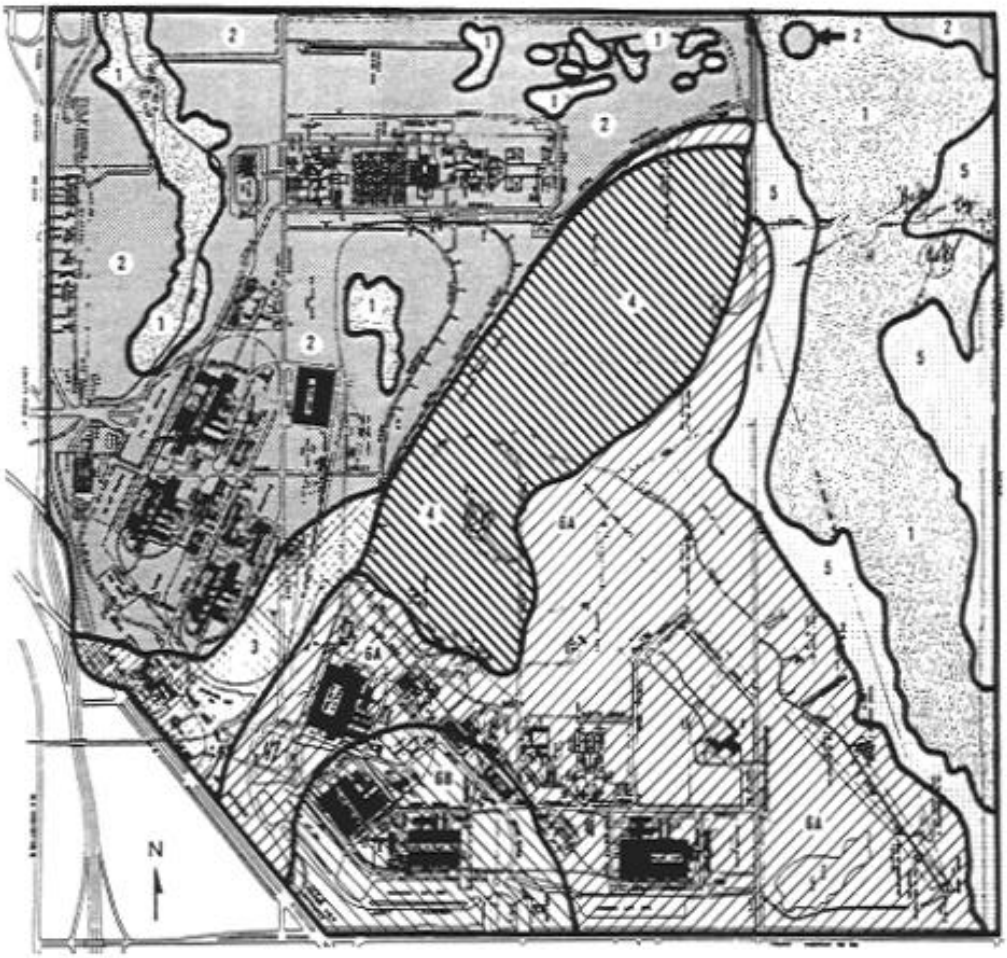
### 3.2.2 Regional and Local Geology

#### 3.2.2.1 Geology Beneath Site C

The local geology of the earth beneath Site C consists of bedrock overlain by three thick layers of deposit. The top deposit, generally referred to as Unit 1, primarily consists of fine sand and silt with an occasional clay layer (Figure 3-5). Unit 1 has a thickness ranging from about 10 to 16 feet. This soil is considered a sandy loam under the U.S. Geologic Survey (USGS) soil classification system. Unit 1 was deposited by ancient Lake Fridley during the retreat of the Grantsburg Sublobe ice. Before the lake was completely drained, the site probably became a wetland, resulting in the deposit of a thin layer of organic material and a layer of clayey material near the land surface.

Below Unit 1 is a layer of Twin Cities Till which is commonly referred to as Unit 2. The till is clayey in nature and ranges in thickness from 64 to 120 feet. Unit 2 provides a good hydraulic barrier between Unit 1 and the underlying Unit 3.

Below Unit 2 is Unit 3. These deposits consist of medium to coarse pebble sand (Hillside Sand) and unnamed layers. Unit 3 increases in thickness to the north as the center of an underlying bedrock valley is approached.




LEGEND

**Swamp and Marsh Deposits** – Organic fine sand, silt, and clay; peat and muck.

**Fridley Formation** – Laminated and cross-laminated fine to medium sand with some silt grading laterally and vertically into large bodies of silt.

**New Brighton Formation** – Laminated and cross-laminated fine to medium sand, silt, and coarse sand with pebbles.

**Arsenal Sand** – Medium to coarse very gravelly sand; intricately cross-bedded.

**Turtle Lake Sand** – Laminated and cross-bedded fine to medium sand with some silt.

**Twin Cities Formation** – Till with local pockets of sand and gravel.

6A – Complex mixture of light-gray till, reddish-brown till, and other related drifts.

6B – Light-gray till at surface, generally underlain by mixed light-gray and reddish-brown tills that are underlain in turn by reddish-brown till.

**Figure 3-5**

**Surface Geology at TCAAP**

A bedrock valley is located beneath Site C (Figure 3-6). Three kinds of bedrock are exposed under the 246-feet thick deposits above the bedrock. The bedrocks are, from north to south, the St. Lawrence Formation, Jordan Sandstone Formation, and Prairie du Chien Group. Their topographic surface dips to the north.

#### 3.2.2.2 Geology Beneath Site 129-3

The local geology of the earth beneath Site 129-3 consists of bedrock overlain by two layers of glacial deposits consisting of Arsenal and Hillside Sands (Figure 3-5). These deposits are generally referred to as Unit 3. This soil is considered a fine sand under the USGS soil classification system. Site 129-3 itself is located on a mound of stratified drift deposited by glacial meltwater. Such mounds are referred to as kames. At Site 129-3, the kame consists of up to 430 feet of unconsolidated glacial deposits. No distinct lithologic break occurs between the Hillside and Arsenal Sands, so it is difficult to determine the thickness of individual units.

The generally overlying Arsenal Sand is a light gray to brown, well-sorted, fine- to coarse-grained sand. The deposits are probably glacial outwash deposited by both the Superior Lobe and the Grantsburg Sublobe ice. These deposits comprise a kame formed on the terminal margin of the retreating Grantsburg Sublobe ice.

The Hillside Sand is very pale brown to brown, poorly sorted, medium- to coarse-grained, and has some pebbles and cobbles. These deposits are thought to be glacial outwash deposited by both the Superior Lobe and the Grantsburg Sublobe ice.

Unit 3 sand overlies a northwest-southeast trending bedrock valley that runs through the center of TCAAP (Figure 3-6).

### 3.2.3 Topography

#### 3.2.3.1 Topography of Site C

Site C is located on a lake plane that was once occupied by ancient Lake Fridley. There is a wetland east of the site. The wetland discharges its water into Rice Creek (located to the west of the site) through a drainage channel that transects about one third of Site C from its northern boundary. The site is very flat with a gentle dip toward the drainage ditch from both the south and north.

#### 3.2.3.2 Topography of Site 129-3

No buildings or structures exist on Site 129-3. An access road was in use during the operation of the lead styphnate leaching pits but has revegetated since it was last used in 1976. The surface topography slopes gently to the northwest. Surface elevations range from about 1,055 feet above sea level at the southwest corner to about 994 feet above sea level along the northern boundary.

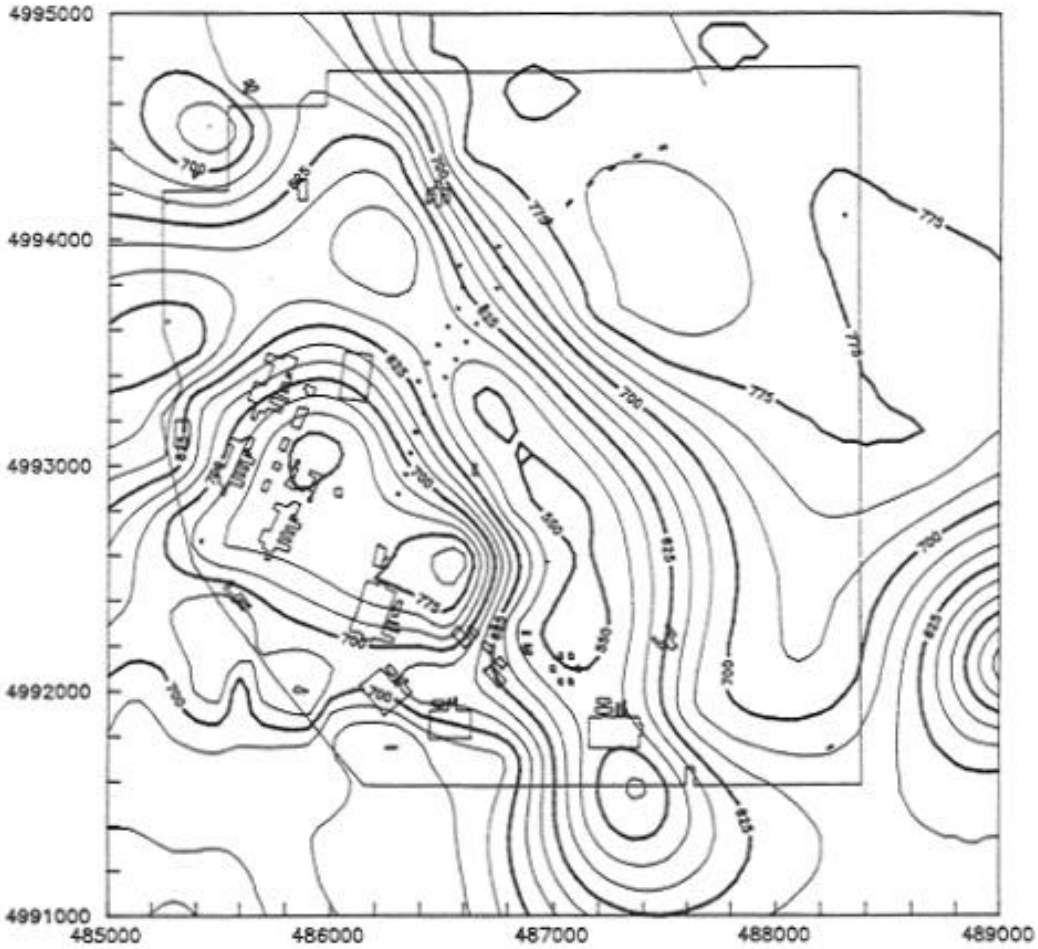



**Figure 3-6**

**Bedrock Surface Topography at TCAAP**

### 3.2.4 Soil Type

#### 3.2.4.1 Soil Type at Site C

Site C is covered by a layer of black decomposed peat, below which are fine sand and sandy clay of lacustrine origin. Oxidation is common in the fine sand and the sandy clay, resulting in molten textures and iron stains for a depth of more than ten feet.

#### 3.2.4.2 Soil Type at Site 129-3

Surface soils on the site consist of brown fine- to medium-grained sand with trace silt and gravel that grade to a light brown fine-grained sand with depth.

### 3.2.5 Hydrogeology

#### 3.2.5.1 Surface Water

With the exception of drainage basins, no surface waters exist within either Sites C or 129-3.

#### 3.2.5.2 Groundwater

Groundwater Beneath Site C - The aquifers below Site C are located in the Unit 1 and 3 formations. The depth of groundwater in Unit 1 may range from two to ten feet below the ground surface. The soils in Unit 1 consist primarily of decomposed peat overlying layers of fine silt and sandy clay of lacustrine origin with a relatively uniform depth of 12 feet. The soil has a horizontal hydraulic conductivity ranging from 0.007 to 22 feet per day, depending on the presence or absence of higher permeability lenses. If it is assumed that the hydraulic conductivity is as above, the porosity of Unit 1 is 0.3, the hydraulic gradient is 0.002, and the horizontal groundwater flow velocity ranges from 0.017 to 55 feet per year. Unit 1 obtains recharge water from the wetland east of the site. The groundwater flow direction in Unit 1 at Site C is not certain due to limited groundwater level data. However, in the area close to the drainage ditch south of the northern edge of Site C, the groundwater flow is dictated by the presence of the ditch. Water from the south and north is thought to discharge to the ditch. The groundwater in Unit 1 is conservatively estimated to flow in a generally northwesterly direction at a rate of 55 feet per year.

In Site C, the condition of the Unit 1 aquifer suggests a potential for migration of contaminants to the unconfined shallow aquifer. However, from the past data, it appears that contaminant migration in Unit 1 is negligible. The presence of organic peat and clayey soils is thought to have deterred the downward transportation of contaminants in Unit 1. Because organic carbon is an effective absorbent for VOC and clay particles for metals, the migration of VOC and metals is expected to be greatly reduced. This may explain why only slight contamination has been detected at certain wells, despite their close proximity to burning pits.

Unit 2, the Twin Cities Till Formation, ranges from 64- to 120-feet thick and underlies Unit 1. Unit 2 is not an aquifer. The clayey nature of the till restricts, if not completely stops, vertical contaminant migration to Unit 3. The downward movement of groundwater through the Unit 2 formation is estimated to range from 0.82 to 8.2 feet per year assuming:

- The vertical hydraulic conductivity of Unit 2 is the same as the horizontal hydraulic conductivity, i.e., 0.001 to 0.01 foot per day.
- The vertical hydraulic gradient is 0.8.
- The formation porosity is 0.35.

At the location of minimum thickness (64 feet), contaminants would take about eight years to pass through Unit 2. Once in Unit 3, contaminants would generally migrate horizontally toward the southwest. The rate of horizontal groundwater flow in Unit 3 has been estimated to be 333 feet per year.

Groundwater Beneath Site 129-3 - Because only two Unit 3 wells exist at Site 129-3, the local characteristics of the aquifer are not clear. Based on the Unit 3 aquifer levels at Sites D to the south and E to the north, the elevation of the aquifer beneath Site 129-3 is between 850 and 859 feet above sea level. Data specifically listing the aquifer depth at Site 129-3 were not found. Sites D and E encounter the same formation (Unit 3) and are relatively close to Site 129-3 (Figures 3-2 and 3-6). Based on an estimated average groundwater elevation of 855 feet above sea level, the groundwater is expected to be at a depth of 140 to 200 feet below ground level. The estimated average linear groundwater velocity through Unit 3 is expected to be 333 feet/year in the horizontal direction and 833 feet/year in the vertical. Groundwater movement through the underlying bedrock, Unit 4, is also expected. Unit 4 consists of the Prairie du Chien Formation. Horizontal movement of groundwater through Unit 4 is estimated at 1,241 feet/year. Vertical movement is estimated at 621 feet/year. Site 129-3 is approximately 4,400 feet upstream of the TCAAP border. Literature data indicating the direction of groundwater flow from Site 129-3 was not found. Unit 3 groundwater flow from Sites D and E is to the southwest. The direction of groundwater flow in Unit 4 is also to the southwest.

### 3.2.6 Distribution of Contaminants

#### 3.2.6.1 Distribution of Contaminants in Site C

The contaminants of primary concern at Site C are solvents, oil, grease, explosives, propellants, and metals.

Geophysical and soil gas surveys at Site C-1 consisted of the excavation of three soil trenches in former disposal and burning areas and collection and analysis of numerous soil, surface water, sediment, and groundwater samples from areas within and outside of Site C-1.[Ref. 20] The resulting data indicated that portions of Site C-1 (i.e., the 1957 pits and 1953 pits) had been used for surface burning. Semi-volatile organic compounds, which commonly occur as residues of grease and oil burning, were detected in the soil. In addition, VOCs were detected semi-quantitatively in the soil gas survey. The affected area extended from the center of Site C to its west boundary, with the highest VOC readings detected at a point immediately west of the 1953 burning pits. The vertical extent of soil contamination by VOCs in the area could not be ascertained. Existing data from Site C-1 indicate no contamination by explosives or PCBs.

Analytical data of composite soil samples collected from the 1962 Pit, located in the southeast corner of Site C, indicate a general absence of contamination by VOCs, semi-volatiles, PCBs,

and pesticides.[Ref. 20] However, heavy metals, particularly lead, arsenic, antimony, beryllium, and thallium were encountered (Figure 3-7 and Table 3-1).

Based on the characteristics of local topography and hydrogeology, contaminants at Site C-1 could migrate via surface runoff and groundwater. The surface water and sediment samples collected from the drainage ditch at a downstream point, however, were found to be relatively free of contamination, indicating that contaminants at the site are currently not migrating offsite through surface runoff.

Sampling of Unit 1 aquifer wells at the site indicates slight contamination by organics in well 0lU085, which is located within the burning area. No sign of contamination was detected in wells 0lU045 and 0lU046, which are just off the major burning areas. From the current data, it appears that contaminant migration in the Unit 1 aquifer at Site C-1 is negligible. It is possible that organic contaminants in the former burning and disposal pits are currently being confined at disposal sites because of the clayey soils and decomposed peat that are common at Site C-1.

The potential for contaminant migration to aquifer Units 3 and 4 is probably not significant. The more than 100 feet of clayey soils in Unit 2 have a tendency to restrict downward migration of pollutants. Sporadic detection before 1988 of organics in down-gradient Unit 3 wells (i.e., wells 03U025 and 03UD83) indicates that contamination may originate from other upgradient sources or that Unit 2 has not been totally effective in blocking the downward migration of a few contaminants from Site C. In any event, large-scale migration of contaminants in deeper aquifers under Site C is currently not occurring.

#### 3.2.6.2 Distribution of Contaminants in Site 129-3

The results of the soil investigations at Site 129-3 indicate that VOCs are present in the soil gas of the unsaturated soil layer beneath Site 129-3.[Ref. 20] No VOCs were detected in soil samples collected at depths up to 3 feet, suggesting a deeper VOC source. Because soil moisture content is not known for the soil in this area, it is not possible to predict the partitioning of VOCs between air, water, and soil. Once in groundwater, the VOCs are expected to move at approximately the same velocity as the average linear groundwater velocity, i.e., 333 feet/year in Unit 3 and 1,241 feet/year in Unit 4 (bedrock).

Elevated concentrations of barium, chromium, lead, and antimony have also been found in the soils at Site 129-3 (Figure 3-8 and Table 3-2). Significant metal contamination has not appeared in the groundwater to date. Soil-bearing data indicate that the metals have remained near the surface (upper 10 feet of soil) and apparently have not migrated downward. Because the adsorptive capacity of soil is a function of factors, such as mineralogy, particle size, soil moisture, pH, and conductivity, it is difficult to predict the mobility of metals in the unsaturated soil layer.

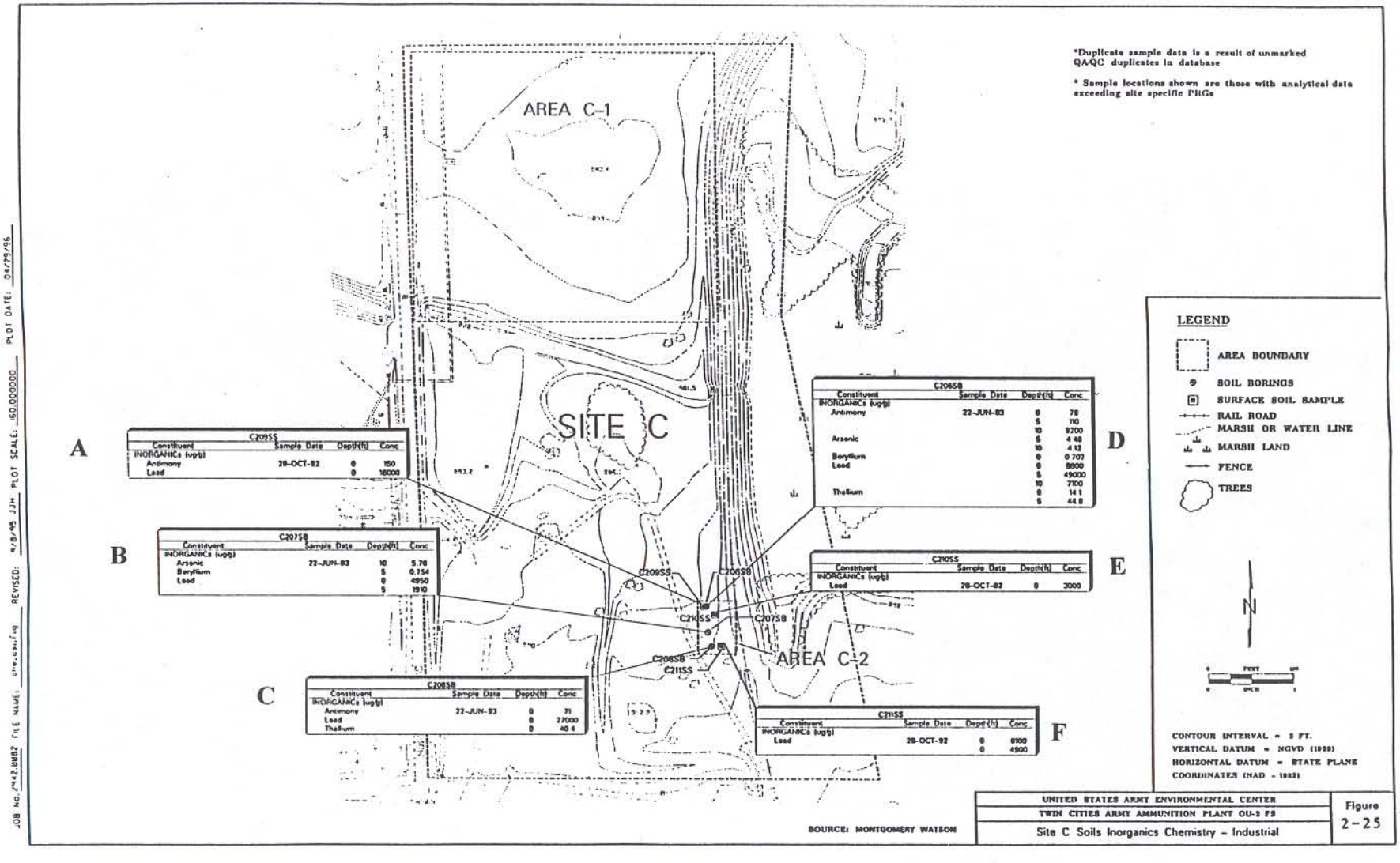



**Figure 3-7**

**Inorganic Contamination at Site C**

**Table 3-1**

**Inorganic Contaminants at Site C**

| Block No.[1] | Depth (ft) | Antimony, mg/kg | Arsenic, mg/kg | Beryllium, mg/kg | Lead, mg/kg | Manganese, mg/kg | Thallium, mg/kg |
|---|---|---|---|---|---|---|---|
| A | 0 | 150 | NA[2] | NA[2] | 16,000 | NA[2] | NA[2] |
| B | 0 | NA[2] | NA | NA | 4,950 | NA | NA |
| | 5 | NA | NA | 0.754 | 1,910 | NA | NA |
| | 10 | NA | 5.76 | NA | NA | NA | NA |
| C | 0 | 71 | NA | NA | 27,000 | NA | 40.4 |
| D | 0 | 78 | NA | 0.702 | 8,800 | NA | 14.1 |
| | 5 | 110 | 4.48 | NA | 49,000 | NA | 44.8 |
| | 10 | 9,200 | 4.12 | NA | 7,100 | NA | NA |
| E | 0 | NA | NA | NA | 3,000 | NA | NA |
| F | 0 | NA | NA | NA | 6,100 | NA | NA |
| | 10 | NA | NA | NA | 4,900 | NA | NA |

(1) References block numbers in Figure 3-7.
(2) NA = Not Applicable.

**Table 3-2**

**Inorganic Contaminants at Site 129-3**

| Block No.[1] | Depth (ft) | Antimony, mg/kg | Lead, mg/kg | Manganese, mg/kg | TCE, mg/kg |
|---|---|---|---|---|---|
| A | 10 | NA[2] | NA[2] | 1,100 | NA[2] |
| B | 0 | 40.4 | NA | NA | NA |
| C | 3 | 362 | 3,700 | NA | NA |
| D | 3 | NA | NA | NA | 120 |

(1) References block numbers in Figure 3-8.
(2) NA = Not Applicable.

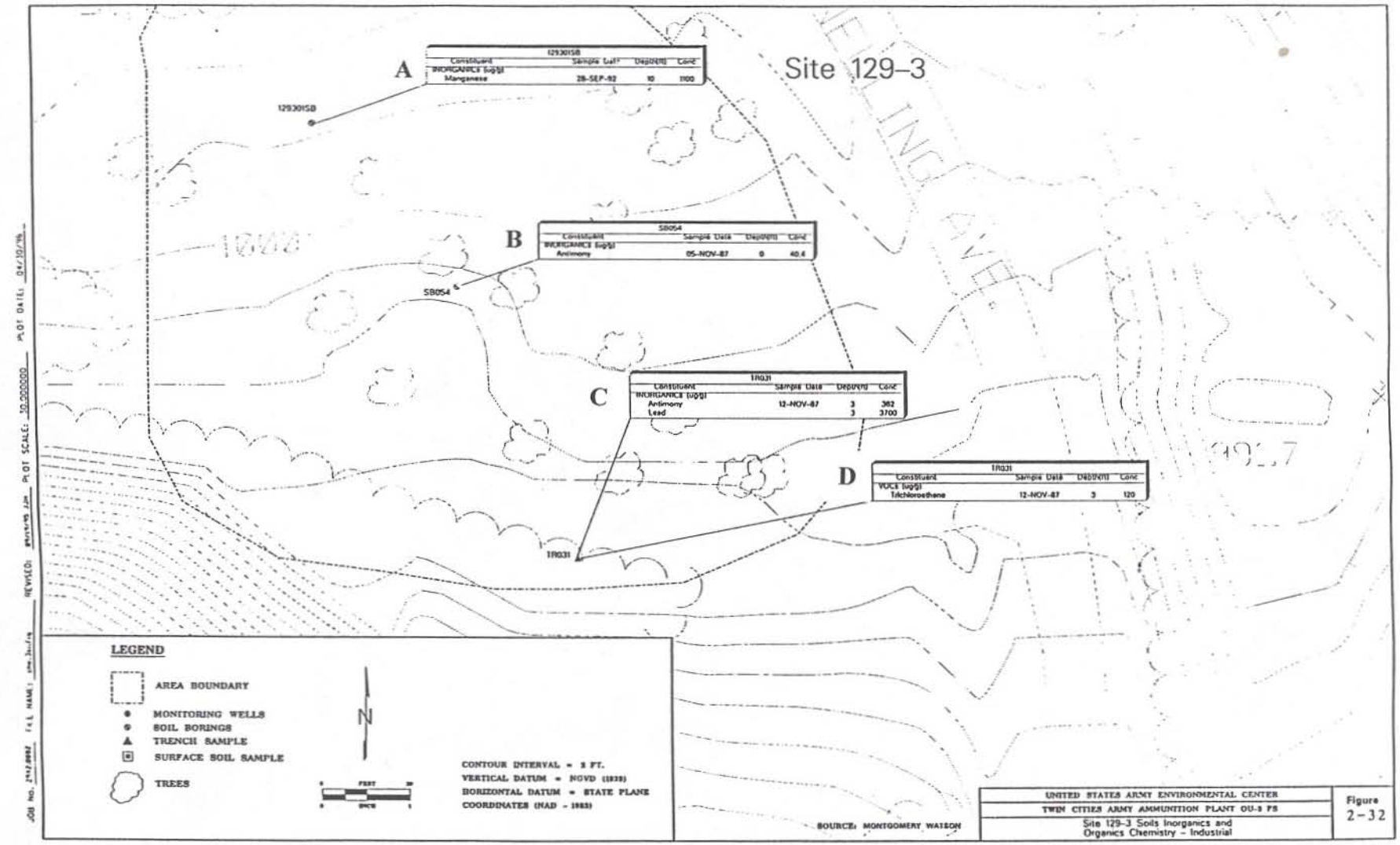



**Figure 3-8**

**Inorganic Contamination at Site 129-3**

In general, due to electrical charge imbalances, metal adsorption in soil (particularly clay) prevents metals from moving very quickly through a soil column. Once in groundwater, however, chromium and antimony are estimated to move at a velocity of 5.3 feet/year and lead at a velocity of 0.5 foot/year in the Unit 3 aquifer. In the Unit 4 aquifer, estimated velocities are 5.2 feet/year for chromium and antimony and 0.5 foot/year for lead.

### 3.3 Information Sources

The technical information presented in this section was obtained from the report "Installation Restoration Program: Remedial Investigation Report for the Twin Cities Army Ammunition Plant (Final Report)," prepared by the U.S. Army Corps of Engineers' Toxic and Hazardous Materials Agency in April 1991.[Ref. 20] Information regarding current operations was updated by ATK.

# Section 4.0
# Demonstration Approach

## 4.1 Performance Objectives

The objective of this project was to evaluate the technical and economic feasibility of *in situ* phytoextraction under the typically difficult and "dirty" conditions found at contaminated military disposal sites. The technical feasibility of the phytoremediation technology was measured by the uptake of lead by plants which, in turn, is a measure of lead removal from soil. The potential of the process to eventually meet a specific regulatory goal was evaluated. Technical criteria considered to evaluate the technology included:

- The concentration of lead in plants (corn and white mustard) after lead uptake was induced. Desired lead concentrations were 1% in corn and 2% in white mustard, based on a previous greenhouse treatability study[Ref. 2] for remediation within a reasonable timeframe.

- Crop total uptake of lead as calculated on the basis of aboveground total biomass production. At the initiation of this project, a desired biomass production target was 6 tons per acre of corn stover prior to grain production and 7 tons per acre for white mustard as cited in the literature[Ref. 6]. The 6 tons of corn stover per acre figure is approximately equivalent to 18 tons per acre of mature corn, including grain.

- The concentrations of lead remaining in the soil after each harvest. The industrial regulatory target for lead concentration at TCAAP is 1,200 mg Pb/kg soil, and the regulatory target for residential use is 400 mg Pb/kg soil. Lead concentrations at Site 129-3 are already below the industrial use standard. The demonstration at Site 129-3 was intended to illustrate remediation at lower lead levels.

- The concentration of lead in soil solutions beneath the plant rooting zone. A soil solution target concentration was not set at Site C due to elevated lead concentrations, up to 49,000 ppm, at deeper (≥3 foot) soil depths.

The performance objective for 7 tons per acre of white mustard was based on literature reference which has since been modified to approximately 2 tons per acre. Two tons per acre is probably a more realistic expectation for white mustard in a single growing season.

Economic feasibility was evaluated by cost analysis (see Section 6.0).

## 4.2 Physical Setup and Operation

### 4.2.1 Introduction

During the course of the demonstration, TVA and ATK were engaged in a number of field activities. A "field activity" is defined here to mean any activity occurring at the demonstration

site which is not directly related to the characterization of the technology performance. With respect to this project, field activities performed at the demonstration sites were:

- Site characterization
- Site preparation
- The conduct of process operations (i.e., personnel and equipment decontamination, crop planting, crop tending, soil amendment addition, crop harvesting, and crop processing.)
- Demobilization and site restoration

The demonstration was originally a three-year project, with two full years planned for cropping. Field activities at TCAAP were initiated on November 18, 1997, when TVA and ATK began to collect soil around Sites C and 129-3 as part of the preliminary site characterization program. The purpose of the site characterization program was to identify two sites which had sufficient lead concentrations to meet the project goals. Based on the preliminary assessment, a suitable site for the Site C demonstration unit was identified (Figure 4-1). However, a suitable site for the Site 129-3 demonstration was not found in the fall of 1997. All field activity was suspended in the winter of 1997/1998 due to the severity of local weather conditions. Field activities resumed in the spring of 1998 and a demonstration site for Site 129-3 was selected at that time (Figure 4-2).

Following the selection of the two demonstration sites, the sites were prepared for use. This task involved installing controlled access zones, eradicating existing grass, installing fences and irrigation systems, and a pre-operational inspection of the site.

Once the operating sites were prepared, process operations began. During this phase, field activities consisted of tilling the soil, fertilizing the soil, planting the crops, installing a soil solution monitoring system, tending of crops planted, irrigation, weeding crops, adding soil amendments, and harvesting the crops. Two crops were planted during the first year of the demonstration: a field corn (*Zea mays*) crop in the spring and a white mustard crop (*Sinapis alba*) in the late summer. One crop of silage corn was planted in the spring of the second year. The extended growing season and late harvest prevented a white mustard crop from being planted in the second year. Plans were made for planting Site 129-3 during a third year. After observing lead and EDTA in groundwater, the third year activities consisted of soil, surface water, and groundwater sampling at Site C in the early spring. Deep core soil sampling was done at Site 129-3 in 2000.

All field operations work on this project were conducted in Modified Level D or Level C personal protective equipment (PPE), as specified in the demonstration Health and Safety Plan located in Appendix B of the Technology Demonstration Plan.[Ref. 21]

### 4.2.2 Site Characterization

Prior to beginning the demonstration, AEC, ATK, and TVA selected two sites which contained suitably contaminated soils. For the site requiring a moderate level of contamination (Site C), a suitable location was defined as a 90- x 90-foot area with lead contamination levels from

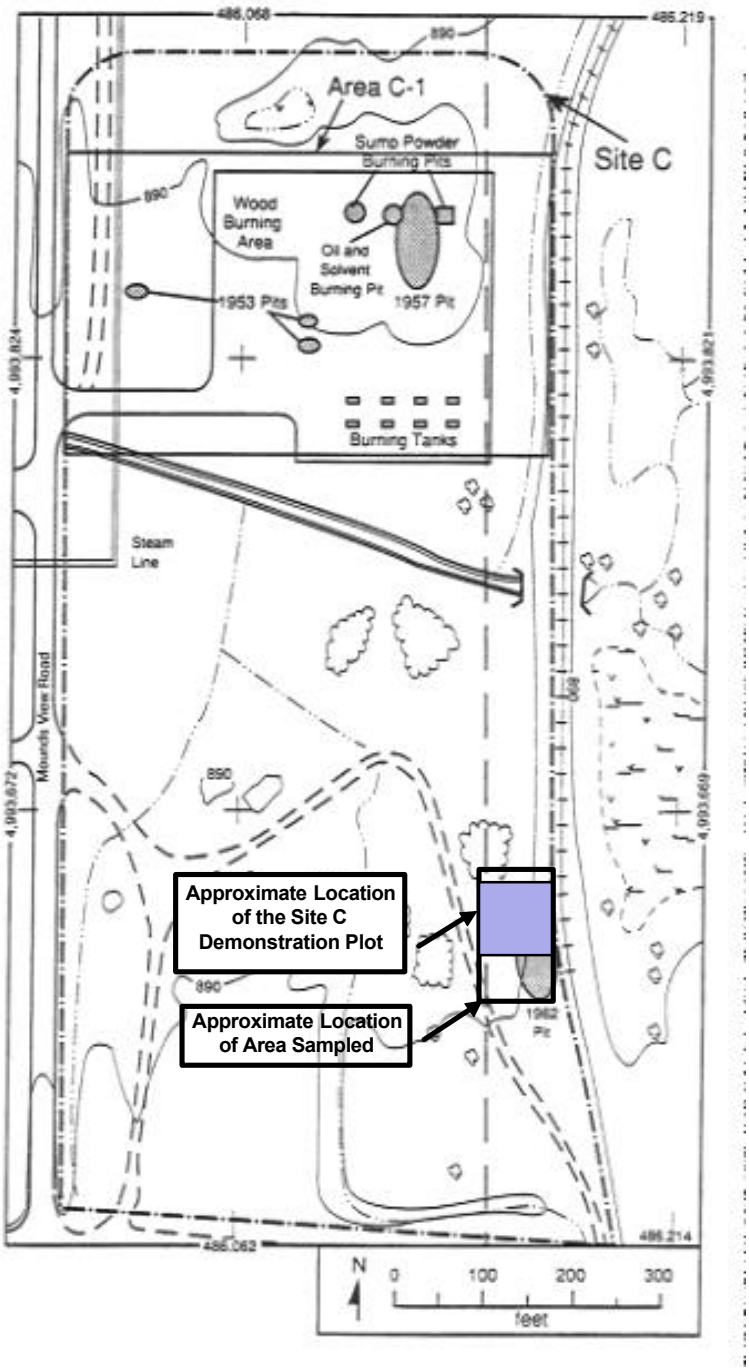
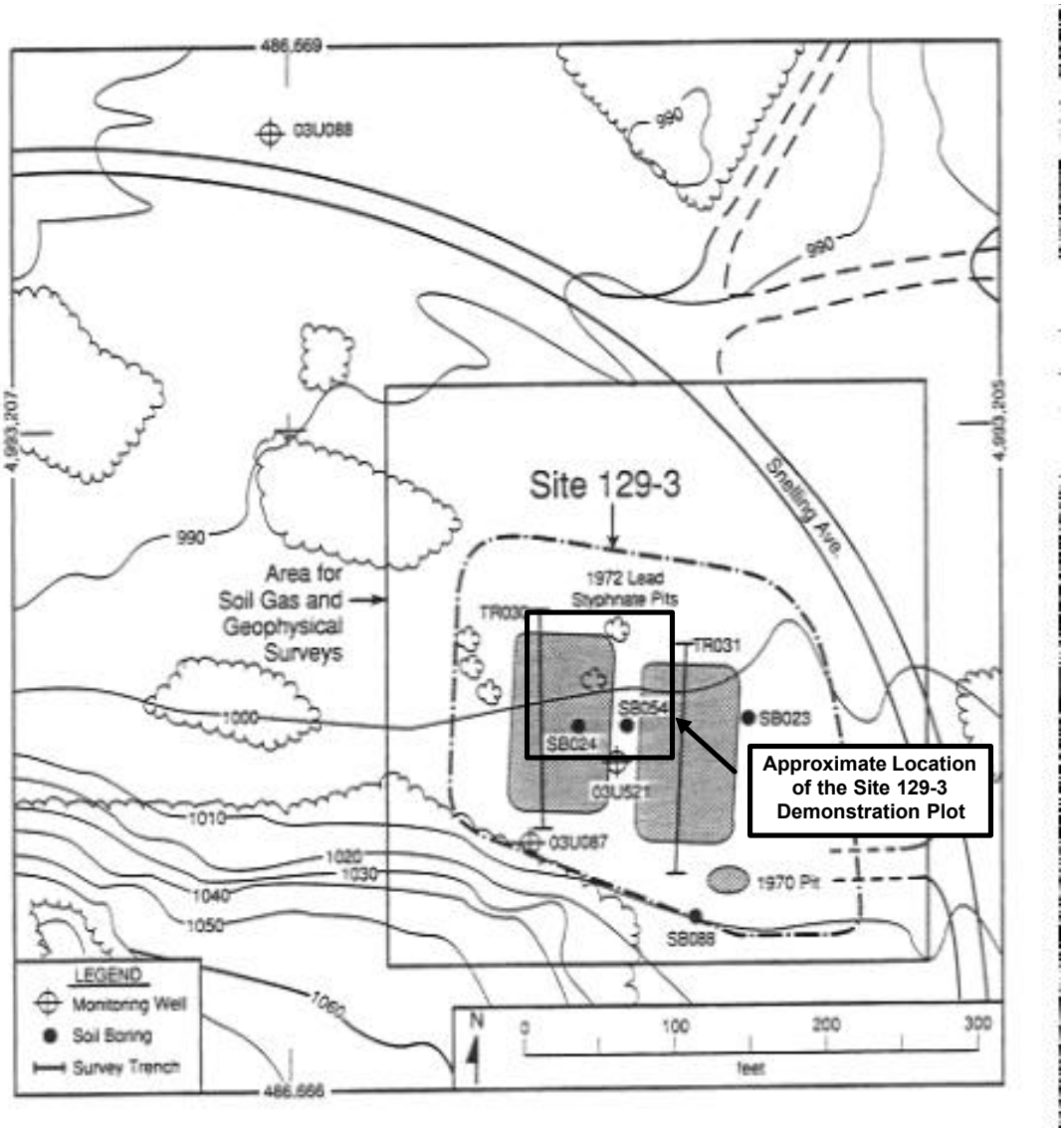



**Figure 4-1**

**Demonstration Site at Site C**




Note: The demonstration is located on the same plot of land sampled during site characterization.

**Figure 4-2**

**Demonstration Site at Site 129-3**

2,000 to 4,000 ppm in the top foot of soil. For the site requiring low levels of contamination (Site 129-3), a suitable location was defined as a 90- x 90-foot site with lead contamination levels from 400 to 700 ppm in the top foot of soil. Samples of the soil from these two sites were collected and analyzed for the purpose of characterizing (mapping) the degree of lead contamination in the immediate area. Initially, these samples were analyzed for lead content and pH (Table 4-1). After selecting the demonstration sites, the soil from each area underwent additional analysis in order to determine fertilization requirements, soil characteristics, and the concentration of other Contaminants of Concern (COC) (Table 4-2). The analytical methods used are listed in Table 4-12 (see Section 4.3.2.1).

Soil sampling was performed by TVA and ATK personnel. Safety precautions and site controls used during the sampling procedure are outlined in the demonstration Health and Safety Plan (see Reference 21, Appendix B, Section B3.2, and Table B1-1). Modified Level D PPE was worn during these procedures. The sampling procedure used at Sites C and 129-3 were as follows:

1. A selected area of Site C (Figure 4-1) was divided into two areas: Site C-North and Site C-South. Site 129-3 was sampled in only one area. The dimensions of these areas were 150 feet x 90 feet at C-North, 90 feet x 90 feet at C-South, and 90 feet x 90 feet at Site 129-3.

2. The C-North Site was subdivided into sixty 15- x 15-foot grids.

3. The C-South and 129-3 sites were subdivided into thirty-six 15- x 15-foot grids.

4. Each 15- x 15-foot grid was further subdivided into four 7.5- x 7.5-foot quadrants.

5. Each 7.5- x 7.5-foot quadrant was sampled to a depth of 12 inches by taking one soil core using a hand-held soil sampling probe. NOTE: during the winter of 1997 and spring of 1998, it was not necessary to wet the soil to prevent the production of Pb-laden dust, as per the demonstration Health and Safety Plan due to the damp condition of the soil.

6. The sample core was subdivided into two portions. One portion represented the depth from 0 inch to 6 inches and the second from 6 inches to 12 inches. Each half core had an approximate wet weight of 100 grams.

7. The quadrant samples from each grid were composited. The 0-inch to 6-inch samples, one from each quadrant of the grid, were composited by placing the four quadrant samples into a single OneZip™ plastic bag. The 6-inch to 12-inch samples from the four quadrants of each grid were composited by placing these samples into another OneZip™ plastic bag (i.e., two 400-gram samples were obtained per grid; 120 soil samples from Site C-North, 72 samples from Site C-South, and 72 samples from Site 129-3). Each plastic bag containing a 400-gram composite sample was labeled as in the following example:

| Site Demonstration Site | Grid | Sample Depth (A = 0"-6", B = 6"-12") |
|---|---|---|
| C-North | 1-60 | A or B |
| C-South | 1-36 | A or B |
| 129-3 | 1-36 | A or B |

8. After sampling all four quadrants in each 15- x 15-foot grid, the soil sampling probe was cleaned by moving to the next grid, taking a soil sample, and discarding the sample collected. The soil sample was discarded within the grid. A field blank was collected by sampling a clean area outside the plot area in the same manner in which other samples were taken.

9. Upon completion of the sampling program, hand tools and all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.

10. Field wastes were packaged in heavy-duty plastic bags and disposed of by ATK.

11. The 400-gram composite samples were packaged for shipment to the TVA Analytical Laboratory in Muscle Shoals, Alabama, in accordance with the TVA chain of custody procedures (Appendix D-17).

12. Upon receipt at TVA, the 400-gram samples were air dried by opening the plastic bag and folding down the top to permit sufficient air movement. The opened bags were placed on tables in a TVA greenhouse and allowed to dry for one week with periodic mixing of the soil in the bag.

13. Upon drying, the soil samples were analyzed for pH and total lead (Table 4-1) by the methods listed in Table 4-12 (see Section 4.3.2.1).

14. After soil from the entire area of Site C was analyzed for total lead content, a 90- x 90-foot area was selected from within Site C-North for use as the demonstration area for Site C. For Site 129-3, the original 90- x 90-foot area of Site 129-3 was selected as the demonstration plot. The soil samples taken from these plots were then further analyzed to fully characterize the site. Analyses conducted are listed in Table 4-2. The methods used are listed in Table 4-12 (see Section 4.3.2.1).

### 4.2.3 Site Preparation and Process Description

Upon completion of the site characterization work, the sites were prepared for conducting the demonstration. Tasks accomplished by ATK during this period included:

**Table 4-1**

**Chemical Analyses for the Initial Soil Characterization Work**

| Sample Type | Minimum Sample Size[1] | Parameter Measured |
|---|---|---|
| Soil | 12 grams | pH<br>Total Metals (Pb)[2] |

(1) Every twentieth sample contained twice the usual amount of sample and was submitted for use in the QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and was used to distinguish it from metals measured following a leaching process.

**Table 4-2**

**Chemical Analyses for the Full Soil Characterization Work**

| Sample Type | Minimum Sample Size[1] | Parameter Measured |
|---|---|---|
| Soil From Site C | 200 grams | Total Organic Carbon (TOC) |
| | | Total Kjeldahl Nitrogen (TKN) |
| | | Extractable P |
| | | Exchangeable K |
| | | Exchangeable Ca |
| | | Exchangeable Mg |
| | | Exchangeable Al |
| | | DTPA-Extractable Fe |
| | | DTPA-Extractable Mn |
| | | Total Metals (As, Be, Pb, Sb, Tl, Mn)[2] |
| | | Bio-Available Pb (Water-Soluble) |
| | | Cation Exchange Capacity (CEC) |
| | | Soil pH |
| | | Soil Moisture |
| Soil From Site 129-3 | 200 grams | Total Organic Carbon (TOC) |
| | | Total Kjeldahl Nitrogen (TKN) |
| | | Extractable P |
| | | Exchangeable K |
| | | Exchangeable Ca |
| | | Exchangeable Mg |
| | | Exchangeable Al |
| | | DTPA-Extractable Fe |
| | | DTPA-Extractable Mn |
| | | Total Metals (Pb, Sb, Mn)[2] |
| | | Bio-Available Pb (Water-Soluble) |
| | | Cation Exchange Capacity (CEC) |
| | | Soil pH |
| | | Soil Moisture |

(1) Every twentieth sample contained twice the usual amount of sample and was submitted for use in the QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and was used to distinguish it from metals measured following a leaching process.

- Installation of controlled access zones
- Mowing grass
- Eradication of existing vegetation within the plots
- Installation of fences
- Installation of sprinkler irrigation systems
- Pre-operational site inspection
- Installation of the soil solution monitoring system (just after planting the 1998 corn crop)

The site preparation work began in mid-March 1998. The first task was the installation of the controlled access zones for the sites. Initially, these zones consisted of a support zone (SZ), a 150- x 180-foot exclusion zone (EZ), and a contamination reduction zone (CRZ) [Figure 4-3]. A 30- x 30-foot CRZ was recommended; however, exact dimensions of the CRZ were left to the discretion of TVA and ATK Health and Safety officers. The EZ consisted of an area 15 feet outside the area where the 120- x 150-foot demonstration site fences were placed. The CRZ consisted of an area outside the area to be fenced, close to the intended location of the fence exit, and upwind of the fenced area.

The SZ consisted of all areas outside the EZ and CRZ. This work was conducted using Modified Level D PPE. Upon setting up the controlled access zones, the area within the EZ and CRZ was mowed. Mowing was conducted using Level C PPE.

Upon clearing the sites, the grass in the 90- x 90-foot farm plots was eradicated with an application of Roundup™ (glyphosate) [Figure 4-3]. These activities were conducted using Level C PPE. Upon completion of these activities, all tools and equipment were decontaminated in accordance with the TCAAP Health and Safety Plan and the demonstration Health and Safety Plan.

After applying the Roundup™, a fence was installed around each of the demonstration sites. Each fence consisted of a 120-foot-wide x 150-foot-long x 8-foot-tall fence with a single exit (Figure 4-4). The sides of the fence consisted of heavy netting. The exit consisted of a gate made of the same netting material. The gate opened outward (away from the interior of the fence). The exit was located on the 120-foot fence wall located furthest from the farm plots. Signs were posted on each exterior wall of the fences reading:

**Warning**
**Lead-Contaminated**
**Soil**
**Poison**

The installation of the fences was conducted using both Modified Level D and Level C PPE. Level C PPE was used for all tasks requiring soil disturbance. All other activities were conducted using Modified Level D PPE. Upon completion of these activities, all tools and equipment were decontaminated by brushing the contaminated soil off the tools and equipment.

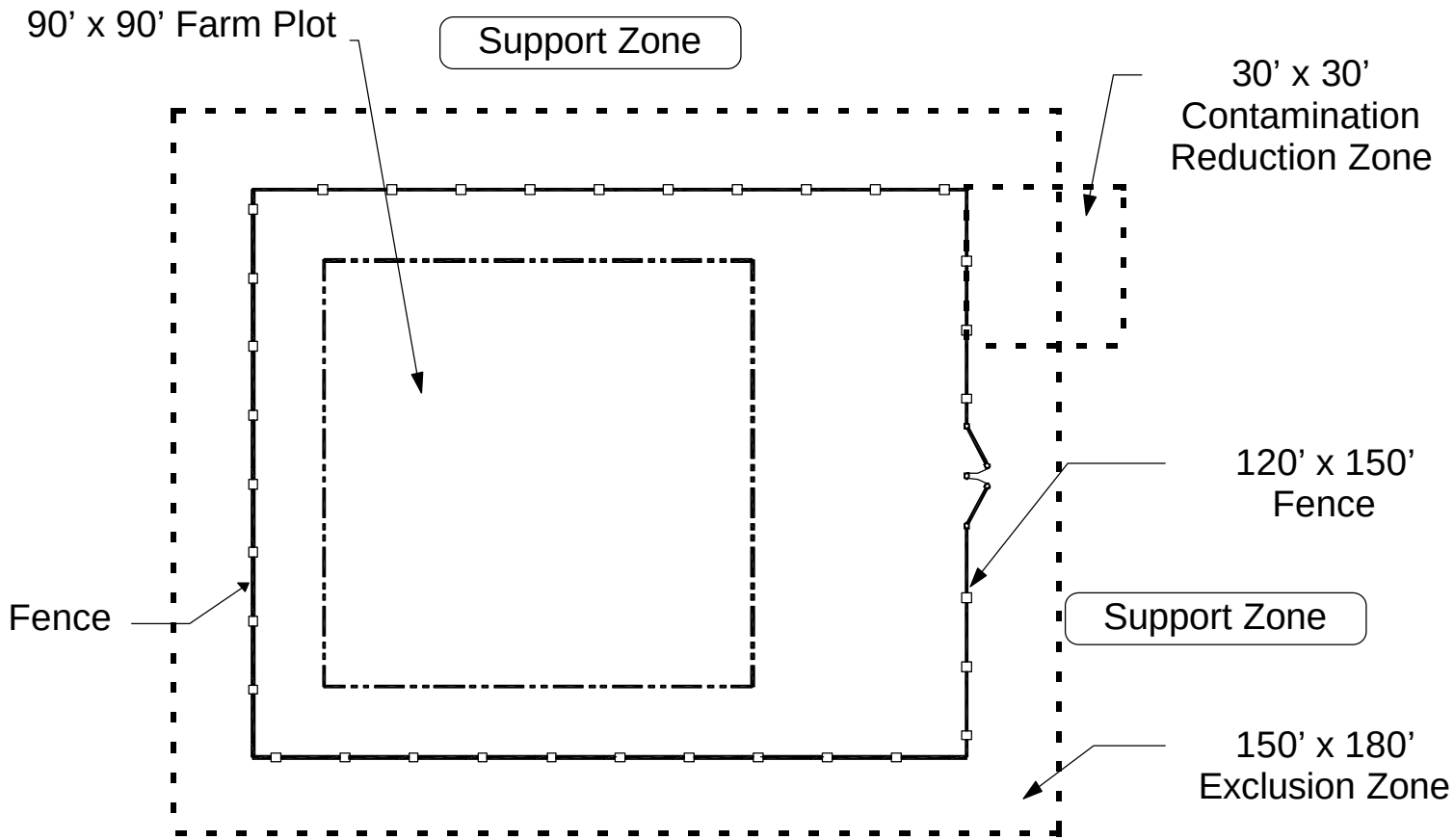



**Figure 4-3**

**Layout for the Initial Site-Controlled Access Zones**

The contaminated soil was swept up and returned to the demonstration plots. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.

Upon completion of the fences, the EZ was moved. The new EZ consisted of the area within the fence located within 15 feet of the 90- x 90-foot plots (Figure 4-5) and was located totally within the fence. The farm plots were located such that the edges of the plots were 15 feet away from the fences. The Work Zone (WZ) was located inside the fence and the CRZ was located immediately outside the fence since the entire area is a CERCLA site. Repositioning of the EZ zone was conducted using Modified Level D PPE.

Upon repositioning the EZ zones, the irrigation systems were installed. These were sprinkler systems supplied by existing water sources located near the demonstration sites. The irrigation systems distributed water over the surface of the farm plots according to the needs of the crop. TVA designed the irrigation system and ATK constructed and installed the system. Modified Level D PPE was used for tasks not requiring soil disturbance. Level C PPE was required for tasks involving soil disturbance. Upon completion of these activities, all tools and equipment were decontaminated by brushing the contaminated soil off the tools and equipment.

The contaminated soil was swept up and placed inside the demonstration plots. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.

After installation of the irrigation system, ATK conducted a visual pre-operational inspection which verified that:

- The sprinkler irrigation systems and related subsystems were functional.
- The fences were in good order and were equipped with the proper signs.
- All tools were removed from the site.
- The controlled access areas were delineated.
- The demonstration fences were properly secured.

At that time, ATK conducted safety inspections in accordance with the TCAAP Health and Safety protocols.

The final site preparation task, installation of the soil solution monitoring systems, was conducted just after planting the 1998 corn crop. A soil solution monitoring system was installed at each demonstration site. Each soil solution monitoring system consisted of 12 porous cup suction lysimeters arranged in three diagonal lines across a 90- x 90-foot plot (Figure 4-6). The soil solution monitoring systems were installed to determine if soil amendments caused the movement of heavy metals and/or EDTA into the soil below the 2-foot sampling depth. Since trichloroethylene (TCE) had been reported as a possible contaminant at Site 129-3, one lysimeter

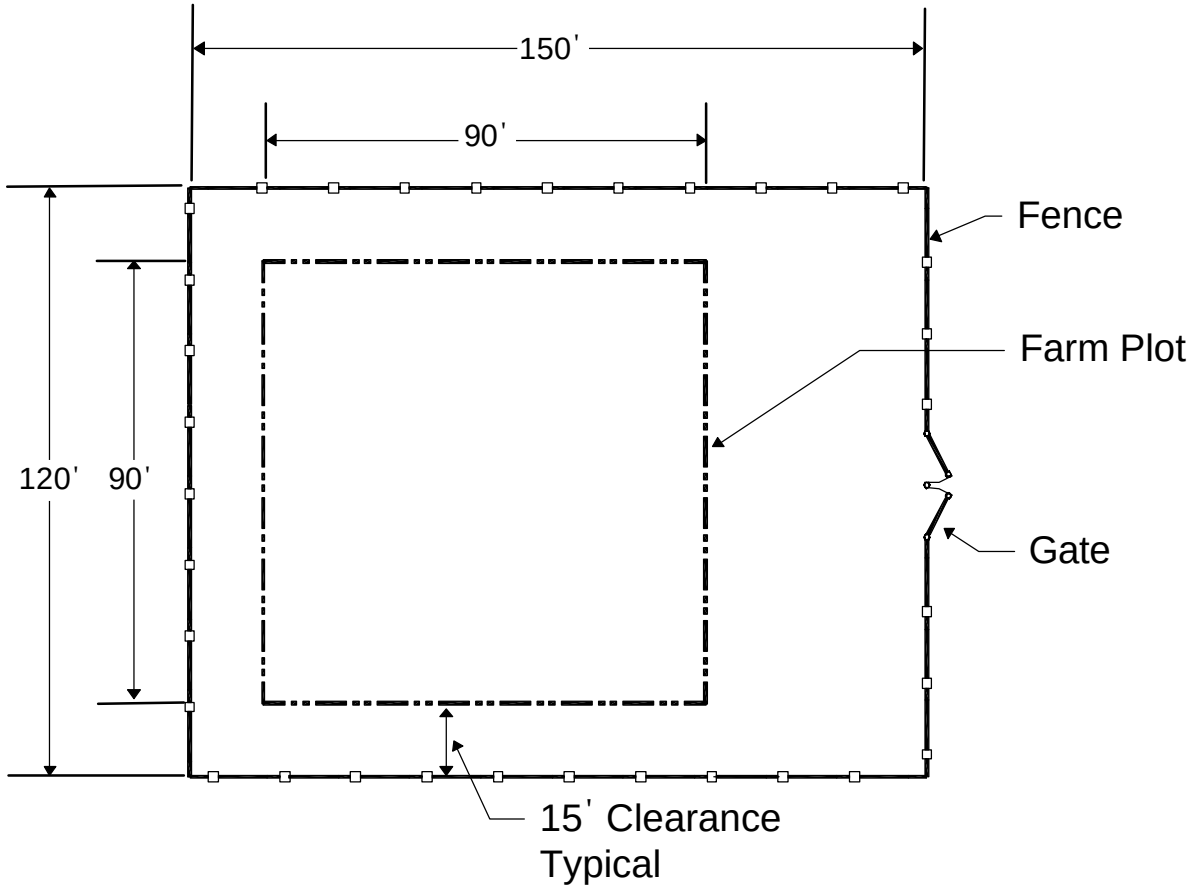



**Figure 4-4**

**Layout of Demonstration Sites**

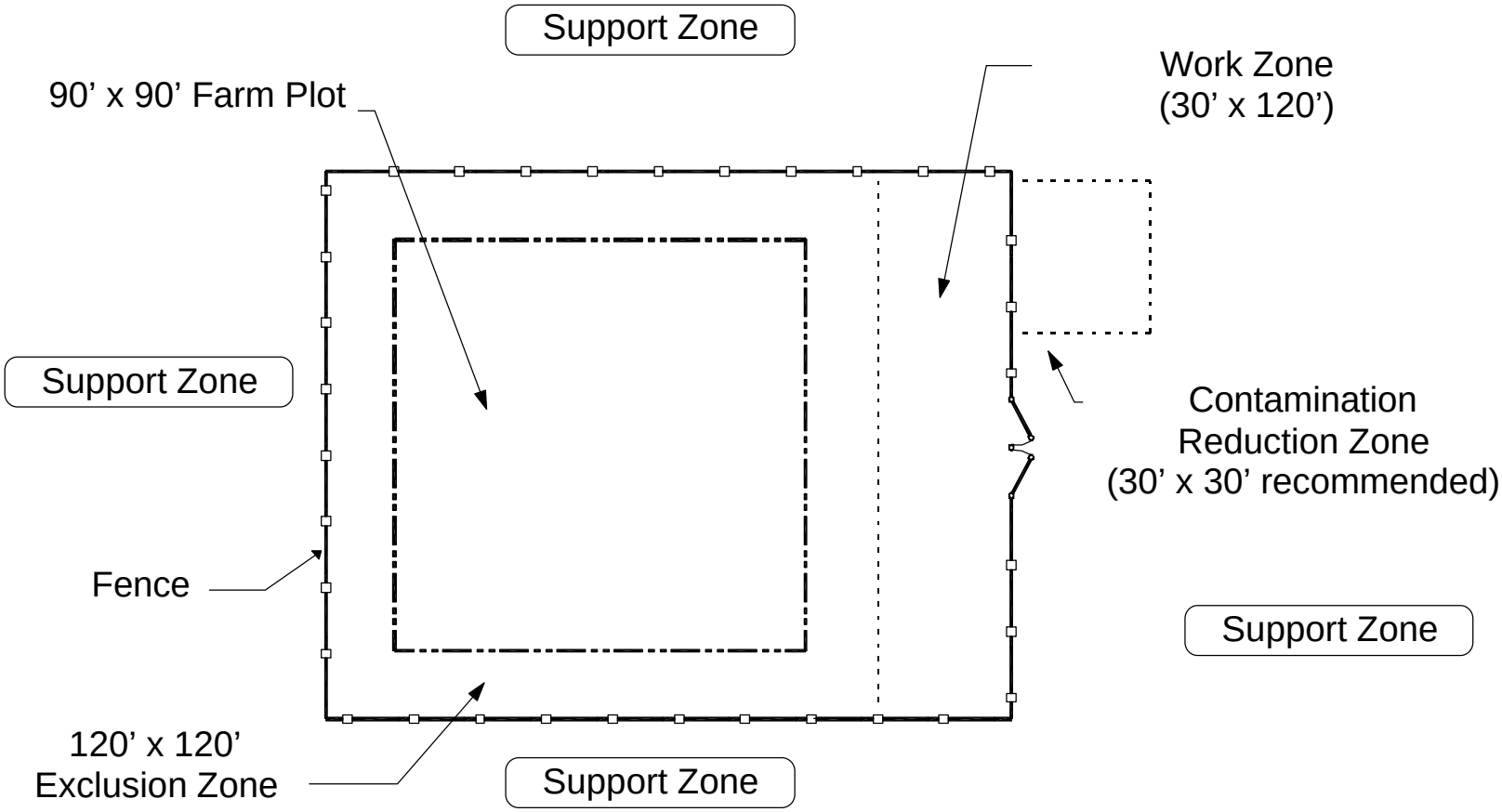



**Figure 4-5**

**Layout for the Final Site-Controlled Access Zones**

at Site 129-3 was dedicated to monitoring potential movement of trichloroethylene. This was done even though the reputed source of trichloroethylene was downslope from the actual plot area.

A power auger was used to create a hole for each lysimeter. Soil recovered by the auger was placed in a bucket and mixed with water and silica flour to create a paste (1 part soil to 1 part water to 1 part silica flour). Next, sufficient paste to fill the annular space between the lysimeter and the hole was poured down the hole. The lysimeter was then placed in the hole. Approximately two inches of the annular space at the top of the lysimeter was re-excavated manually and plugged with a separate paste made with bentonite clay to prevent water infiltration from the surface into the lysimeter. The purpose of the bentonite plug was to provide a water- and air-tight seal. Any paste remaining in the buckets was poured onto the surface of the 90- x 90-foot plot.

Each porous cup suction lysimeter consisted of a 2-inch diameter inert polyvinyl chloride (PVC) tube, approximately 60 inches in length, with a rubber stopper attached at the top of the tube and a porous ceramic vessel (cup) attached at the bottom (Figure 4-7). A small glass tube passed through the center of the rubber stopper and PVC tube and ended just short of the bottom of the cup. When positioned in the soil, the top of the lysimeter was one foot above the soil surface and the bottom lay approximately 48 inches below the soil surface. To obtain a soil solution sample for metals analysis, suction was applied to the glass tube at the surface, which caused water from the soil to move into the porous cup. The solution collected in the porous ceramic cup then flowed though the glass tube to the surface where it was collected in a Buchner side arm suction flask. A hand-held, battery-powered drill with pump attachment was used to create the suction.

The lysimeters were installed using Level C PPE until air monitoring showed that Level D PPE was appropriate. The air monitoring was performed on June 3, 1998, and consisted of one sample collected in the morning and one sample collected in the afternoon. Under the sampling conditions (digging and rototilling), lead exposure was well below the current OSHA PEL and Action Limit, thus, the use of respirators was discontinued. ATK personnel were responsible for installation of the lysimeters. Upon completion of these activities, all tools and equipment were decontaminated by brushing the contaminated soil off the tools and equipment and rinsing the buckets. Any contaminated soil recovered during decontamination was swept up and returned to the demonstration plots. Upon leaving the site, all personnel involved in the installation underwent decontamination in accordance with the demonstration Health and Safety Plan.

### 4.2.4 Process Operations

#### 4.2.4.1 1998 Demonstration

##### 4.2.4.1.1 1998 Crop Planting

Two crops were planted during the first year of the two-year demonstration. Corn (*Zea mays* cv. Mexican June) was planted May 11, 1998, and white mustard (*Sinapis alba*) on August 17, 1998.

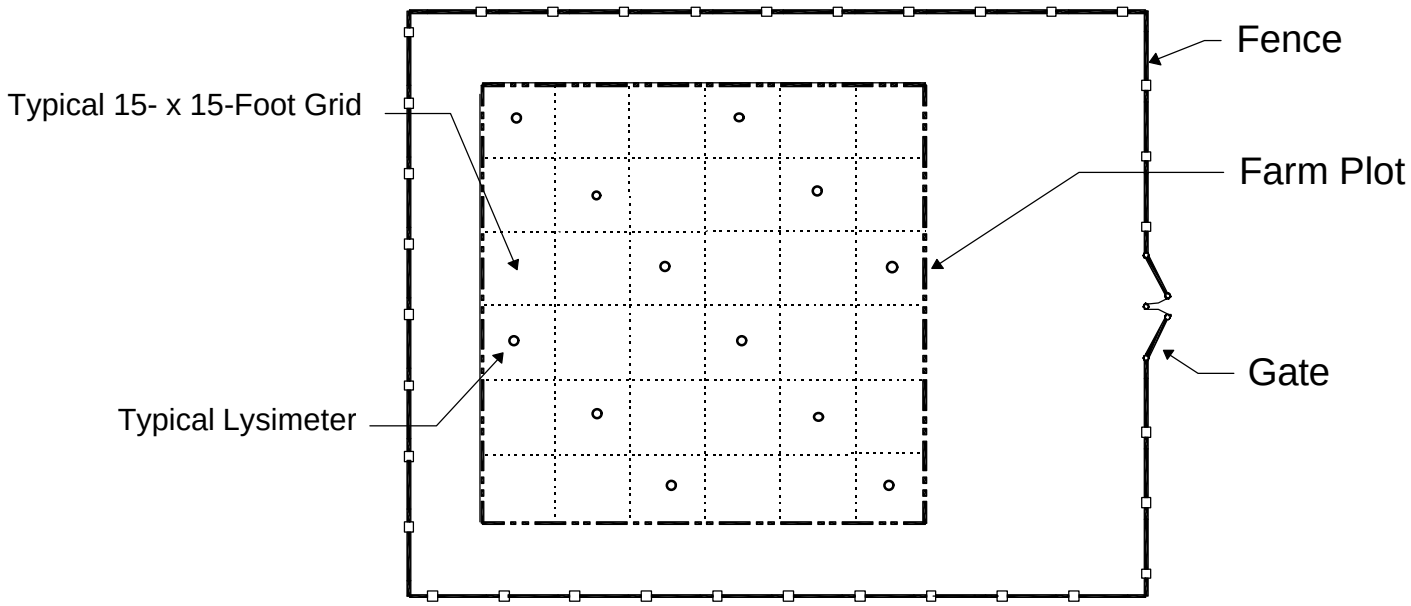



**Figure 4-6**

**Position of Lysimeters in a Soil Solution Monitoring System**

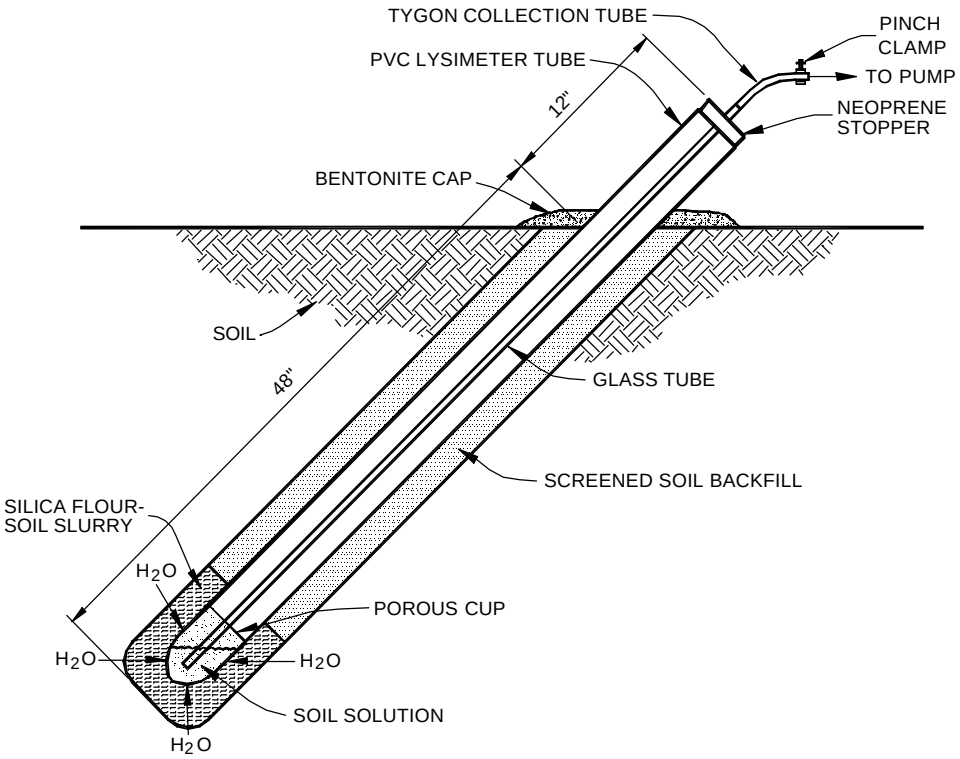



**Figure 4-7**

**Diagram of a Lysimeter**

Tasks accomplished during the planting periods included:

- Tilling the soil
- Removing debris and cobbles from soil
- Fertilizing the soil
- Planting the crop
- Irrigating the plots

Soil tilling was done using a Rototiller or tractor with a power takeoff (PTO) Rototiller attachment. Soil tilling was conducted using Level C PPE. ATK personnel tilled the soil.

Following tilling, the soil was fertilized with granular nitrogen (N), potassium (K), and phosphorus (P) fertilizer. The fertilizer was applied either by hand application or with a drop-type spreader, depending upon the amount to be applied. All fertilizers were applied at agronomic rates for the specific crop, taking into account the amount of nutrient already present in the soil (based on soil analyses), and the removal rates of each nutrient from the soil by each crop. The fertilizer for corn was applied in a split application to optimize fertilizer use by the crop and to prevent movement of unused fertilizer out of the root zone. A split application is one of two equal applications of the granular nitrogen and potassium fertilizers in which each application is applied at one-half of the recommended agronomic rate. The first application was applied to the soil just before planting and the second application was made midway through the growing season (at approximately four weeks for corn). Due to the planting method used for white mustard (broadcast seeding), this crop was fertilized as a single application during planting. Soil fertilization was conducted using Modified Level D PPE. ATK and TVA personnel performed fertilization tasks.

The nitrogen fertilizer used for corn was ammonium nitrate ($NH_4NO_3$, 34% N) applied at a N rate of 150 pounds per acre (88 pounds of $NH_4NO_3$ to provide 30 pounds of N per plot). The potassium fertilizer was potassium sulfate ($K_2SO_4$ - 45% K) applied at a K rate of 150 pounds of K per acre (67 pounds of $K_2SO_4$ to provide 30 pounds of K per plot). Additionally, a small amount of phosphate fertilizer in the form of triple superphosphate (TSP-21% P) was band-applied as a "starter" fertilizer for corn on Site C at a rate of 14 pounds of TSP per 0.2-acre plot to provide 3 pounds of P per plot (15 pounds of P per-acre basis). Corn is more susceptible to phosphate deficiency than mustard, and phosphate levels in soil at Site C were very low (16 pounds per acre available P). The corn crop developed signs of phosphate deficiency early in the season (purple coloration of the stems and leaves) and two foliar applications of a 0.5% P solution were made to correct the problem. Phosphate was soil-applied for corn only at Site C. Phosphate levels at Site 129-3 were sufficient for corn, and no additional phosphate was applied for that corn crop. In addition, the corn at Site C exhibited iron deficiency (interveinal chlorosis - a whitening of the leaf between the leaf veins) three weeks into the growing season. This was corrected by a foliar application of a 2% iron sulfate solution.

Granular (prilled) urea (44% N) was used as the nitrogen fertilizer for white mustard at a rate of 260 pounds N per acre (118 pounds of urea for 52 pounds of N per plot). The potassium source was potassium sulfate applied at a rate of 150 pounds K per acre (67 pounds potassium sulfate to

give 30 pounds K per plot). The N and K were applied at the same rate for both Site C and for Site 129-3. However, at Site C, phosphate fertilizer was applied at a rate of 100 pounds of TSP per plot to give 21 pounds P per plot (105 pounds of P per acre); at Site 129-3, the P rate was 50 pounds TSP per plot (55 pounds of P per acre).

Planting was done after fertilization. Corn was planted by hand using a push-type hand planter equipped with a seed plate for large-seeded crops. White mustard was planted using a hurricane seeder for small-seeded crops. Planting was conducted using Modified Level D PPE.

Immediately after planting, the plots were irrigated with ½-inch of water to prevent 'burning' of emerging plant seedlings. Soil irrigation was conducted using Modified Level D PPE. ATK personnel irrigated the soil.

TVA supplied all seed, pesticides, and fertilizer for use throughout the project. TVA also provided guidance during the planting and fertilization phases of the project.

**4.2.4.1.2 1998 Crop Tending**

Tasks accomplished during the crop-tending periods included:

- Inspecting the crops
- Cultivating soil and weeding (corn crop only)
- Applying foliar iron and phosphate fertilizers, pesticides, fungicides, and herbicides (as required)
- Fertilizing the soil (second half of split application for corn)
- Irrigating the crops

Both the corn and white mustard were tended on a weekly basis.

As indicated above, two crops were grown. Corn was grown for a total of 10 weeks (9 weeks to achieve crop maturity followed by 1 week after soil amendment addition). White mustard was scheduled to be grown for a total of 7½ weeks (7 weeks to maturity plus 2 days after soil amendment application). However, poor germination of white mustard, particularly at Site C, necessitated two additional spot replantings. Therefore, the white mustard crop was not at the same stage of growth over the entire plot area at the end of the 7-week growth period.

Crop inspection consisted of examining the crop and recording significant observations. Items to inspect included, but were not limited to:

- The condition of the crop including:
  - The appearance of predatory insects
  - The appearance of fungi or other plant diseases
  - The impact of unusual weather conditions on plants (i.e., drought, frost, or hailstorm damage, etc.)
  - Unusual color
  - Evidence of wildlife intrusion

- Presence of weeds

- The condition of the surrounding fence, including verification that the fence was intact

- The mechanical condition and maintenance requirements of the irrigation subsystem

Observations made during inspections were recorded in a logbook. Inspections were conducted using Modified Level D PPE. ATK personnel made the inspections. TVA personnel provided assistance with interpreting inspection results and developing an appropriate response to unusual conditions, i.e., P deficiency, lodging (i.e., storm knockdown of vegetation), pestilence, peculiar coloration, etc.

The corn crop was cultivated once with a Rototiller. Cultivation consisted of tilling the soil between the corn rows to minimize weed growth. Since the white mustard crop was solid broadcast-seeded instead of planted in rows, no cultivation was required for that crop. Cultivation for corn was conducted using Level C PPE. ATK personnel cultivated the corn crop.

ATK consulted with TVA on the need to apply foliar iron and phosphate fertilizers, since inspection of the corn crop indicated the iron and phosphate deficiencies in the early stage of growth. Fertilizer solutions (0.5% phosphate and 1% iron) were manually applied using a hand sprayer. Solutions were applied by ATK personnel.

The second half of the split fertilizer application for corn was conducted four weeks after planting the corn crop on June 8, 1998. The fertilizer was applied in a manner identical to that described above for fertilization during planting (Section 4.2.4.1.1). Soil fertilization was conducted using Modified Level D PPE. ATK personnel applied fertilizer to the corn crop.

Both crops were irrigated (watered) so that the plots received at least one inch of moisture per week, or according to the needs of the crop. This was done in two applications of ½ inch per week. To determine if a plot needed watering, a rain gauge was installed at each demonstration site and the amount of natural rainfall was measured. If supplemental moisture was required, irrigation was conducted using the irrigation system installed on each farm plot. ATK, in consultation with TVA, determined when to discontinue and restart artificial irrigation. Irrigation was conducted using Modified Level D PPE. ATK personnel were responsible for irrigating the crops.

#### 4.2.4.1.3 1998 Soil Amendment Addition

After the corn and white mustard crops reached a full vegetative state, acetic acid and EDTA for corn, and EDTA only for white mustard, were applied to the soil to solubilize heavy metals. For corn, acetic acid was applied first followed immediately by the EDTA. Soil amendment additions to corn were completed the week of July 20, 1998, after pre-amendment sampling. Pre-amendment sampling activities for white mustard were completed on October 7 and 8, 1998. Soil amendments were added on October 9 and 10, 1998.

Acetic acid was applied to acidify the soil to a pH of 5.5. The amount of acetic acid needed was calculated from buffer curves determined on bulk soil collected from the sites. The volume of acetic acid solution applied was sufficient to bring the soil to field capacity to a depth of two feet, assuming uniform movement of water down through the soil. Field capacity is the percentage of water remaining in a soil 2 or 3 days after having been saturated and after free drainage has practically ceased. The application rate of acetic acid at both Site C and at Site 129-3 was 4,018 pounds per plot. The application was hand-applied using a hose applicator connected to a 5,000-gallon stainless steel tanker truck.

The EDTA was added to optimize the solubilization of lead in the first two feet of soil (root zone). EDTA was dissolved in a solution of potassium hydroxide to form the potassium salt in order to obtain the desired concentration of EDTA for application to soil. The potassium salt of EDTA is preferred to other salts, such as sodium, since a previous greenhouse study[Ref. 2] showed that use of the potassium salt of EDTA did not affect the physical structure of soil and considerably reduced the risk of poor seed germination and poor plant growth associated with the sodium salt. The EDTA was added on an equimolar (i.e., 1:1) basis of EDTA to the average total lead concentration (about 3,100 ppm) in the plot. Although higher amounts of EDTA were added in greenhouse tests (1.5:1 EDTA to lead), this amount was considered to be excessive in this field situation and the ratio was maintained at 1:1 EDTA:lead. At Site C, the EDTA application rate was 6,750 pounds for corn and 3,375 pounds for white mustard. This was determined by calculating the average number of moles of soil lead from the average soil lead concentration [i.e., 3,140 ppm ÷ 207.2 (molecular weight of lead) = 15.2] and matching with an equal number of moles of EDTA (i.e., 6,750 lb EDTA ÷ 445 (molecular weight $K_3EDTA \cdot 2H_20$ that was used) = 15.2 moles EDTA). The rate for white mustard was reduced by half to account for reduced plot coverage due to poor stand establishment that occurred with white mustard at this site. The application rate for both crops at Site 129-3 was 850 pounds. The lower rate at Site 129-3 resulted from the lower average soil lead concentration at that site. Applications to the corn crops were made with the same equipment used for application of acetic acid.

EDTA application to the white mustard crop was made through drip delivery systems installed on Site C and on Site 129-3 prior to planting the white mustard crop. The system at Site C consisted of a 90-foot-long main header across the south end of the field with 90-foot-long strips of drip tubing attached every two feet along the length of the header. These strips extended northerly across the entire field and provided the means for chelate delivery for the white mustard. The system was the same at Site 129-3, except that the header was placed on the north end of the field and drip tubing extended from it across the demonstration area in a southerly direction.

Soil amendment activities were conducted using Level C PPE. TVA determined the amounts of soil amendments to be applied based on the lead content, buffering capacity, and field capacity of the soil, and conducted the field applications with assistance by ATK.

#### 4.2.4.1.4 1998 Crop Harvesting and Processing

After senescence due to excessive lead uptake (and possibly coincident uptake of EDTA which resulted in an ion imbalance within the plant), the corn and white mustard crops were sampled for analysis of lead and other COCs (see Section 4.3.2.1), then the entire crop was harvested for processing. Post-amendment sampling and harvest for corn was conducted the week of July 27, 1998. Post-amendment sampling and harvest for white mustard was conducted beginning on Octbober 14, 1998. In addition to lead, COCs at Site C included arsenic (As), beryllium (Be), manganese (Mn), antimony (Sb), and thallium (Tl). COCs at Site 129-3 were lead, manganese, and antimony.

Harvesting consisted of the following tasks:

- Placing plastic tarps in the WZ
- Cutting the plant shoots
- Air-drying the plant shoots
- Transporting the plant shoots to a smelter
- Weighing the shoots
- Smelting the shoots

After crop senescence, plants were cut and placed on plastic tarps in the WZ and allowed to dry over a 5- to 7-day period. The corn was cut by holding the plant to ensure it did not contact contaminated soil and cutting the stalk near the base using a corn knife. The white mustard was cut down with a bladed weedeater. Tarp placement activities were conducted using Modified Level D personal protective equipment. Cutting activities were conducted using Level C personal protective equipment. ATK and TVA personnel conducted these activities.

After air-drying, random grab samples were taken for analysis of moisture content to determine yields, and the crops were loaded onto a truck for transportation to the smelter. The smelter was Gopher Resource Corporation, located at 3385 South Highway 149, Eagan, Minnesota. At Gopher Resource Corporation, the loaded truck was weighed, unloaded, and reweighed. These activities were conducted using Level C personal protective equipment. ATK reported the crop weight to TVA and recorded it in the ATK logbook. Truck-loading activities were conducted using Modified Level D personal protective equipment. ATK personnel conducted these loading activities. Gopher Resource Corporation personnel conducted the unloading activities and were responsible for truck decontamination. Upon arrival at the Gopher Resource Corporation, the crops were processed by smelting, and "Certificates of Waste Material Consumption" were provided to ATK to document this phase of operations.

After harvesting the warm season corn crop, the soil microbial activity was stimulated by irrigating and tilling the soil in cycles to encourage the degradation of residual EDTA. Each irrigation/tillage cycle consisted of first irrigating the soil with ½ inch of water and then cultivating (tilling) the soil with a tractor equipped with a power takeoff Rototiller attachment. Three irrigation/tillage cycles were performed prior to planting the white mustard. Each irrigation/tillage cycle was conducted at least three days apart. Irrigation activities were conducted using Modified Level D personal protective equipment. Tilling activities were

conducted using Level C personal protective equipment. ATK personnel conducted both of these activities.

#### 4.2.4.2 1999 Demonstration

##### 4.2.4.2.1 1999 Crop Planting and Tending

The initial planting attempt was made on May 3, 1999, with a silage corn variety (Novartis Mycogen 345 hybrid). The silage variety was used instead of the previous grain variety in an attempt to improve biomass yields and rooting depth and density. Planting was done with a Covington one-row tractor-pulled planter. Seed was planted on 15-inch row spacings (12 rows per fifteen foot grid) for a desired plant population of 180 plants per grid. Heavy rainfall interrupted planting, however, and subsequent periods of heavy rainfall thereafter prevented completion of planting until May 26-27. The data in Table 4-3 shows that precipitation was 3.17 inches above normal during May 1999. Even though precipitation was about normal for June, actual conditions at the sites stayed wet and unfavorable for good crop growth. Temperatures were cool at planting, during germination, and during seedling emergence, causing low germination, poor stand establishment, and reduced growth rates. Extensive bird damage greatly reduced the plant population at both sites, and several replantings during June resulted in a stand of various growth stages.

Stalk counts (Tables 4-4 and 4-5) were taken at both plots immediately prior to amendment addition to determine growth stages and the reduction in plant coverage. At Site C, these measurements were taken in the eastern half of the plot only, since growth in the western half of the plot was very poor and non-uniform. Of the eastern half, there was sufficient growth only on the eastern-most third of that area to justify amendment application. Stalk counts and plant heights were recorded for the grids to be treated and sampled at Site C. At Site 129-3, only 2 grids (1 & 2) had sufficient plant population for soil amendment applications and sampling.

At Site C, fertilizers were applied at the following rates: N - 200 pounds/acre as ammonium nitrate; K - 150 pounds per acre as potassium sulfate; P - 44 pounds per acre as triple super phosphate. Nitrogen and K fertilizers were broadcast-applied and tilled in, and P was band-applied at planting two inches below the seed row. Fertilizer rates at Site 129-3 were the same, except P was decreased to 31 pounds per acre. The N and K fertilizer at both sites was applied as a two-way split application, with half being applied at planting, and the rest applied approximately 4 weeks later.

No mustard crop was planted in 1999 because of the extended growing season and the late harvest of the corn.

##### 4.2.4.2.2 1999 Soil Amendment Addition

At Site C, soil amendments (acetic acid and EDTA) were applied via a drip delivery system consisting of 90-ft lengths of drip tubing connected every ten inches to a two-inch header. The header was connected by hose to a 5,000-gallon stainless steel tanker truck. This system contrasts with the 1998 system in that the number of tubes (108) was triple the number used with the white mustard in 1998. The tubing network extended across the entire plot oriented parallel with the corn rows. The increased number of delivery tubes allowed adequate saturation

of the soil with the amendment solutions in a short period of time (approximately 2 hours). Due to bare areas in the plot at Site C, only the 36 tubes extending across grids 5, 6, 11, 12, 17, 18, 23, 24, 29, 30, 35, and 36 were used for amendment delivery. The other tubes were blocked off to prevent application of amendments to bare soil.

Since only two grids were selected, amendments were applied at Site 129-3 using a hand-held hose applicator connected to the tanker truck.

On August 11, 1999, 1,700 gallons of a 15% acetic acid solution was applied to the designated grids at Site C through the drip delivery system over a two hour time period, followed by 1,600 gallons of aqueous potassium EDTA solution applied over one hour and forty-five minutes. The soil was visibly wet after application of the acetic acid, and saturated after application of the EDTA. This amount of EDTA reflected a one-third reduction from the amount of EDTA applied to 1998 corn, based on the frequency of occurrence of a given lead concentration. The total amount of EDTA applied was 1,500 pounds.

Amendments were applied to the two grids at Site 129-3 on August 11, 1999, immediately following the amendment application at Site C. Due to the lower concentration of soil lead at Site 129-3, the acetic acid and EDTA solutions used at Site C were diluted. Forty gallons of the 15% acetic acid solution was diluted to 280 gallons and 50 gallons of the potassium EDTA was diluted to 500 gallons, and the solutions were applied with the hose applicator to the two selected grids. Diluting the solutions gave a 1:1 ratio of EDTA:Pb based on a frequency of occurrence of lead concentrations across the grids of 140 mg/kg. The mole ratio of EDTA was maintained at 1:1, but the amount applied was reduced by one-third as compared to 1998.

#### 4.2.4.2.3 1999 Crop Harvesting and Processing

Crops were harvested according to the procedure for the 1998 demonstration year (Section 4.2.4.1.4).

#### 4.2.4.3 2000 Field Activities - Soil, Surface Water, and Groundwater Sampling

A field demonstration was not conducted in 2000. A field demonstration at Site 129-3 was planned in 2000. However, after observation of lead and EDTA in groundwater, the project was modified to soil, surface water, and groundwater sampling, as discussed in Section 4.3.4.

#### 4.2.4.4 Personnel and Equipment Decontamination

Two temporary decontamination areas were installed at each site; one for personnel and one for equipment. Since the soil around each site was considered contaminated, the areas consisted of a zone marked off and designated for decontamination procedures. The exact dimensions and placement of the decontamination equipment were left to the discretion of TVA and ATK Health and Safety Officers. A general guide to the decontamination procedures and the placement of decontamination equipment is provided in Attachment C of the demonstration Health and Safety Plan.[Ref. 21] ATK personnel were responsible for disposing of the residuals

**Table 4-3**

**Precipitation and Temperature Data at the Minneapolis-St. Paul International Airport for the 1998 and 1999 Demonstration Years**

| Month | Precipitation Equivalent (in.) | Precipitation Normal (in.) | Departure from Normal (in.) | Mean Temperature (°F) |
|---|---|---|---|---|
| (1998) | | | | |
| | | | | |
| Jan | 1.64 | 0.95 | +0.69 | 19 |
| Feb | 0.80 | 0.88 | -0.08 | 32 |
| Mar | 4.56 | 1.94 | +2.62 | 32 |
| Apr | 1.56 | 2.42 | -0.86 | 51 |
| May | 4.40 | 3.39 | +1.01 | 63 |
| Jun | 6.52 | 4.05 | +2.47 | 65 |
| Jul | 2.63 | 3.53 | -0.90 | 73 |
| Aug | 5.99 | 3.62 | +2.37 | 72 |
| | | | | |
| Total | 26.78 | | +7.32 | |
| | | | | |
| | | | | |
| (1999) | | | | |
| | | | | |
| Jan | 2.67 | 0.95 | +1.72 | 12 |
| Feb | 0.40 | 0.88 | -0.48 | 28 |
| Mar | 1.86 | 1.94 | -0.08 | 34 |
| Apr | 3.43 | 2.42 | +1.01 | 49 |
| May | 6.56 | 3.39 | +3.17 | 60 |
| Jun | 3.68 | 4.05 | -0.37 | 67 |
| Jul | 4.55 | 3.53 | +1.02 | 76 |
| Aug | 2.64 | 3.62 | -0.98 | 70 |
| | | | | |
| Total | 25.79 | | +5.01 | |

**Table 4-4**

**Plant Count and Height for Grids in Site C (1999)**

| Grid Number | Plants per Grid | Average Height (ft) |
|---|---|---|
| | | |
| 4 | 20 | 6 |
| 5 | 46 | 6 |
| 6 | 58 | 4 |
| 10 | 15 | 4.5 |
| 11 | 51 | 6 |
| 12 | 75 | 5 |
| 16 | 21 | 2 rows 4.5 |
| 17 | 45 | 6 |
| 18 | 64 | 3-4.5 |
| 22 | 29 | 4.5 |
| 23 | 48 | 4.5 |
| 24 | 57 | 4.5 |
| 28 | 38 | 4.5 |
| 29 | 49 | 5-6 |
| 30 | 56 | 6 |
| 34 | 38 | 4-6 |
| 35 | 50 | 4-6 |
| 36 | 53 | 6 |

(1) Planting was conducted to provide a maximum possible plant density of 180 plants per grid.

**Table 4-5**

**Plant Count and Height in Grids at Site 129-3[1] (1999)**

| Grid Number | Plants per Grid | Average Height (ft) |
|---|---|---|
| 1 | 34 | 7 |
| 2 | 66 | 7 |
| 3 | 18 | 7 |
| 4 | 25 | 5 |
| 5 | 4 | 5 |
| 6 | 15 | 5 |
| 7 | 20 | 3 |
| 8 | 30 | 3 |
| 9 | 37 | 3 |
| 10 | 14 | 5 |
| 11 | 30 | 2 |
| 12 | 8 | 5 |
| 13 | 9 | 7 |
| 14 | 15 | 3 |
| 15 | 30 | 2-7 |
| 16 | 36 | 3 |
| 17 | 25 | 7 |
| 18 | 8 | 7 |
| 19 | 36 | 3 |
| 20 | 18 | 7 |
| 21 | 23 | 7 |
| 22 | 8 | 7 |
| 23 | 40 | 7 |
| 24 | 13 | 6-7 |
| 25 | 8 | 3 |
| 26 | 10 | 4 |
| 27 | 32 | 5 |
| 28 | 20 | 7 |
| 29 | 10 | 6 |
| 30 | 20 | 3-6 |
| 31 | 44 | 7 |
| 32 | 16 | 3 |
| 33 | 46 | 6 |
| 34 | 53 | 3-6 |
| 35 | 44 | 7 |
| 36 | 74 | 7 |

(1) Planting was conducted to provide a maximum possible plant density of 180 plants per grid.

produced by decontamination procedures. Both TVA and ATK personnel were responsible for the decontamination of their respective personnel and equipment after all process operations. All decontamination procedures were done in accordance with the demonstration Health and Safety Plan[Ref. 21] and the TCAAP installation-wide Health and Safety Plan.[Ref. 22] The demonstration Health and Safety Plan[Ref. 21] was considered a part of the TCAAP installation-wide Health and Safety Plan.[Ref. 22]

#### 4.2.4.5 Record Keeping

A description of activities occurring at Sites C and 129-3 was maintained in field logbooks located in Building 105 at TCAAP. Both TVA and ATK were responsible for recording their activities in logbooks. ATK supplied TVA with copies of the field logbooks.

#### 4.2.4.6 Demobilization and Site Restoration

Demobilization activity consisted of removing extraneous plant material, clearing the site, dismantling the amendment delivery system and the irrigation system, and removing the fence and the lysimeters.

#### 4.2.4.7 Residuals Management for Field-Related Activities

Residuals consisted of plant tissues, contaminated plant and soil sample wastes, rinse water, and contaminated articles of clothing (Tyvek® suits, booties, gloves, masks, respirator filters, etc.). These materials were disposed of as follows:

- The plant tissues were smelted at Gopher Resource Corporation, located at 3385 South Highway 149, Eagan, Minnesota, (612) 454-3310. (ATK activity)

- Sample wastes were disposed of by TVA Analytical Laboratory in a manner consistent with the nature of the waste. (TVA activity)

- Contaminated soil collected during the process of decontaminating personnel and equipment was returned to the demonstration plots. (TVA and ATK activity)

- Contaminated rinse water generated during the process of decontaminating personnel or equipment was poured onto the demonstration plots. (TVA and ATK activity)

- Contaminated plastic tarps or pads and articles of clothing (Tyvek® suits, booties, gloves, masks, respirator filters, etc.) were disposed of in a manner appropriate to the nature of the waste. (ATK activity)

## 4.3 Sampling Procedures

### 4.3.1 Introduction

The sampling objectives for the 1997-1998 site characterization, the 1998 and 1999 demonstrations were to:

- Initially characterize the soil at two TCAAP sites to map total lead content.

- Additionally, characterize the soils at the selected sites for other chemical and physical properties.

- Determine metal and chelate levels in the soil and plants during the demonstration period.

- Determine whether any downward movement of heavy metals, trichloroethylene, or chelate occurred at depths below the plant root structures during the demonstration period.

Field activities were conducted in 2000 to:

- Determine soil physical properties (soil types) three-dimensionally across the plot area to determine the effect on movement of water and EDTA and Pb.

- Characterize the soil profile for amount and type of debris in the subsurface soils, which potentially affect downward movement of EDTA and Pb.

- Determine the movement of lead, EDTA, and other cations in groundwater and surface water within the Site C plot and into areas adjacent to the plot.

- Determine the concentrations of cations that compete with lead for complexation by EDTA, which affects lead transport in water.

Sampling methods for achieving the first two objectives (i.e., soil characterization) are outlined in Section 4.2.2. The lead concentrations in the soils of Sites C and 129-3 were mapped during the initial soil characterization phase prior to growing the crops. This data was collected by TVA. Sampling methods for the next two objectives are documented here since they are indicators of system performance. For the purpose of this document, these two objectives are referred to as the "demonstration objectives" since they refer to objectives that were to be accomplished during the demonstration phases of the project. The last four objectives address the environmental impact of demonstration activities. A listing of the characteristics to be monitored to meet these objectives is provided in Table 4-6.

### 4.3.2 Experimental Design for 1998 Demonstration Phases

#### 4.3.2.1 Experimental Design for 1998 Soil and Plant Sampling

During the 1998 demonstration, crops of corn, followed by crops of white mustard, were grown and harvested at both sites. Two 90- x 90-foot plots were used for growing these crops. The plots in Sites C and 129-3 were divided into thirty-six 15- x 15-foot grids (Figure 4-6). This grid system was retained throughout the demonstration.

Immediately before adding soil amendments for corn, the soil in every fourth grid was sampled at depths of 0 to 12 inches and 12 to 24 inches and analyzed for total lead, bioavailable lead, other COCs, moisture, and pH. The corn tissue was sampled and analyzed for lead and other COCs (Tables 4-7 and 4-8). The limited number of grids were sampled because plants were not

expected to take up much lead in the absence of a chelator. An overview of the experimental design for soil and plant sampling is given in Table 4-9 and 4-10. The corn was ready for harvest approximately four days after adding the soil amendments. Immediately prior to harvest, soil was sampled from every grid at depths of 0 to 12 inches and 12 to 24 inches and analyzed for total lead, bio-available lead, other COCs, and soil moisture. The soil samples from every other grid were analyzed for chelate concentration and soil pH. Plant samples from every grid were analyzed for total lead and other heavy metals. Plants from every fourth grid were analyzed for chelate. After sampling, the corn was harvested and removed from the site.

After harvesting the corn and aerating the soil by irrigation/tillage, white mustard was planted and grown for seven weeks to full vegetative biomass. Prior to adding the chelate, soil and plant samples were obtained from 18 of the 36 grids in each plot. The analytes measured were the same as for corn, as outlined above, except chelate concentration in the soil was also analyzed. Soil amendment additions were conducted without soil acidification for white mustard. Post-harvest sampling, analyses, and harvesting methods for white mustard were the same as outlined for corn. Details for the experimental design for sampling are given in Table 4-11. A listing of the methods used to conduct the chemical analyses is provided in Table 4-12.

Analysis of the plant data was used to quantify the amount of lead taken up by the plants and was intended to be the primary means to verify lead removal from the soil. The soil sampling results were used to assess the rate of chelate disappearance due to degradation, plant uptake, or movement out of the rooting zone. Soil was also analyzed for lead to see if a reduction of lead levels could be observed over the two-year period. The combined results of plant and soil sampling were intended to be used to estimate the number of crops needed to reduce the soil lead concentration to acceptable levels.

#### 4.3.2.2 Experimental Design for 1998 Soil Solution Sampling

The soil solution data was intended to estimate potential environmental effects of the technology. During the warm and cool growing seasons, soil solution was collected from the soil solution monitoring systems under Sites C and 129-3. Soil solution sampling began three weeks before the chelate was added to each crop. For four weeks after this point, the lysimeters comprising the soil solution monitoring system were sampled after the first significant rainfall of each week. A significant rainfall was defined as any 24-hour rainfall event exceeding 0.25 inch of rain. If sufficient soil solution was present in the lysimeter, the samples were collected and analyzed for heavy metals and chelate. Soil solutions were composited for each site. Regulators requested analysis for TCE because of a previous TCE finding located outside of the demonstration plot at Site 129-3. A single lysimeter at Site 129-3 was designated for collection of soil solution for trichloroethylene analysis. The negative results were the basis for elimination of this sampling from future work in the demonstration. The specific analytes for each site are listed in Table 4-7 and 4-8. A listing of the methods for the chemical analyses is provided in Table 4-12. Details of the sampling procedures are given in Section 4.3.5.3.

#### 4.3.2.3 1998 Statistical Analysis of Data

It was recognized that it would be difficult to discriminate between differences in soil lead concentration below initial levels after only two growing seasons. Therefore, the data analysis emphasized plant uptake of lead and was based on the lead concentrations in the plants.

The approach for the statistical analysis was based on a design developed by Dr. Julio Henao, of the International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama. The statistical analysis of the data produced was based on the following assumptions:

1. There were two treatments (amendment application). These corresponded to Site 129-3 (treatment T1), a site with low concentration of lead, and Site C (treatment T2), a site with high concentration of lead.

2. Measures of the concentration of lead in plants and soil were done on each plot.

3. Total lead uptake was estimated on each plot at harvest.

4. A normal distribution was assumed for lead concentration and total lead uptake. If high variation or a non-normal distribution was observed, a test of additivity and homogeneity of variances was done and an appropriate data transformation was then used to test the hypothesis.

Data evaluation was based on the following statistical models:

- Model 1 - A general investigation of the variability of lead content, including site effects, variability across rows within a site, and variability across columns within a site.

- Model 2 - A paired t-test to compare soil lead concentrations only in the grids analyzed before and after soil amendment additions.

- Model 3 - Changes in lead concentration in soil over the two-year period.

##### 4.3.2.3.1 Model 1 - Variability of Soil and Plant Lead Content

The analysis of variability (comparisons) tested the variation due to:

- Site effects: to test the hypothesis that changes in concentration or total lead uptake are due to site concentration.

- Rows within sites: to test the hypothesis of variability of concentration or total lead uptake across rows.

- Columns within sites: to test the hypothesis of variability of concentration or total lead across columns.

**Table 4-6**

**Sampling Goals for the TCAAP Demonstration**

| Study Goal | General Characteristic Measured | Specific Characteristic Measured or Calculated | Activity Timeframe | Sampling Frequency |
|---|---|---|---|---|
| Initial Soil Characterization | Beginning lead levels in soil | Lead Concentration in Soil | Site Characterization | Once |
| | Soil characteristics | Soil pH | | |
| Additional Soil Characterization | Fertilizer requirements | TKN; Extractable P, Exchangeable K; DTPA-Extractable Fe & Mn | Site Characterization | Once |
| | Soil characteristics | TOC and Soil Moisture; Exchangeable Ca, Mg, Al; CEC, pH | | |
| | Initial heavy metals contaminant concentrations | Total Metals (As, Be, Pb, Sb, Tl, Mn); Bio-available Pb | | |
| Document plant uptake of lead and other heavy metals | Heavy metals concentration in soil before and after soil amendment additions | Total Metals (As, Be, Pb, Sb, Tl, Mn) in soil; Bio-available Pb | 1998 & 1999 Demonstrations | 2 times/yr. for 1998; once for 1999 |
| | Heavy metals concentration in plants before and after soil amendment additions | Total Metals (As, Be, Pb, Sb, Tl, Mn) in plant shoots | | |

**Table 4-6 (Continued)**
**Sampling Goals for the TCAAP Demonstration**

| Study Goal | General Characteristic Measured | Specific Characteristic Measured or Calculated | Activity Timeframe | Sampling Frequency |
|---|---|---|---|---|
| Document chelate levels in soil and plants | Chelate concentrations in soil before and after soil amendment additions | Chelate in soil | 1998 & 1999 Demonstrations | 2 times/yr. for 1998; once for 1999 |
| | Chelate concentrations in plants after soil amendment additions | Chelate in plants | | |
| Document heavy metal, trichloroethylene, and chelate movement | Metals in soil solution, chelate, and trichloroethylene | Total Metals (As, Be, Pb, Sb, Tl, Mn); Trichloroethylene; chelate | 1998 & 1999 Demonstrations | 14 times/yr. for two years [1] |
| Document heavy metal and chelate movement | Metals, cations, and chelate in groundwater, surface water, and subsurface soils | Total Metals (As, Be, Pb, Sb, Tl, Mn), cations, and chelate | 2000 Field Activities | Groundwater - 3 times<br>Surface Water - 2 times<br>Subsurface Soil - 1 time |

(1) If TCE was not detected, the analysis would not be continued.

**Table 4-7**

**Chemical Analyses for Soil, Plant, and Soil Solution Samples From Site C in 1998**

| Sample Location | Sample Period | Sample Type | Minimum Sample Size[1] | Preservative Added | Number of Grids Sampled | Parameter Measured |
|---|---|---|---|---|---|---|
| Site C | Before adding soil amendments | Soil | 40 grams | None | 9 grids for corn; 18 grids for white mustard | Total Metals (As, Be, Pb, Sb, Tl, Mn)[2] |
| | | | | | | Plant-available Pb |
| | | | | | | pH |
| | | | | | | Chelate (EDTA) (Except for corn) |
| | | | | | | Moisture |
| | | Plants (Aerial) | 100 grams | None | 9 grids for corn; 18 grids for white mustard | Total Metals (As, Be, Pb, Sb, Tl, Mn)[2] |
| | | Soil Solution | 250 mL | Nitric Acid | Not Applicable | Total Metals (As, Be, Cu, Pb, Sb, Tl, Mn)[2] |
| | | | 40 mL | None | Not Applicable | Chelate (EDTA) |
| Site C | After adding soil amendments | Soil | 40 grams | None | 36 grids | Total Metals (As, Be, Pb, Sb, Tl, Mn)[2] |
| | | | | | | Plant-available Pb |
| | | | | | | Moisture |
| | | | | | 18 grids | pH |
| | | | | | | Chelate (EDTA) |
| | | Plants (Aerial) | 100 grams | None | 36 grids | Total Metals (As, Be, Pb, Sb, Tl, Mn)[2] |
| | | | | | 9 grids | Chelate (EDTA) |
| | | Soil Solution | 250 mL | Nitric Acid | Not Applicable | Total Metals (As, Be, Cu, Pb, Sb, Tl, Mn)[2] |
| | | | 40 mL | None | Not Applicable | Chelate (EDTA) |

(1) Every twentieth sample containing twice the usual amount of sample was submitted for use in the QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

**Table 4-8**

**Chemical Analyses for Soil, Plant, and Soil Solution Samples From Site 129-3 in 1998**

| Sample Location | Sample Period | Sample Type | Minimum Sample Size[1] | Preservative Added | Number of Grids Sampled | Parameter Measured |
|---|---|---|---|---|---|---|
| Site 129-3 | Before adding soil amendments | Soil | 40 grams | None | 9 grids for corn; 18 grids for white mustard | Total Metals (Pb, Sb, Mn)[2] |
| | | | | | | Plant-available Pb |
| | | | | | | pH |
| | | | | | | Chelates (EDTA) (Except for corn) |
| | | | | | | Moisture |
| | | Plants (Aerial) | 100 grams | None | 9 grids for corn; 18 grids for white mustard | Total Metals (Pb, Sb, Mn)[2] |
| | | Soil Solution | 250 mL | Nitric Acid | Not Applicable | Total Metals (Pb, Sb, Mn)[2] |
| | | | 80 mL | HCl | Not Applicable | Trichloroethylene |
| | | | 40 mL | None | Not Applicable | Chelate (EDTA) |
| Site 129-3 | After adding soil amendments | Soil | 40 grams | None | 36 grids | Total Metals (Pb, Sb, Mn)[2] |
| | | | | | | Plant-available Pb |
| | | | | | | Moisture |
| | | | | | 18 grids | pH |
| | | | | | | Chelates |
| | | Plants (Aerial) | 100 grams | None | 36 grids | Total Metals (Pb, Sb, Mn)[2] |
| | | | | | 9 grids | Chelate (EDTA) |
| | | Soil Solution | 250 mL | Nitric Acid | Not Applicable | Total Metals (Pb, Sb, Mn)[2] |
| | | | 80 mL | HCl | Not Applicable | Trichloroethylene |
| | | | 40 mL | None | Not Applicable | Chelate (EDTA) |

(1) Every twentieth sample containing twice the usual amount of sample was submitted for use in the QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

**Table 4-9**

**An Overview of Experimental Design for Soil Sampling in Sites C and 129-3 for 1998**

- 1st Planting (Corn) - before soil amendment addition - 9 grids per site for two sites with two soil depths (36 samples total).

- 1st Planting (Corn) - after soil amendment addition - 36 grids per site for two sites with two soil depths (144 samples total).

- 2nd Planting (White Mustard) - before soil amendment addition - 18 grids per site for two sites with two soil depths (72 samples total).

- 2nd Planting (White Mustard) - after soil amendment addition - 36 grids per site for two sites with two soil depths (144 samples total).

Total: 396 samples

**Table 4-10**

**An Overview of Experimental Design for Plant Sampling in Sites C and 129-3 for 1998**

- 1st Planting (Corn) - before soil amendment additions - 9 grids per site for two sites (18 samples total).
- 1st Planting (Corn) - after soil amendment additions - 36 grids per site for two sites (72 samples total).
- 2nd Planting (White Mustard) - before soil amendment additions - 18 grids per site for two sites (36 samples total).
- 2nd Planting (White Mustard) - after soil amendment additions - 36 grids per site for two sites (72 samples total).

Total: 198 samples

**Table 4-11**

**Experimental Design Details for 1st Growing Season (1998) for Soil and Plant Sampling**

| Plot | Crop | Sampling Time | Soil pH Adjustment | Chelate Concentration | Number of Grids Sampled | Soil Depths | Chemical Analyses | Number of Soil Samples | Number of Plant Samples |
|---|---|---|---|---|---|---|---|---|---|
| C | Corn | Before Soil Amendments | Not Applicable | Not Applicable | 9 | 2 | See Table 4-7 | 9 grids X 2 depths = 18 | 9 |
| | | After Soil Amendments | 5.5 | 1:1 molar ratio of EDTA:Lead | 36 | 2 | | 36 grids X 2 depths = 72 | 36 |
| | White Mustard | Before Soil Amendments | Not Applicable | Not Applicable | 18 | 2 | | 18 grids X 2 depths = 36 | 18 |
| | | After Soil Amendments | Not Applicable | 1:1 molar ratio of EDTA:Lead | 36 | 2 | | 36 grids X 2 depths = 72 | 36 |
| | | | | | | | Total | 198 | 99 |
| 129-3 | Corn | Before Soil Amendments | Not Applicable | Not Applicable | 9 | 2 | See Table 4-8 | 18 | 9 |
| | | After Soil Amendments | 5.5 | 1:1 molar ratio of EDTA:Lead | 36 | 2 | | 72 | 36 |
| | White Mustard | Before Soil Amendments | Not Applicable | Not Applicable | 18 | 2 | | 36 | 18 |
| | | After Soil Amendments | Not Applicable | 1:1 molar ratio of EDTA:Lead | 36 | 2 | | 72 | 36 |
| | | | | | | | Total | 198 | 99 |
| | | | | | | | Grand Total | 396 | 198 |

**Table 4-12**

**Methods for Analyzing Soils, Plants, and Soil Solution**

| Parameter Measured | Extraction or Preparation Method[2] | Analytical Method[2] |
|---|---|---|
| **Soil and Plant Analyses** | | |
| pH | N/A | ASA 12-2.6 |
| Total Organic Carbon (TOC) | N/A | ASA 29-3.5.2 |
| Total Kjeldahl Nitrogen (TKN) | N/A | Lachat QuikChem 13-107-06-2-D |
| Extractable P | ASA 24-5.2 | 6010B |
| Exchangeable K | ASA 9-3.1 | 6010B |
| Exchangeable Ca | ASA 9-3.1 | 6010B |
| Exchangeable Mg | ASA 9-3.1 | 6010B |
| Exchangeable Al | ASA 9-4.2 | 6010B |
| DTPA-Extractable Fe | ASA 17-4.3 | 6010B |
| DTPA-Extractable Mn | ASA 17-4.3 | 6010B |
| Total Metals (Be, Pb, Sb, Tl, Mn)[1] | 3050B | 6010B |
| Total Metals (As)[1] | 3050B | 7060A |
| Bio-Available Pb (Water-Soluble) | ASA 21-5 | 6010B |
| Chelate (EDTA) | AP-0057 (soil) | AP-0047 |
| Cation Exchange Capacity (CEC) | ASA 9-3.1/9.4.2 | 6010B/AP-0059 |
| Soil Moisture | N/A | ASA 21-2.2.2 |
| **Soil Solution Analyses** | | |
| Total Metals (Be, Cu, Pb, Sb, Tl, Mn)[1] | 3005A | 6010B |
| Total Metals (As)[1] | 7060A | 7060A |
| Chelator (EDTA) | N/A | AP-0047 |
| Trichloroethylene | N/A | 8021B |

(1) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

(2) The methods and procedures listed are provided in Appendix D.

The general model used to test the hypotheses was:

$$Y_{ijk} = u + p_i + \iota_{ji} + F_{ki} + e_{ijk} \qquad \text{(Model 1)}$$

$Y_{ijk}$: Lead concentration in plant
$u$: Concentration mean or uptake mean for the two sites
$p_i$: Site effect
$\iota_{ji}$: Variability of rows within sites
$F_{ki}$: Variability of columns within sites
$e_{ijk}$: Random variation assumed N (0, $\sigma$)

**4.3.2.3.2 Model 2 - Changes in Soil Concentrations in Sampled Grids**

Since not all of the grids were sampled before soil amendments were applied, Model 2 was used to compare the change in soil lead concentration only in the grids sampled both before and after soil amendment addition and crop harvest. A paired t-test was used to determine whether the mean of the differences between soil lead concentrations before and after soil amendments was significantly different from zero, so the null hypothesis is:

$$H_0{:}u_D = 0 \text{ (Model 2)}$$

and the test criterion is:

$$t = \frac{D}{s_D}$$

where D is the mean of the differences and $s_D$ is the standard deviation of the differences.

**4.3.2.3.3 Model 3 - Changes in Lead Concentrations in Soil Over the Two-Year Period**

Model 3 included the factor of time (periods) to evaluate changes in soil lead concentration at each sampling period as discrete variables so that changes in soil Pb might be detected at a specified confidence level.

$$Y_{ijk} = u + \gamma_{ji} + \iota_{ji} + F_{ki} + e_{ijkl} \qquad \text{(Model 3)}$$

$\gamma_{ji}$: Variability of periods

The analysis of variance tested the variation due to sampling periods. Regression analysis was used to determine whether any of the measured parameters showed a statistically significant response to another parameter.

The above-discussed parametric statistical analysis provided a practical and realistic assessment of the 1998 data for the sites under the existing conditions. However, a detailed geostatistical analysis and evaluation was also performed. This analysis incorporated soil lead concentration data in the treatment plots prior to the commencement of the phytoremediation study and subsequent to applying the final treatments in 1998. The geostatistical analysis included development of appropriate variogram models and two-dimensional kriging to develop contour plots of the data for both the upper (0- to 12-inch) and lower (12- to 24-inch) soil horizons

(assuming the random field is stationary). A detailed explanation of the theory, methodology, and results of the geostatistical analysis is presented in Appendix H.

### 4.3.3 Experimental Design for 1999 Demonstration Phases

#### 4.3.3.1 Experimental Design for 1999 Soil and Plant Sampling

Due to insufficient or poor growth of corn which resulted in bare areas in the plots, only selected areas in the plots were designated to receive amendments, and only these areas were used for pre-amendment soil sampling. Twelve grids at Site C (5, 6, 11, 12, 17, 18, 23, 24, 29, 30, 35, and 36) designated to receive amendments were sampled on August 10, 1999, following the procedure described in Section 4.3.5.1.1. Two grids (1 and 2) were sampled at Site 129-3. Sampling was done by dividing each grid into quadrants and, with a power auger, taking one sample from each quadrant at depths of 0 to 12 inches and 12 to 24 inches. The four samples were composited by depth into one sample for analysis.

For pre-amendment plant sampling, plant samples were taken from each of the grids designated for treatment in accordance with Section 4.3.5.2. Plant sampling was done by dividing each grid into quadrants and taking two whole stalk samples from each quadrant. The four samples were composited into one sample for analysis.

After soil amendments were added and the corn had senesced due to the treatments, post-amendment soil and plant samples were taken. For Site C, the grids receiving amendment applications, plus four locations within grids in the plot immediately adjacent to the treated area, were sampled for lead, EDTA, and other COCs on August 17, 1999. Post-amendment sampling of the two selected grids at Site 129-3 was also performed on August 17. The sampling procedure for the post-amendment soils was the same as used for pre-amendment soil sampling.

Plant samples were taken from each of the grids that received soil amendments in accordance with Section 4.3.5.2. The sampling procedure for plant samples taken after amendment additions was the same as for the pre-amendment samples.

No mustard crop was planted in 1999 because of the extended growing season and the late harvest of the corn. Hence, no samples were collected.

#### 4.3.3.2 Experimental Design for 1999 Soil Solution Sampling

Sampling attempts were carried out as described in Section 4.3.5.3. However, all attempts to collect soil solution samples were unsuccessful. The reasons for the lack of success were not apparent. Possibly, over the winter months of 1998-1999, freezing and thawing of water in the surrounding soil resulted in loosening of the seal between the fill soil and the porous cup of the lysimeter so that water did not flow into the cup.

#### 4.3.3.3 Experimental Design for Soil Sequential Extraction Analyses

Midway through 1999, information became available for use of a sequential soil fractionation analysis that could be used to revise the amount of EDTA to add to soil.[Ref. 23] Therefore, in 1999, post-amendment soil samples were analyzed by a modification of a sequential extraction procedure (Appendix J) employed for lead-contaminated soils in another study [Ref. 2] to determine

the concentrations of the more plant-available fractions of lead in the soil. This analysis may be used as a basis for calculating the amount of EDTA needed to solubilize only the plant-available fraction of lead in soil, which will result in a more conservative amount of EDTA being added to the soil. Soil lead can be fractionated into water-soluble, exchangeable, carbonate-bound, oxide-bound, organically-bound, and residual mineral fractions. The fractions generally considered to be the more readily plant-available forms are the water-soluble, exchangeable, carbonate-bound, and oxide-bound fractions. However, the oxide-bound fraction is usually much less plant-available than the other fractions, and therefore is not included as part of the total plant-available lead concentration.

#### 4.3.3.4 1999 Statistical Analysis of Data

Due to the limited data collected from the small number of grids at both sites (12 of the 36 grids at Site C and two of the 36 grids at Site 129-3), statistical analysis of the data by use of parametric statistics was not performed. Geostatistical analysis and evaluation was performed on data obtained at Site C. The analysis is presented in Appendix E. However, the extreme variability in lead content prevented an accurate accounting of the total lead status of the soil with the use of geostatistics.

### 4.3.4 2000 Field Activities - Groundwater, Surface Water, and Deep Core Soil Sampling

Plans were modified to include phytoextraction at Site 129-3 in 2000. After observation of lead and EDTA in the groundwater, the plans were changed to sampling only. Groundwater, surface water, and soil were sampled in 2000 to determine if the EDTA applications to the plot at Site C in 1998 and 1999 had impacted groundwater beneath and outside the plot area, or surface water in a drainage ditch to the southwest, west and northwest of the plot.

Three groundwater sampling events and two surface water sampling events were performed at Site C (Table 4-13). The groundwater samplings were performed on April 11, May 17, and May 30, 2000. A single surface water sample was collected from the drainage ditch on April 11 in conjunction with groundwater sampling. A second, more comprehensive set of surface water samples was collected on May 4, 2000. The sampling locations for the ground and surface water samples are shown in Figure 4-8. Groundwater samples were not collected at Site 129-3. The groundwater samples were taken at increasing distances from the demonstration plot in order to track the extent of lead and EDTA movement away from the plot. Samples were taken from the drainage ditch to determine if groundwater that flowed beneath the demonstration plot subsequently flowed up into the ditch.

Samples sent to the TVA Analytical Laboratory were unfiltered and unacidified. The samples were unfiltered in order to determine the contribution (if any) of lead adsorbed on silt, clay, or colloidal particulates to the total concentration of lead in the sample. The samples were initially unacidified to prevent interference with EDTA determination, but upon receipt by TVA, the sample was subdivided and a portion was acidified to preserve the sample for metals determination.

**Table 4-13**

**Chronology of Groundwater and Surface Water Sampling Events at Site C in 2000**

| Sampling Event | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) |
|---|---|---|---|---|
| 1 | FB1 | Field Blank | 11-Apr-00 | |
| 1 | RB1 | Rinse Blank | 11-Apr-00 | |
| 1 | RB2 | Rinse Blank | 11-Apr-00 | |
| 1 | GW1 | Groundwater | 11-Apr-00 | 7 - 7.5 |
| 1 | GW2 | Groundwater | 11-Apr-00 | 5 - 5.5 |
| 1 | GW3 | Groundwater | 11-Apr-00 | 5 |
| 1 | GW4 | Groundwater | 11-Apr-00 | 4 |
| 1 | GW5 | Groundwater | 11-Apr-00 | 6 |
| 1 | GW6 | Groundwater | 11-Apr-00 | 5.5 |
| 1 | SW1 | Surface Water | 11-Apr-00 | |
| | | | | |
| 2 | PRB2-1-U | Pre-Rinse Blank | 4-May-00 | |
| 2 | PRB2-1-F | Pre-Rinse Blank | 4-May-00 | |
| 2 | FB2-1-U | Field Blank | 4-May-00 | |
| 2 | FB2-1-F | Field Blank | 4-May-00 | |
| 2 | RB2-1-U | Rinse Blank | 4-May-00 | |
| 2 | RB2-1-F | Rinse Blank | 4-May-00 | |
| 2 | SW2-1-U | Surface Water Sample -Unfiltered | 4-May-00 | |
| 2 | SW2-1-F | Surface Water Sample - Filtered | 4-May-00 | |
| 2 | SW2-2-U | Surface Water Sample -Unfiltered | 4-May-00 | |
| 2 | SW2-2-F | Surface Water Sample - Filtered | 4-May-00 | |
| 2 | SW2-3-U | Surface Water Sample -Unfiltered | 4-May-00 | |
| 2 | SW2-3-F | Surface Water Sample - Filtered | 4-May-00 | |
| 2 | SW2-4-U | Surface Water Sample -Unfiltered | 4-May-00 | |
| 2 | SW2-4-F | Surface Water Sample - Filtered | 4-May-00 | |
| 2 | SW2-4-UD | Surface Water Sample -Unfiltered Duplicate | 4-May-00 | |

**Table 4-13 (Continued)**

**Chronology of Groundwater and Surface Water Sampling Events at Site C in 2000**

| Sampling Event | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) |
|---|---|---|---|---|
| 2 | SW2-4-FD | Surface Water Sample - Filtered Duplicate | 4-May-00 | |
| 2 | PRB 2-1U | Pre-Rinse Blank Unfiltered | 17-May-00 | |
| 2 | PRB 2-1F | Pre-Rinse Blank Filtered | 17-May-00 | |
| 2 | FB2-1U | Field Blank | 17-May-00 | |
| 2 | FB2-1F | Field Blank Filtered | 17-May-00 | |
| 2 | RB2-1U | Rinse Blank | 17-May-00 | |
| 2 | RB2-1F | Rinse Blank Filtered | 17-May-00 | |
| 2 | GW2-1U | Groundwater Sample - Unfiltered | 17-May-00 | 9.5 - 10 |
| 2 | GW2-1F | Groundwater Sample - Filtered | 17-May-00 | 9.5 - 10 |
| 2 | GW2-2 | DID NOT SAMPLE | 17-May-00 | DID NOT SAMPLE |
| 2 | GW2-3 | DID NOT SAMPLE | 17-May-00 | DID NOT SAMPLE |
| 2 | GW2-4U | Groundwater Sample - Unfiltered | 17-May-00 | 9 - 9.5 |
| 2 | GW2-4F | Groundwater Sample - Filtered | 17-May-00 | 9 - 9.5 |
| 2 | GW2-5U | Groundwater Sample - Unfiltered | 17-May-00 | 5 |
| 2 | GW2-5F | Groundwater Sample - Filtered | 17-May-00 | 5 |
| 2 | GW2-6U | Groundwater Sample - Unfiltered | 17-May-00 | 8 |
| 2 | GW2-6F | Groundwater Sample - Filtered | 17-May-00 | 8 |
| 2 | GW2-7 | DRY | 17-May-00 | DRY |
| 2 | GW2-8U | Groundwater Sample - Unfiltered | 17-May-00 | 7.5 |
| 2 | GW2-8F | Groundwater Sample - Filtered | 17-May-00 | 7.5 |
| 2 | GW2-9 | DRY | 17-May-00 | DRY |

**Table 4-13 (Continued)**

**Chronology of Groundwater and Surface Water Sampling Events at Site C in 2000**

| Sampling Event | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) |
|---|---|---|---|---|
| | | | | |
| 3 | FB3-1U | Field Blank | 30-May-00 | |
| 3 | FB3-1F | Field Blank Filtered | 30-May-00 | |
| 3 | PRB3-1U | Pre-Rinse Blank Unfiltered | 30-May-00 | |
| 3 | PRB3-1F | Pre-Rinse Blank Filtered | 30-May-00 | |
| 3 | GW3-1U | Groundwater Sample - Unfiltered | 30-May-00 | 8 |
| 3 | GW3-1F | Groundwater Sample - Filtered | 30-May-00 | 8 |
| 3 | GW3-2U | Groundwater Sample - Unfiltered | 30-May-00 | 6 |
| 3 | GW3-2F | Groundwater Sample - Filtered | 30-May-00 | 6 |
| 3 | GW3-3U | Groundwater Sample - Unfiltered | 30-May-00 | 8 |
| 3 | GW3-3F | Groundwater Sample - Filtered | 30-May-00 | 8 |
| 3 | GW3-4U | Groundwater Sample - Unfiltered | 30-May-00 | 8 |
| 3 | GW3-4F | Groundwater Sample - Filtered | 30-May-00 | 8 |
| 3 | GW3-4U-DUP | Groundwater Sample - Unfiltered | 30-May-00 | 8 |
| 3 | GW3-4F-DUP | Groundwater Sample - Filtered | 30-May-00 | 8 |
| 3 | GW3-5U | Groundwater Sample - Unfiltered | 30-May-00 | 3 |
| 3 | GW3-5F | Groundwater Sample - Filtered | 30-May-00 | 3 |
| 3 | GW3-6U | Groundwater Sample - Unfiltered | 30-May-00 | 6 |
| 3 | GW3-6F | Groundwater Sample - Filtered | 30-May-00 | 6 |

The first set of groundwater samples and the first surface water sample were analyzed by the TVA Analytical Laboratory for lead, EDTA, pH, and 19 other cations. A laboratory of the Minnesota Department of Health performed analyses for lead only on splits of these samples. The samples were analyzed for other cations by TVA to determine the degree of competition by other cations with lead for complexation by EDTA, and the potential speciation of EDTA with other cations in addition to lead.

The second and third set of groundwater samples were analyzed for EDTA by the TVA Analytical Laboratory. A commercial laboratory (CompuChem), one of the TCAAP Quality Assurance Project Plan (QAPP)-approved laboratories used for CERCLA cleanup, performed analyses for lead on these samples.

The TVA Analytical Laboratory performed analyses on the second set of surface water samples (taken May 4, 2000) for lead, EDTA, pH, and 19 other cations. CompuChem performed the analysis for lead on these samples.

The sampling procedure for collection of the groundwater and surface water samples is detailed in Section 4.3.5.4. The quality assurance/quality control procedures used by TVA in the ground and surface water analyses were the same as those identified in the phytoremediation demonstration plan. [Ref. 21]

The method used by TVA for EDTA analysis was TVA Method AP-0047, as provided in the Technology Demonstration Plan and the 1998 data report. There was no standard EPA method for EDTA analysis, so TVA developed this method in-house based on literature research. The EPA method for lead analysis was SW846-6010. EPA Method 150.1 was used to determine pH.

EDTA in all sampling results is reported as $Na_2EDTA$ and as EDTA. For EDTA, analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is: (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

#### 4.3.4.1 First Groundwater and Surface Water Sampling - April 11, 2000

Six groundwater samples were taken with a Geoprobe® from the locations shown in Figure 4-9 and designated as GW1-1 through GW1-6. A field blank and two equipment rinse blanks were also taken at this time. The depth to groundwater ranged from 4 feet to 7.5 feet (Table 4-13).

Six temporary boreholes were advanced inside and outside the plot using a Geoprobe® instrument. Attempts were made to collect a groundwater sample from each borehole. ATK contracted with American Engineering and Testing, Inc. (AET) to perform the drilling and sample collection.

The borehole locations were agreed upon by USAEC and MPCA representatives in a March 30, 2000 conference call. A map (Figure 4-8) was constructed showing the locations of the boreholes before sampling commenced. These borehole locations provided one upgradient sample, three downgradient samples, and two samples from within the demonstration plot. ATK marked the locations in the field prior to the sampling event. A duplicate sample was collected

from borehole GW-5 (within the demonstration plot) and a rinsate sample was collected when the equipment was decontaminated between sampling at GW-5 and GW-6.

The boreholes were advanced to the bottom of Unit 1 as determined by the on-site geologists from AET and ATK. Unit 1 is estimated to be approximately 15 feet thick at Site C. By agreement between AEC and MPCA, any Geoprobe® advances to the bottom of Unit 1 without encountering water constituted a complete sampling event at that location.

Also, by agreement, incomplete penetration of the Geoprobe® would result in the borehole being offset 5 feet to the northwest. If refusal continued, the borehole was to be offset in the following order: 5 feet to the northeast; 5 feet to the southeast; and finally, 5 feet to the southwest. In the event that these five attempts failed to advance a borehole, the location was considered complete.

To avoid cross-contamination of samples, new equipment was used at each borehole location or equipment was decontaminated between borings. Since Site C was already scheduled for shallow soil remediation, decontamination water was poured onto the site. After the groundwater samples were collected, the boreholes were filled with bentonite grout, as required by Minnesota Department of Health Rules.

The MPCA requested that split samples be collected, and all equipment pertinent to that exercise was provided by the MPCA.

One split of each sample was sent to the TVA laboratory where the groundwater samples and blanks were filtered through a 0.2 micron pore size Millipore® syringe filter and divided into two equal portions. One portion was acidified and analyzed for lead and 19 other cations. The other, unacidified portion was analyzed at its indigenous pH for EDTA and pH.

A single surface water sample was collected from the drainage ditch at this time by dipping a large container into the standing surface water, and then transferring to sample containers.

**4.3.4.2 Second Surface Water Sampling - May 4, 2000**

Surface water samples were collected from four locations in the drainage ditch as described in Section 4.3.5.4. The sample locations are designated as SW2-1 through SW2-4 on Figure 4-8. A duplicate sample was collected from the location designated SW2-4. One equipment pre-rinse blank, one equipment rinse blank, and one field blank also were collected in conjunction with this sampling. Each sample, including blanks, was divided into two portions, and one portion was filtered through a 0.45 micron pore size Millipore® filter at the time of collection in the field, then acidified, while the other portion was unfiltered and unacidified.

The filtered, acidified samples were sent to an outside lab, CompuChem, for analysis of lead. The unfiltered, unacidified samples were sent to the TVA Analytical Laboratory for EDTA analysis. These samples were then divided into two portions. One portion was filtered through a 0.45 micron pore size Millipore® filter, analyzed for EDTA, then acidified and analyzed for

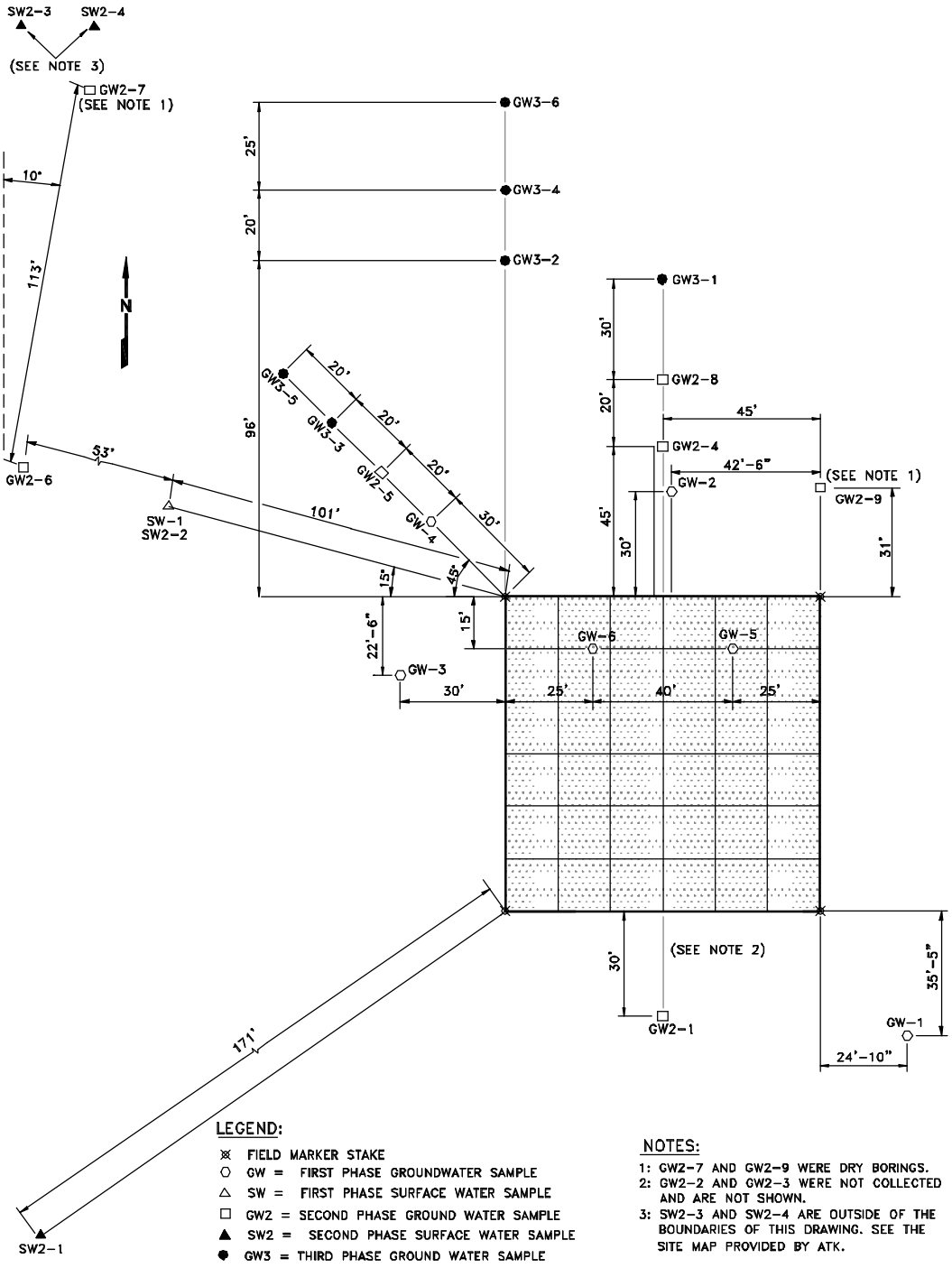



**Figure 4-8**
**Groundwater and Surface Water Sampling Locations**
**Site C - April 2000**

lead. The other portion was filtered through a 0.2 micron pore size Millipore® filter, analyzed for EDTA, then acidified and analyzed for lead and other cations that could potentially compete with lead for complexation by EDTA. The dual filtration was done to test for adsorption and transport of EDTA and lead on particulates in the water.

#### 4.3.4.3 Second Groundwater Sampling - May 17, 2000

Attempts were made to collect groundwater samples from 9 locations (shown on Figure 4-8) at this sampling. The samples were collected as outlined in Section 4.3.5.4 using the GeoProbe®. The sample locations are designated as GW2-1 through GW2-9 as shown on Figure 4-8. However, due to difficulties in the field and bad weather, two of the locations (GW2-2 and GW2-3) were not sampled, and groundwater was not found at two other locations (GW2-7 and GW2-9). One equipment pre-rinse blank, one equipment rinse blank, and one field blank also were collected in conjunction with this sampling. The depth to groundwater ranged from 5 feet to 10 feet (Table 4-13).

Each sample and blank was divided into two portions. One portion was filtered through a 0.45 micron pore size Millipore® filter at the time of collection in the field, then acidified, while the other portion was unfiltered and unacidified.

The filtered, acidified samples were sent to CompuChem for analysis of lead. The unfiltered, unacidified samples were sent to the TVA Analytical Laboratory for EDTA analysis. Analyses for other elements were not conducted. However, TVA split the samples and retained an acidified portion in case additional analyses were requested.

#### 4.3.4.4 Third Groundwater Sampling - May 30, 2000

Groundwater samples were collected from six locations (designated as GW3-1 through GW3-6 on Figure 4-8). A duplicate sample was collected from location GW3-4. One equipment pre-rinse blank and one field blank were collected. The samples were collected using the Geoprobe® as outlined in Section 4.3.5.4. The depth to groundwater at this sampling ranged from 3 to 8 feet (Table 4-13).

As before, each sample was divided into two portions, with the filtered and acidified portion sent to CompuChem for determination of the lead concentration in the sample, and the unfiltered, unacidified portion sent to the TVA Analytical Laboratory for EDTA analysis.

#### 4.3.4.5 2000 Deep Core Soil Sampling at Site C and Site 129-3

Since the experimental plots were shown to be extremely heterogeneous with respect to soil type and the type and amount of debris present, particularly at Site C, deep core soil samples (to a 4-foot depth) were taken at Site C from 12 locations within the plot and from 6 locations outside the plot (Figure 4-9). Deep core samples were taken from 4 locations within the plot at Site 129-3, (Figure 4-10) but none were taken outside the plot. All samples were taken with the GeoProbe® on April 11, 2000, in conjunction with the groundwater sampling. The sampling protocol is detailed in Section 4.3.5.1.2.

The intact cores were characterized by visual and tactile means to determine the broad soil textural class and also to determine the amount and type of debris present in order to gain a three-dimensional perspective of the soil. The soil was analyzed in increments of one foot to determine the amount of solubilized lead and EDTA in the surface and subsurface soil after the winter of 1999, to determine background concentrations of lead and EDTA outside the plot, and to determine concentrations of total lead present at the lower soil depths.

### 4.3.5 Sampling Plan

#### 4.3.5.1 Soil Sampling

##### 4.3.5.1.1 Soil Sampling in 1998 and 1999

Soil sampling was performed by TVA personnel, with assistance from ATK personnel. The sampling procedure was as follows:

1. The Site C and 129-3 farm plots were each subdivided into thirty-six 15- x 15-foot grids, as described above in Section 4.3.2. Each 15- x 15-foot grid was then subdivided into four 7.5- x 7.5-foot quadrants.

2. All of the grids were sampled during most sampling periods during the 1998 season. However, only every second or fourth 15- x 15-foot grid was sampled during sampling periods conducted prior to the addition of soil amendments (see Tables 4-7 and 4-8). Those 15- x 15-foot grids were designated with a flag. In 1999, only twelve grids were sampled at Site C and two at Site 129-3.

3. The 0-inch to 12-inch soil sample from each grid was a composite sample comprised of soil taken from the four quadrants within each grid. Each grid quadrant was sampled by creating a 12-inch-deep hole using a power soil sampling auger and then scraping a soil sample from the length of the hole using a spoon. Each soil sample weighed approximately 200 grams. Use of the power sampling equipment was a modification of the Technology Demonstration Plan.

4. The four 0-inch to 12-inch soil samples from each grid were composited by placing the four quadrant samples into a single OneZip™ plastic bag. Each plastic bag contained approximately one 800-gram composite sample and was labeled, as indicated in Section 4.3.5.7.

5. A 12-inch to 24-inch soil sample was obtained from each quadrant of each grid sampled above. Each 12-inch to 24-inch quadrant sample was obtained from the sampling hole used to obtain the 0-inch to 12-inch sample by placing the soil auger into the original hole, drilling a 24-inch deep hole, and then scraping a soil sample from the length of the 12- to 24-inch hole using a spoon. Each soil sample weighed approximately 200 grams.

6. The 12-inch to 24-inch soil samples from each grid were composited by placing the four quadrant samples into a single OneZip™ plastic bag. Each plastic bag contained approximately one 800-gram composite sample and was labeled, as indicated in Section 4.3.5.7.

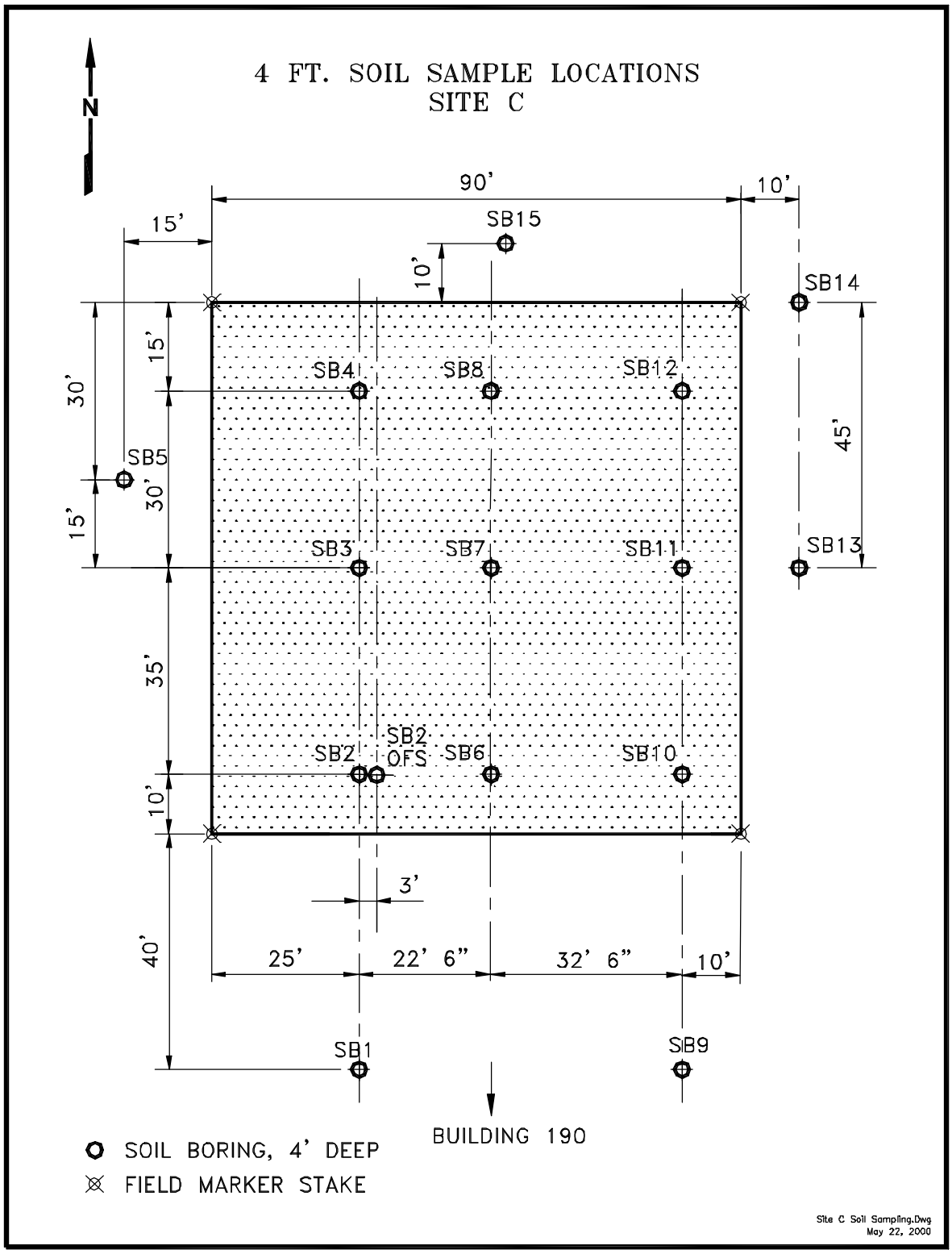



**Figure 4-9**
**Locations for Deep Core Soil Samples Taken at Site C**

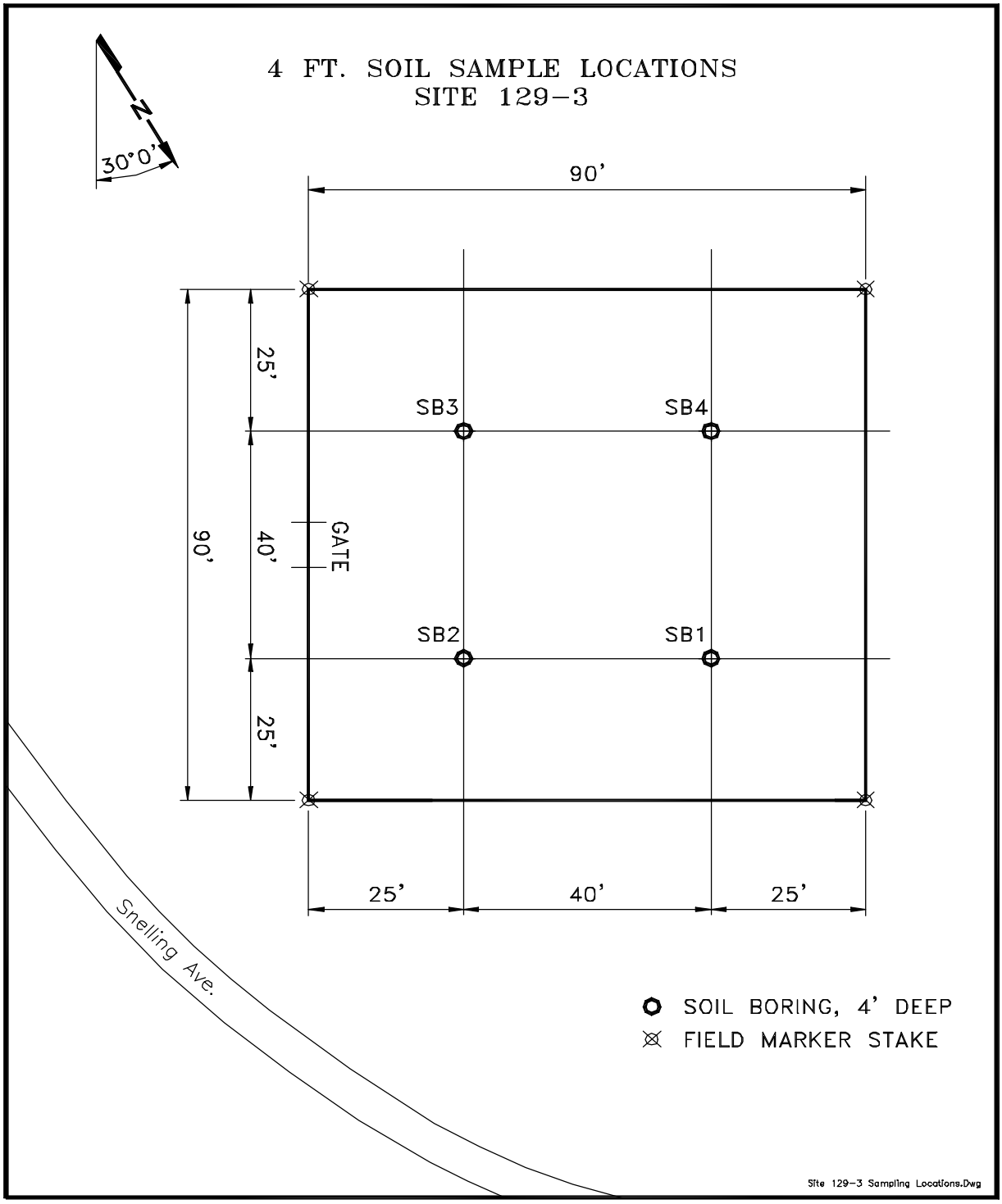



**Figure 4-10**
**Locations for Deep Core Soil Samples Taken at Site 129-3**.

7. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.[Ref. 21]

8. Field wastes were packaged in suitably sized heavy-duty plastic bags and placed in a designated satellite area until disposal in a hazardous waste landfill.

9. The soil samples were packaged for shipment to the TVA Analytical Laboratory in Muscle Shoals, Alabama, in accordance with the TVA chain of custody procedures (Appendix D-17).

10. Upon receipt at the TVA facility, the 800-gram soil samples were air-dried by opening the plastic bag and folding down the top to permit sufficient air movement. The opened bags were placed on tables in a greenhouse and allowed to dry for one week with periodic mixing of the soil in the bag.

11. Upon drying, the soil samples were analyzed, as outlined in Tables 4-7 and 4-8. The specific analytical methods used are shown in Table -12. A total of 396 soil samples were taken during the 1998 demonstration year (Table 4-9). Fifty-six samples were taken during the 1999 season.

No field QC samples were collected for soil sampling, but a laboratory duplicate of every twentieth sample was analyzed when sample size allowed.

**4.3.5.1.2 Soil Sampling in 2000**

Soil samples down to the four foot depth were collected from Site C and from Site 129-3 using the Geoprobe®. The sampling was performed by American Engineering and Testing, Inc. (AET).

The sampling procedure was as follows:

1. The sample locations were determined as shown in Figure 4-9 and 4-10.

2. 48" Geoprobe® Macro-Core Sample Tubes with liners (MC PETG Liner, heavy duty) were used to sample continuously to depth of exactly 4 feet from ground surface. If significant obstructions were encountered (evidenced by lifting of Geoprobe®), then the sample tube was removed, the liner discarded, and the sampling point was offset 1 to 2 feet.

3. Compression of the soil in the tubes to less than 40 inches necessitated collection of two separate samples at each of the sample locations. One sample was collected from the ground surface to exactly 2 feet deep. The second sample was collected from 2 feet to 4 feet via the same sample hole (the probe was inserted through the void left by the 0- to 2-foot sample collection).

4. Probe rods were retracted and the sample liner removed. Length of sample material within the liner was measured to the nearest inch and recorded. Before cutting, a permanent marker was used to write "Top" and "Bottom" directly on the sample liner. Any empty liner material was cut away, (use Macro-Core Circular Cutting Tool or knife) and a black (black, b for bottom) vinyl end cap was placed on the end with the deepest soil and a red vinyl end cap on the end with the shallowest soil. A permanent marker was used to label each tube.

The label identified the sample location and the respective depth range (0 to 2 feet or 2 to 4 feet). Probe rods and other downhole equipment were decontaminated between each use.

5. Each deep core soil sample (i.e., MC PETG Liner) was labeled as to

   - Site C or Site 129-3
   - Sample location
   - Top or bottom of sample
   - Date
   - Depth range at which sample was collected
   - Sampler's initials

6. Any soil from the outside of the sample liner was wiped away with a dry cloth or paper towel. Up to six core samples (12 liner halves) were placed in a large plastic bag and a knot was tied in the opening. This bag was placed in a 2nd plastic trash bag, which was knotted, and then again in a third bag, which was knotted. The triple-bagged samples were placed in a cooler on top of Blue Ice.

7. Immediately before relinquishing samples to the shipping company (UPS or FEDEX), the old Blue Ice was removed and new frozen Blue Ice was added. The chain of custody form was completed and placed in a sealable bag inside cooler. The custody seal was applied across the opening of the cooler and signed and dated. The ice chests were shipped over night for delivery by 10:00 a.m. to:

   Tennessee Valley Authority
   Attention: **David Phillips**
   Reservation Road, CTR-1K
   Muscle Shoals, Alabama 35661
   Phone 256-386-3358

8. The format for the Field Log used during collection of deep core soil samples was as follows:

| Date | Location | Start Time | End Time | Recovery (inches) | Comments |
|---|---|---|---|---|---|

#### 4.3.5.2 Plant Sampling

Plant sampling was performed primarily by TVA personnel with assistance from ATK personnel. The sampling procedure was as follows:

1. Each 15- x 15-foot grid was divided into four 7.5- x 7.5-foot quadrants, as in Step 1 for soil sampling (Section 4.3.5.1.1).

2. A 15- x 15-foot (minimum) plastic tarp was placed on an area within the WZ (see description of WZs in Section B 6.4 of the demonstration Health and Safety Plan[Ref. 21]).

3. All of the grids were sampled during most sampling periods in 1998. However, only every second or fourth 15- x 15-foot grid was sampled during sampling periods prior to the addition of soil amendments (see Tables 4-7 and 4-8). These 15- x 15-foot grids were designated with a flag. In 1999, only twelve grids were sampled at Site C and two at Site 129-3.

4. Two plants from each of the four 7.5- x 7.5-foot quadrants were harvested by cutting the plant at the stalk near the base (eight plants total). Each plant was cut down by carefully holding the plant to prevent contact with contaminated soil, cutting the stalk using a corn knife or shears, and carrying the harvested plants to the tarp in the WZ.

5. At the WZ, the eight plants harvested from each grid were cut into small pieces using hand tools and placed into large paper bags. Each paper bag was labeled, as indicated in Section 4.3.5.7. After processing the plants from each grid, but prior to processing plants from the next grid, the plant debris on the tarp was brushed into a dust bin using a broom and deposited into the paper bag. Each paper bag was folded at the top and sealed (stapled).

6. Upon completion of the sampling program, hand tools were decontaminated by either wiping off the tool or rinsing with potable water.

7. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.[Ref. 21]

8. The plant samples were packaged for shipment to the TVA Analytical Laboratory in Muscle Shoals, Alabama, in accordance with the TVA chain of custody procedures (Appendix D-17).

9. Upon receipt at the TVA facility, the plant tissue samples were oven-dried for 72 hours at 55°C in the original paper bags. The tissue was then ground to less than 2.0-mm particle size using a Wiley Mill. The dried, ground tissue was stored in large glass bottles and labeled.

10. A representative plant sample was obtained from the glass bottles and analyzed, as outlined in Tables 4-7 and 4-8. The specific analytical methods that were used are provided in Table 4-12. A total of 198 plant samples were taken in 1998 (Table 4-10). Twenty-eight plant samples were taken in 1999.

No field QC samples were collected for plant sampling, but a laboratory duplicate of every twentieth sample was collected when sample size allowed.

#### 4.3.5.3 Soil Solution Sampling

Soil solution sampling was performed by ATK personnel. The sampling procedure is described below.

#### 4.3.5.3.1 Soil Solution Sampling at Site C

Samples were collected from the lysimeters at Site C whenever the lysimeters contained a sufficient volume of soil solution to obtain an approximate 80-mL sample. However, on numerous occasions, there was insufficient solution in the lysimeters to collect a sample. Each 80-mL sample was obtained by applying a suction to the glass tube at the top of the lysimeter. The system was designed so that soil solution in the porous ceramic cup at the bottom of the lysimeter flowed through the glass tube to the surface, through a plastic tube, and into a 250-mL Buchner side arm suction flask. A hand-held, battery-operated drill with pump attachment was used to create the suction.

All of the 80-mL samples collected were composited in a pre-cleaned 1-liter stainless steel beaker for distribution to other containers. Approximately 40 mL of the soil solution from the stainless steel beaker was transferred to one 40-mL glass bottle. The contents of this bottle were analyzed for EDTA. Approximately 250 mL of the soil solution from the stainless steel beaker was transferred to one 250-mL plastic bottle. The contents of this bottle were analyzed for total metals (Be, Pb, Sb, Tl, Mn). In addition, the solution from the lysimeter in the extreme northwest corner of the demonstration plot was analyzed for copper (total metals - Cu), since the collected solution exhibited a blue coloration, which sometimes indicates the presence of copper. This blue coloration varied in intensity from faint blue to sky blue and persisted over a period of 7 weeks. Next, approximately 500 mL of the soil solution from the stainless steel beaker was transferred to one 500-mL glass bottle. The contents of this bottle were analyzed for arsenic. The contents of the 250- and 500-mL bottles were preserved by adding four drops of nitric acid to each bottle. Any remaining soil solution in the 1-liter stainless steel beaker was poured onto the soil in the 90- x 90-foot plot.

During the first sampling day at the demonstration site, a rinse blank, trip blank, and field duplicate (for each bottle) also were collected. Thereafter, a rinse blank, trip blank, and field duplicate were collected for every twentieth composite sample collected.

Each sample container was affixed with a label indicating: the demonstration site the sample was taken from, the purpose for taking the sample (demonstration, rinse blank, trip blank, or field duplicate), the date the sample was taken, and the type of crop growing at the time (see labeling instructions in Section 4.3.5.7). All of the containers were transported to the TVA Analytical Laboratory in Muscle Shoals, Alabama. All samples were refrigerated upon arrival at the lab. All samples received from the demonstration site were handled in accordance with the TVA chain of custody procedures.

Upon completion of the sampling program, all hand tools were decontaminated either by wiping off the tool or rinsing with clean water. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with Section B3.2 of the demonstration Health and Safety Plan.[Ref. 21]

#### 4.3.5.3.2 Soil Solution Sampling at Site 129-3

As described for Site C, soil solution at Site 129-3 was collected from lysimeters using a 250-mL Buchner side arm suction flask and a hand-held, battery-operated drill with suction pump attachment. However, due to the volatile nature of trichloroethylene, the sampling procedure varied from that described for Site C for the sample designated for trichloroethylene sampling as

requested by the regulators. The lysimeter closest to trench TR031, i.e., the lysimeter located in the northwestern corner of the 90- x 90-foot plot area (grid #6) was designated for trichloroethylene sampling. Had sample collection been possible, the sampling procedure would have been as follows:

Lower a 50-mL glass sample bottle, attached to a probe, to the bottom of the lysimeter. Carefully fill the bottle and bring to the soil surface. Carefully and quickly transfer 40 mL of the contents to one 40-mL glass screw cap volatile organic analyte (VOA) vial containing four drops of concentrated hydrochloric acid and quickly seal with the cap. Analyze the contents of the 40-mL VOA vial for trichloroethylene. The VOA vial is labeled to indicate that this is the first VOA sample collected at this sampling. HCl is added to preserve the sample for trichloroethylene analyses. Any excess water is poured into a 250-mL Buchner side arm suction flask.

The 50-mL glass sample bottle is lowered into the lysimeter a second time, carefully filled, and brought to the surface. The contents (40-mL) are carefully and quickly transferred to a second 40-mL glass screw cap VOA vial containing four drops of concentrated hydrochloric acid. The contents of this vial are analyzed for trichloroethylene for quality control purposes. The VOA vial is labeled to indicate that this is the second VOA sample collected. Again, any excess water is poured into the 250-mL Buchner side arm suction flask.

Next, up to 80 mL of sample is collected by lowering a glass sample bottle, attached to a probe, to the bottom of the lysimeter. The sample is poured into a 250-mL flask. Any soil solution in the flask is poured into a precleaned 1-liter stainless steel beaker.

For analysis of metals and EDTA, approximately 80 mL of soil solution was collected from each of the remaining 11 lysimeters at Site 129-3 (if lysimeters contained sufficient solution for sampling). Each 80-mL sample was obtained by applying a suction to the glass tube at the top of the lysimeter. Soil solution in the lysimeter porous ceramic cup flowed through the glass tube to the top of the lysimeter, through a plastic tube, and into a 250-mL Buchner side arm suction flask. A hand-held, battery-operated drill with pump attachment was used to create the suction.

At a given sampling event, all 80-mL samples collected were composited in the 1-liter stainless steel beaker described above. Approximately 40 mL of the soil solution from the stainless steel beaker was transferred to one 40-mL glass bottle. The contents of this bottle were analyzed for EDTA. Approximately 250 mL of the soil solution from the stainless steel beaker were transferred to a 250-mL plastic bottle, preserved by addition of four drops of nitric acid, and analyzed for total metals (Pb, Sb, Mn). Any remaining soil solution in the 1-liter stainless steel beaker was poured onto the soil in the 90- x 90-foot plot.

During the first soil solution sampling day at the demonstration site, a rinse blank, trip blank, and field duplicate also were collected. Thereafter, a rinse blank, trip blank, and field duplicate were collected for every twentieth composite sample collected. For the trichloroethylene sample, a trip blank would have been collected each time.

Each sample container was affixed with a label indicating: the demonstration site the sample was taken from, the purpose for taking the sample (demonstration, rinse blank, trip blank, or field duplicate), the date the sample was taken, and the type of crop growing at the time (see labeling instructions in Section 4.3.5.7). All of the containers were transported to the TVA Analytical Laboratory in Muscle Shoals, Alabama, for analysis. All samples were refrigerated upon arrival at the laboratory. All samples received from the demonstration site were handled in accordance with the TVA laboratory chain of custody procedures.

Upon completion of the sampling program, all hand tools were decontaminated either by wiping off the tool or rinsing with clean water. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination.

#### 4.3.5.4 Ground and Surface Water Sampling in 2000

##### 4.3.5.4.1 Groundwater Sampling at Site C

Subsurface water sampling was arranged by ATK. Sample containers (250-mL Nalgene® bottles) were cleaned by TVA personnel prior to use by acid-washing and then rinsing with deionized water. The bottles were then shipped to TCAAP.

A log was maintained by ATK which appropriately described all aspects of the actual sampling, and the characteristics of each sample. This included any difficulties encountered in obtaining the sample, and the color, odor, and appearance of each sample. The sampling procedure is described below.

1. Using the Geoprobe® sampling equipment in accordance with manufacturer's instructions, the access hole was bored or drilled to the expected subsurface water level.

2. After location of water was achieved, a water sample of at least 200 mL in volume was withdrawn from the collection device and place in the sample container.

3. Care was taken to ensure that no soil or other solid or liquid contaminant was introduced into the sample or sample bottle. However, if such contamination had occurred, the contaminated sample would have been discarded and another sample obtained.

4. The sample was not filtered, acidified, or altered in any way from the natural state.

5. Each sample was labeled as to the following:
    a) Site C
    b) sample location
    c) date
    d) time
    e) depth at which sample was collected
    f) physical appearance of sample, i.e., clear, turbid, etc.
    g) name of person collecting the sample

6. Each sample bottle label was covered with plastic tape so that moisture would not obliterate the label.

7. Each sample was placed in an ice chest containing crushed ice or Blue Ice for cooling the samples in the field.

8. Immediately before relinquishing samples to the shipping company (FEDEX), the old Blue Ice (or crushed ice) was removed and new frozen Blue Ice was added. The sample bottles were cushioned by wrapping in plastic bubble wrap, placing on Blue Ice, and the ice chest was sealed for shipment.

9. A chain of custody form was completed and placed in a sealable bag inside the cooler. A custody seal was placed across the opening of the cooler and signed and dated. The container was shipped over night for delivery by 10:00 a.m. to:

   Tennessee Valley Authority
   Attention: **David Phillips**
   Reservation Road, CTR-1K
   Muscle Shoals, Alabama 35661
   Phone 256-386-3358

10. The format for the field log used during collection of groundwater samples was as follows:

| Date | Location | Start Time | End Time | Recovery (inches) | Comments |
|---|---|---|---|---|---|

**4.3.5.4.2 Surface Water Sampling at Site C**

Surface water sampling was arranged by ATK. Sample containers (250 mL Nalgene® bottles) were cleaned by TVA personnel prior to use by acid-washing and then rinsing with deionized water. The bottles were then shipped to TCAAP.

A log was maintained by ATK which appropriately described all aspects of the actual sampling, and the characteristics of each sample. This included any difficulties encountered in obtaining the sample, and the color, odor, and appearance of each sample. The sampling procedure is described below.

For the single surface water sample - April 11, 2000:

1. Water was collected from the drainage ditch by dipping a large plastic bucket into the standing water in the ditch.

2. A water sample of at least 200 mL in volume was poured from the collection device into the sample container.

3. Care was taken to ensure that no soil or other solid or liquid contaminant was introduced into the sample or sample bottle. However, if such contamination had occurred, the contaminated sample would have been discarded and another sample obtained.

4. The sample was not filtered, acidified, or altered in any way from the natural state.

5. Rinse blanks were collected in similar fashion.

6. The sample was labeled as to the following:
    a) Site C
    b) Sample location
    c) Date
    d) Time
    e) Depth at which sample was collected
    f) Physical appearance of sample, i.e., clear, turbid, etc.
    g) Name of person collecting the sample

7. The sample bottle label was covered with plastic tape so that moisture would not obliterate the label.

8. The sample was placed in the same ice chest containing the groundwater samples and packed in Blue Ice and shipped to TVA along with the groundwater samples.

<u>For the surface water sampling - May 4, 2000:</u>
The protocol for this sampling was the same as for the single sample collected on April 11, except that water was collected from the drainage ditch by pumping with a peristaltic pump fitted with Tygon® tubing into the 250 mL Nalgene® sample containers.

**4.3.5.5 Sampling Team Structure and Qualifications**
The sampling team collecting soil and plant samples consisted of at least one team leader and one technician. This team consisted of both TVA and ATK personnel. All sampling team members had completed the Occupational Safety and Health (OSHA) 40-hour HAZWOPER training program in accordance with 29 CFR 1910.120. The team leader had also completed the 8-hour supervisor training.

The ATK sampling team collecting soil solution samples consisted of one team leader and one technician. All sampling team members had completed the OSHA 40-hour HAZWOPER training program. The team leader had also completed the 8-hour supervisor training.

The sampling team for the groundwater and surface water sampling consisted of a team leader from ATK, a representative from MPCA, and personnel from AET. For the first groundwater sampling, a representative for AEC and a representative for TVA were also present as observers.

#### 4.3.5.6 Site Health and Safety Procedures

Level D PPE was deemed appropriate for sampling operations. Monitoring for lead in ambient air indicated that under the conditions of sampling, lead exposure was well below the current OSHA PEL and Action Limit, thus, no respirator was required during sampling.

#### 4.3.5.7 Sample Labeling

Soil samples were labeled with the date of sampling, the plot designation, the grid the soil sample was taken from, and the soil depth. An example of the labeling of a soil sample taken in the first sampling period is: 7-1-98, plot C, grid 16, 0-12 inches.

Plant samples were labeled with the date of sampling, the plant species, the plot designation, and the grid from which the plant sample was taken. An example of the labeling of a plant sample taken in the first sampling period is: 7-1-98, corn, Site C, grid 16.

A label was affixed to each bottle containing a soil solution sample indicating: the date the sample was taken, the demonstration site the sample was taken from, and the purpose for taking the sample (demonstration, rinse blank, trip blank, or field duplicate). An example of labeling for a soil solution sample being taken for demonstration purposes taken in the 1998 crop would be: date, Site C, rinse blank.

Each ground and surface water sample was labeled as to the following:

a) Site C
b) sample location
c) date
d) time
e) depth at which sample was collected
f) physical appearance of sample, i.e., clear, turbid, etc.
g) name of person collecting the sample

Each sample bottle label was covered with plastic tape so that moisture would not obliterate the label.

#### 4.3.5.8 Sample Documentation

All samples shipped from the site by TVA or received by TVA were handled in accordance with Procedure SP-0001, “Sampling Chain of Custody” (Appendix D-17).

#### 4.3.5.9 Sample Storage, Packaging, and Shipping

Soil samples were transported in the appropriately identified and labeled sealed plastic bags (OneZip™-type) into which they were placed immediately after sampling. The bags were placed into containers for shipping. Soil samples remained in these bags for storage.

Plant samples were shipped in the paper bags into which they were placed immediately after harvesting. The bags were folded at the top, sealed (stapled), and placed into sealed containers for shipping. After plant samples were dried and ground, they were stored in glass bottles.

Soil solution and ground and surface water samples were placed in plastic bottles, and shipped in ice chests containing blue ice.

Deep core soil samples were placed in triple plastic bags, and shipped in ice chests containing blue ice.

All samples shipped or received by TVA were handled in accordance with TVA chain of custody procedures (Appendix D-17).

## 4.4 Analytical Procedures

### 4.4.1 Laboratory Procedures

Standard analytical procedures for data collected in the laboratory are provided in Appendices D-1 through D-19. For EDTA, analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is: (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

### 4.4.2 Analytical Equipment

The equipment used for collecting laboratory data at TVA is outlined in Table 4-17. The pH of soil samples taken in the laboratory were analyzed with a glass electrode and pH meter. Total Organic Carbon (TOC) was analyzed by a manual titrimetric method. Total Kjeldahl Nitrogen (TKN) was determined colorimetrically via an automatic analyzer. For Cation Exchange Capacity (CEC) analysis, both an automatic analyzer and inductively coupled plasma (ICP) were used. Extractable P, Exchangeable K, Ca, Mg, and Al; DTPA-Extractable Fe and Mn; Bio-available Pb; and Total Metals (Be, Pb, Sb, Tl, Mn) were determined by ICP spectrometry. Arsenic (As) was determined by atomic absorption (AA). The EDTA chelate was analyzed by high performance liquid chromatography (HPLC). Trichloroethylene was to be determined by gas chromatography (GC).

### 4.4.3 Residuals Management of Laboratory- and Sampling-Related Wastes

Residuals consisted of lead-contaminated soil, plant tissue, soil solutions, ground and surface water samples, rinse water, laboratory waste, and contaminated articles of clothing (Tyvek® suits and booties, gloves, masks, respirator filters, etc.). The fate of these materials was as follows:

- Contaminated soil, water, and plant samples sent to TVA, as well as related laboratory wastes, were disposed of through TVA's existing hazardous waste disposal contracts. (TVA activity)

- Contaminated soils collected during the process of decontaminating personnel and equipment decontamination were returned to the demonstration plots. (TVA and ATK activity)

- Contaminated rinse water collected during the process of decontaminating personnel and/or equipment was poured onto the demonstration plots. (TVA and ATK activity)

Contaminated soils, plastic tarps or pads, articles of clothing (Tyvek® suits, booties, gloves, masks, respirator filters, etc.) produced during the sampling process were disposed of in a manner appropriate to the nature of the waste. (ATK activity)

**Table 4-14**

**Equipment Used for Data Collection**

| Parameter Measured | TVA Equipment | ATK-Designated Lab Equipment |
|---|---|---|
| **Soil and Plant Analyses** | | |
| pH | Orion pH meter | NA[1] |
| Total Kjeldahl Nitrogen (TKN) | Lachat QuikChem 8000 or Technicon AutoAnalyzer II | NA |
| Extractable P | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Exchangeable K | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Exchangeable Ca | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Exchangeable Mg | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Exchangeable Al | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| DTPA-Extractable Fe | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| DTPA-Extractable Mn | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Total Metals (Be, Cu, Pb, Sb, Tl, Mn) | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Total Metals (As) | AA | NA |
| Bio-Available Pb (Water-Soluble) | Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Chelator (EDTA) | HPLC | NA |
| Cation Exchange Capacity (CEC) | Lachat QuikChem 8000 or Technicon AutoAnalyzer II and Perkin Elmer or Thermo Jarrel Ash ICP | NA |
| Soil Moisture | Analytical Balance | NA |
| **Soil Solution Analyses** | | |
| Total Metals (Be, Pb, Cu, Sb, Tl, Mn) | ICP | |
| Total Metals (As) | AA | |
| Trichloroethylene | GC | |

(1) NA = Not Applicable.

# Section 5.0
# Performance Assessment

## 5.1 Performance Data

### 5.1.1 Analytical Methods Employed

Standard analytical procedures for data collected in the laboratory are provided in Appendices D-1 through D-19. EDTA in all sampling results is reported as $Na_2EDTA$ and as EDTA. For EDTA, analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is: (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692. On a molar basis, there is no difference: one mole of disodium EDTA is equivalent to one mole of EDTA.

## 5.2 Data Assessment

### 5.2.1 Preliminary Site Characterization

At the beginning of the demonstration, preliminary soil characterization samples were collected from both Site C and Site 129-3 to map the extent and location of lead contamination in the soil at the proposed demonstration sites (Figures 5-1 and 5-2). Each demonstration site was divided into 36 grids. A soil sample was collected from each of the 36 grids and the samples were analyzed for pH and total lead (Tables 5-1 and 5-2). These results indicate that the soil at both sites was uniformly alkaline (pH approximately 8.2) down to the depth sampled (12 inches).

The lead concentrations in the soil at both sites varied extensively. At Site C, the lead concentration averaged 2,610 mg/kg at the 0- to 6-inch depth and ranged from 1,240 mg/kg to 8,170 mg/kg. The average lead concentration at the 6- to 12-inch depth was 2,850 mg/kg and ranged between 1,050 mg/kg to 7,150 mg/kg. The lead concentrations at Site C are consistent with those of a site with a moderate level of lead contamination. Based on the state of development of the technology at the onset of the demonstration, the soil contained lead concentrations which were reported to be just within the practical and economic limits of the technology. However, results of this demonstration showed that remediation of soil at these lead concentrations under the conditions of the site was not technologically and economically practical.

Much of the lead in the soil at Site 129-3 was present at concentrations below the regulatory residential use target of 400 mg/kg. The lead concentrations averaged 329 mg/kg at the 0- to 6-inch depth and ranged from 6 mg/kg to 1,730 mg/kg; the average lead concentration at the 6- to 12-inch depth was 249 mg/kg, with a range of 3 mg/kg to 918 mg/kg (Table 5-2). For demonstration purposes, the lower lead concentrations at this site would be similar to those which would be encountered near the end of a remediation effort. Demonstrating remediation at

| Grid # | 31 | 32 | 33 | 34 | 35 | 36 |
|---|---|---|---|---|---|---|
| 0-6 in. | 1,840 | 1,780 | 2,980 | 4,200 | 3,010 | 1,820 |
| 6-12 in. | 2,820 | 2,100 | 1,300 | 2,620 | 4,050 | 1,580 |
| Grid # | 25 | 26 | 27 | 28 | 29 | 30 |
| 0-6 in. | 1,760 | 2,340 | 1,240 | 3,490 | 2,400 | 2,010 |
| 6-12 in. | 3,550 | 3,630 | 1,500 | 4,800 | 2,550 | 1,200 |
| Grid # | 19 | 20 | 21 | 22 | 23 | 24 |
| 0-6 in. | 2,030 | 2,870 | 8,170 | 6,340 | 2,360 | 2,730 |
| 6-12 in. | 4,270 | 4,540 | 1,050 | 7,150 | 1,990 | 2,160 |
| Grid # | 13 | 14 | 15 | 16 | 17 | 18 |
| 0-6 in. | 1,340 | 2,510 | 1,810 | 2,390 | 3,000 | 2,670 |
| 6-12 in. | 2,570 | 4,060 | 2,030 | 3,640 | 2,430 | 2,620 |
| Grid # | 7 | 8 | 9 | 10 | 11 | 12 |
| 0-6 in. | 1,800 | 2,200 | 2,410 | 1,940 | 1,720 | 2,130 |
| 6-12 in. | 2,360 | 2,820 | 2,870 | 2,110 | 2,000 | 2,800 |
| Grid # | 1 | 2 | 3 | 4 | 5 | 6 |
| 0-6 in. | 2,690 | 3,650 | 2,420 | 1,410 | 1,590 | 3,090 |
| 6-12 in. | 1,100 | 5,320 | 4,670 | 1,680 | 2,000 | 2,710 |

**Figure 5-1**
**Map of Initial Lead Contamination (mg/kg) at Site C**

| Grid # | 31 | 32 | 33 | 34 | 35 | 36 |
|---|---|---|---|---|---|---|
| 0-6 in. | 353 | 682 | 130 | 170 | 490 | 973 |
| 6-12 in. | 784 | 802 | 20 | 237 | 396 | 6 |
| Grid # | 25 | 26 | 27 | 28 | 29 | 30 |
| 0-6 in. | 1,730 | 349 | 311 | 41 | 117 | 300 |
| 6-12 in. | 249 | 549 | 45 | 17 | 133 | 300 |
| Grid # | 19 | 20 | 21 | 22 | 23 | 24 |
| 0-6 in. | 1,050 | 221 | 356 | 232 | 365 | 117 |
| 6-12 in. | 301 | 344 | 495 | 13 | 521 | 516 |
| Grid # | 13 | 14 | 15 | 16 | 17 | 18 |
| 0-6 in. | 56 | 101 | 402 | 98 | 44 | 149 |
| 6-12 in. | 41 | 289 | 377 | 23 | 218 | 299 |
| Grid # | 7 | 8 | 9 | 10 | 11 | 12 |
| 0-6 in. | 705 | 6 | 169 | 126 | 41 | 85 |
| 6-12 in. | 122 | 3 | 3 | 194 | 57 | 20 |
| Grid # | 1 | 2 | 3 | 4 | 5 | 6 |
| 0-6 in. | 206 | 206 | 913 | 178 | 188 | 188 |
| 6-12 in. | 151 | 196 | 918 | 321 | 224 | 133 |

**Figure 5-2**
**Map of Initial Lead Contamination (mg/kg) at Site 129-3**

**Table 5-1**

**Initial Soil pH and Total Lead at Site C**

| Grid No. | pH | | Pb, mg/kg | |
|---|---|---|---|---|
| | Depth, inches | | Depth, inches | |
| | 0-6 | 6-12 | 0-6 | 6-12 |
| 1 | 8.1 | 8.3 | 2,690 | 1,100 |
| 2 | 8.3 | 8.4 | 3,650 | 5,320 |
| 3 | 8.0 | 8.1 | 2,420 | 4,670 |
| 4 | 8.4 | 8.5 | 1,410 | 1,680 |
| 5 | 8.3 | 8.0 | 1,590 | 2,000 |
| 6 | 8.6 | 8.0 | 3,090 | 2,710 |
| 7 | 8.5 | 8.4 | 1,800 | 2,360 |
| 8 | 8.1 | 8.3 | 2,200 | 2,820 |
| 9 | 8.3 | 8.5 | 2,410 | 2,870 |
| 10 | 8.7 | 8.0 | 1,940 | 2,110 |
| 11 | 8.3 | 8.1 | 1,720 | 2,000 |
| 12 | 8.0 | 8.4 | 2,130 | 2,800 |
| 13 | 8.3 | 8.3 | 1,340 | 2,570 |
| 14 | 8.3 | 8.7 | 2,510 | 4,060 |
| 15 | 8.3 | 8.6 | 1,810 | 2,030 |
| 16 | 8.2 | 8.2 | 2,390 | 3,640 |
| 17 | 8.5 | 8.3 | 3,000 | 2,430 |
| 18 | 8.4 | 8.5 | 2,670 | 2,620 |
| 19 | 8.1 | 7.9 | 2,030 | 4,270 |
| 20 | 8.3 | 8.0 | 2,870 | 4,540 |
| 21 | 8.6 | 8.9 | 8,170 | 1,050 |
| 22 | 8.7 | 8.4 | 6,340 | 7,150 |
| 23 | 8.3 | 8.1 | 2,360 | 1,990 |
| 24 | 8.2 | 8.4 | 2,730 | 2,160 |
| 25 | 8.5 | 8.3 | 1,760 | 3,550 |
| 26 | 8.3 | 8.5 | 2,340 | 3,630 |
| 27 | 8.3 | 8.6 | 1,240 | 1,500 |
| 28 | 8.4 | 8.3 | 3,490 | 4,800 |
| 29 | 8.3 | 8.2 | 2,400 | 2,550 |
| 30 | 8.6 | 8.3 | 2,010 | 1,200 |
| 31 | 8.7 | 8.4 | 1,840 | 2,820 |
| 32 | 8.5 | 8.0 | 1,780 | 2,100 |
| 33 | 8.5 | 8.0 | 2,980 | 1,300 |
| 34 | 8.7 | 8.3 | 4,200 | 2,620 |
| 35 | 8.7 | 8.2 | 3,010 | 4,050 |
| 36 | 8.7 | 8.1 | 1,820 | 1,580 |
| **Mean** | ***8.2*** | ***8.1*** | ***2,610*** | ***2,850*** |
| **Std. Dev.** | ***0.3*** | ***0.4*** | ***1,340*** | ***1,340*** |

**Table 5-2**

**Initial Soil pH and Total Lead at Site 129-3**

| Grid No. | pH | | Pb, mg/kg | |
|---|---|---|---|---|
| | Depth, inches | | Depth, inches | |
| | 0-6 | 6-12 | 0-6 | 6-12 |
| 1 | 8.6 | 8.1 | 206 | 151 |
| 2 | 8.3 | 8.2 | 206 | 196 |
| 3 | 8.0 | 8.1 | 913 | 918 |
| 4 | 8.4 | 8.6 | 178 | 321 |
| 5 | 8.3 | 8.1 | 188 | 224 |
| 6 | 8.1 | 8.0 | 188 | 133 |
| 7 | 8.5 | 8.4 | 705 | 122 |
| 8 | 8.1 | 8.3 | 6 | 3 |
| 9 | 8.2 | 8.5 | 169 | 3 |
| 10 | 8.8 | 8.1 | 126 | 194 |
| 11 | 8.4 | 8.1 | 41 | 57 |
| 12 | 8.1 | 8.2 | 85 | 20 |
| 13 | 8.2 | 8.3 | 56 | 41 |
| 14 | 8.2 | 8.9 | 101 | 289 |
| 15 | 8.2 | 8.3 | 402 | 377 |
| 16 | 8.2 | 8.2 | 98 | 23 |
| 17 | 8.5 | 8.8 | 44 | 218 |
| 18 | 8.4 | 8.5 | 149 | 299 |
| 19 | 8.1 | 8.1 | 1,050 | 301 |
| 20 | 8.3 | 8.0 | 221 | 344 |
| 21 | 8.6 | 8.9 | 356 | 495 |
| 22 | 8.7 | 8.4 | 232 | 13 |
| 23 | 8.6 | 8.1 | 365 | 521 |
| 24 | 8.2 | 8.4 | 117 | 516 |
| 25 | 8.5 | 8.3 | 1,730 | 249 |
| 26 | 8.2 | 8.5 | 349 | 549 |
| 27 | 8.3 | 8.6 | 311 | 45 |
| 28 | 8.4 | 8.3 | 41 | 17 |
| 29 | 8.3 | 8.2 | 117 | 133 |
| 30 | 8.6 | 8.1 | 300 | 300 |
| 31 | 8.7 | 8.4 | 353 | 784 |
| 32 | 8.6 | 8.0 | 682 | 802 |
| 33 | 8.5 | 8.0 | 130 | 20 |
| 34 | 8.7 | 8.3 | 170 | 237 |
| 35 | 8.7 | 8.2 | 490 | 396 |
| 36 | 8.8 | 8.1 | 973 | 6 |
| **Mean** | ***8.2*** | ***8.3*** | ***329*** | ***249*** |
| **Std. Dev.** | ***0.3*** | ***0.4*** | ***358*** | ***244*** |

low-end concentrations was an important aspect of the phytoextraction demonstration, since removal of lead by plants can vary with soil concentration.[Ref. 24]

Lead concentrations across the plots were analyzed statistically using Model 1 (Section 4.3.2.3.1) to test for a difference in site lead concentrations and for variability across grid rows and grid columns within each site. Since site differences were significant, the sites were analyzed separately for row and column variability (Appendix E, Table E-1). The lead concentrations in rows and columns for both Site C and Site 129-3 were not significantly different because the variability in the data was too great. If the variability of the grids within each row and column is large, it would give a large error term for testing for significance. A large error term makes detecting differences in row and column variability more difficult. The large standard deviations for both sites (Tables 5-1 and 5-2), which indicates a large amount of variability in lead concentrations, suggested that differences in row and column variability were not detected due to a large error term in the statistical analysis for both sites.

After selecting the demonstration sites, the soils from each area were further analyzed to determine fertilization requirements, various chemical and physical properties, and COCs (Table 5-3). The alkaline soil pH (pH >8.0) at both sites is the principle factor in the naturally low solubility and plant availability of lead. The sandy texture, low cation exchange capacity, and low organic matter of the soils make it difficult for nutrients to be retained. Most of the soil fertility parameters at Site C were low. Overall, soil fertility parameters at Site 129-3 were adequate for crop growth. Low extractable P levels at Site C indicated a potential for P deficiency in crops grown on this plot. Levels of P at Site 129-3 appeared adequate for good crop growth.

The iron levels at Site C were high which usually indicates a significant level of iron hydroxides and oxides in the soil mineralogy at the site. Although the soil class at Site C (Mollic Hapludalf) is not usually characterized by a high iron oxide content, the concentration reported here could reasonably be found in this soil. The soil survey also indicated aluminum oxides in the subsurface B horizon mineralogy, as indicated by exchangeable Al in the soil analysis. The specific mineralogy of the soil at Site 129-3 is normally characterized by a significant iron oxide content and aluminum oxides may also be present in quantities that would dominate the mineralogy.

Iron and aluminum minerals play a major role in primary sorption reactions in the soil, particularly those involving multivalent cations, such as antimony and thallium, and organic compounds such as EDTA. In addition, iron will effectively compete with lead for complexation by EDTA. High concentrations of iron will result in displacement of lead from the EDTA complex in the neutral to acidic soil pH range, with subsequent re-precipitation of lead as insoluble compounds in the soil. Analysis of cation-EDTA equilibria reactions indicate that EDTA will eventually predominate as the iron (III) chelate in acidic to neutral soils, and as the calcium chelate in alkaline soils. The abundance of calcium in the soil at Site C and the neutral to slightly alkaline soil pH would support formation of both calcium and iron complexes of EDTA.

### 5.2.2 Soil Sampling 1998 - Corn Crop

#### 5.2.2.1 Pre-Amendment Soil Sampling - 1998 Corn Crop

Pre-amendment plant and soil sampling for the corn crop at Sites C and 129-3 were completed the week of July 20, 1998.

Soil samples were taken from Sites C and 129-3 immediately prior to adding the soil amendments to determine if any changes had occurred from the time the soil was initially sampled to the point at which the corn was ready for soil amendment addition. During this period, the soil pH at both sites decreased from approximately 8.2 (Tables 5-1 and 5-2) to pH 7.7 (Tables 5-4 and 5-5). Such decreases commonly occur in soils after fertilization and tilling due to the nitrification process. Tilling kills soil microbes and breaks up organic matter; decomposition of the microbes provides an ammonium source in addition to the ammonium ions from the added fertilizer. Nitrification (oxidation) of the ammonium ions to nitrate then provides the protons which are responsible for the decrease in pH. The reaction is as follows:

$2NH_4^+ + 3O_2 \rightarrow 2NO\text{-}_2 + 2H_2O + 4H^+ + \text{energy};$
$2NO_2 + O_2 \rightarrow 2NO_3\text{-} + \text{energy}$

Organic acids are produced during decomposition of organic matter, which provides a secondary source of acidity. In addition, the sandy soils at TCAAP have a fairly low buffering capacity against change in pH and this has also contributed to the decrease in pH.

At both sites, the lead concentrations obtained prior to soil amendment addition varied significantly from the initial soil characterization. At Site C, the average lead concentration across all grids at the 0- to 12-inch depth was about 46% higher than the initial characterization (compare Tables 5-1 and 5-4). Just prior to soil amendment addition, the average lead concentration for Site C was 4,000 mg/kg and 3,830 mg/kg at the 0- to12-inch and 12- to 24-inch depths, respectively. In contrast, the average lead concentrations at the 0- to 12-inch depth at Site 129-3 were 76% lower than the levels found during the initial characterization (compare Tables 5-2 and 5-5). The differences in lead concentrations were observed at both sites even though the samples were taken in close proximity to each other in the grids at each sampling. The differences in concentration were likely due to the non-uniform distribution of lead as a result of the random placement of the contaminants over a period of many years. Tilling during plot preparation and planting might also account for some of the variability. Information in the RI/FS indicates that lead-contaminated waste was disposed of over much of the demonstration plot area. The higher lead concentrations in the 12- to 24-inch depth could indicate a downward movement of lead deposited by surface disposal and burning of such lead-contaminated waste. More likely, however, the lead in the 12- to 24-inch zone was placed there over years of disposal activities, since historical data indicates lead is at 5 and 10 ft in the general area. Further, lead-contaminated soil from other areas of TCAAP may well have been dumped into the area of the 1962 Pit as fill soil after the original soil had been excavated during equipment decontamination activities.

An average of 2 mg/kg arsenic was detected in the Site C soil (Table 5-4). Since the arsenic content in a typical non-contaminated glacial till sandy soil may be 6 mg/kg and range between

2-12 mg/kg,[Ref. 24] the concentrations reported may be of natural origin and not the result of disposal practices.

Although beryllium is listed as a COC for Site C, concentrations of the element in the soil were <0.15 mg/kg (Table 5-4), less than the 0.7 mg/kg figure reported in the Record of Decision (ROD). At these concentrations, the element does not appear to be cause for concern. The normal range of concentration for beryllium in uncontaminated soils is from <1 to 15 mg/kg and averages 1.6 mg/kg.[Ref. 25] Beryllium occurs most often in a divalent oxidic-bonded form. In the alkaline environment at TCAAP, it would likely be present as a complex carbonate anion. Beryllium is usually immobile in soil and does not leach readily. In the anion form, it is not easily taken up and concentrated in plants. However, relatively low concentrations of beryllium in a soluble form, in the range of 2-16 mg/kg ($10^{-3}$ to $10^{-4}$ M), are highly toxic to plants. Symptoms of toxicity include inhibited seed germination and inhibition of P absorption. When there is appreciable uptake, toxicity is manifested in mature leaves at a concentration range from 10 to 50 mg/kg.

Manganese concentrations were considerably less than the concentration of 2,500 mg/kg at Site C and 850 mg/kg at Site 129-3, as reported in the ROD (Tables 5-4 and 5-5). Concentrations were fairly uniform with soil depth across the field at both sites, averaging 297 mg/kg at Site C and 314 mg/kg at Site 129-3. It is difficult to discern if these concentrations are indigenous levels in the soil or a result of contamination. An average manganese concentration for soils that is usually cited is 600 ppm.[Ref. 26]

Antimony concentrations in the pre-amended soil at both sites were below the detection limit of the analytical method employed (Tables 5-4 and 5-5). Apparently, the concentrations reported in the ROD of 67 mg/kg at Site C and 22 mg/kg at Site 129-3 do not accurately reflect actual antimony concentrations across the demonstration areas. Antimony may be part of lead bullet composition and manufacture and antimony would be a likely soil contaminant at the site. However, the values reported in the ROD were based on a limited number of samples. Concentrations of antimony in the original waste may have been very low and the area of deposition limited, which may account for the present low concentrations. A typical concentration range for antimony in sandy soils is 0.05-1.33 mg/kg, with a mean of 0.19 mg/kg,[Ref. 27] so the low concentrations may be the natural concentrations in these soils. However, the mobility of antimony in sandy soil can be relatively high, particularly if the element is in association with Fe hydroxides,[Ref. 27] and the iron hydrous oxide content in these type soils may be appreciable.[Ref. 28] Thus, movement out of the surface soil to lower depths could account for the low antimony concentrations observed in these samples. In addition, the samples for the ROD were taken in the summer of 1990. The time differential between sampling for the ROD and subsequently occurring events such as tillage, planting, and irrigation operations, as well as adequate rainfall, may have caused the levels of antimony observed here.

**Table 5-3**

**Characterization of Bulk Soil from Sites C and 129-3**

| | **Site C** | **Site 129-3** |
|---|---|---|
| Texture | various | sand |
| pH | 8.2 | 8.0 |
| CEC, cmol/kg | 4.9 | 2.4 |
| Field capacity, % | 12 | 10 |
| Organic carbon, % | 0.6 | 0.4 |
| TKN, % | 0.008 | 0.007 |
| Total Pb, mg/kg | 3,200 | 400 |
| Exchangeable Al, mg/kg | 7 | 5 |
| " Ca " | 1,447 | 1,120 |
| " Mg " | 88 | 116 |
| " K " | 51 | 58 |
| Extractable P, mg/kg | 16 | 38 |
| " Fe " | 21 | 8 |
| " Mn " | 16 | 3 |
| Total As, mg/kg | <4.5 | <4.5 |
| " Be " | <0.6 | <0.6 |
| " Mn " | 260 | 250 |
| " Sb " | <40 | <40 |
| " Tl " | <50 | <50 |
| Plant-available Pb, mg/kg | 12 | 4 |

## Table 5-4

## Soil pH, Water-Soluble Pb, and Contaminants of Concern at Site C Prior to Adding Soil Amendments to 1998 Corn

| Grid No. | pH | | Water-Soluble Pb, mg/kg | | Pb[1], mg/kg | | As[1,2], mg/kg | | Be[1,2], mg/kg | | Mn[1,2], mg/kg | | Sb[1,2], mg/kg | | Tl[1,2], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 4 | 7.3 | 7.3 | 1.9 | <0.5[3] | 2,110 | 2,510 | 1.5 | 1.5 | <0.15[3] | <0.15[3] | 324 | 275 | <40[3] | <40[3] | <50[3] | <50[3] |
| 8 | 7.4 | 7.6 | 1.1 | 0.7 | 12,700 | 3,310 | 1.8 | 1.0 | <0.15 | <0.15 | 205 | 252 | <40 | <40 | <50 | <50 |
| 12 | 7.9 | 7.9 | 0.7 | <0.5 | 3,210 | 1,280 | 2.4 | 1.7 | <0.15 | <0.15 | 541 | 264 | <40 | <40 | 213 | <50 |
| 16 | 8.0 | 8.0 | 1.4 | 0.8 | 5,470 | 7,120 | 2.1 | 5.4 | <0.15 | <0.15 | 261 | 207 | <40 | <40 | <50 | <50 |
| 20 | 7.4 | 7.5 | 1.7 | 1.6 | 3,390 | 4,060 | 1.8 | 1.4 | <0.15 | <0.15 | 220 | 205 | <40 | <40 | 73 | <50 |
| 24 | 7.6 | 7.7 | 1.8 | <0.5 | 2,330 | 266 | 2.1 | 1.6 | <0.15 | <0.15 | 240 | 222 | <40 | <40 | <50 | <50 |
| 28 | 8.0 | 7.9 | <0.5[3] | 1.6 | 1,910 | 6,090 | 1.9 | 1.3 | <0.15 | <0.15 | 213 | 203 | <40 | <40 | <50 | <50 |
| 32 | 7.9 | 8.1 | 1.3 | <0.5 | 2,400 | 6,320 | 1.8 | 1.7 | <0.15 | <0.15 | 252 | 898 | <40 | <40 | <50 | <50 |
| 36 | 8.1 | 7.8 | 0.6 | 1.6 | 2,470 | 3,530 | 2.3 | 1.5 | <0.15 | <0.15 | 365 | 198 | <40 | <40 | <50 | <50 |
| | | | | | | | | | | | | | | | | |
| **Mean** | ***7.7*** | ***7.8*** | ***1.1*** | ***0.7*** | ***4,000*** | ***3,830*** | ***2.0*** | ***1.9*** | ***NA[4]*** | ***NA*** | ***291*** | ***302*** | ***NA*** | ***NA*** | ***32*** | ***NA*** |
| **Std. Dev.** | ***0.3*** | ***0.3*** | ***0.6*** | ***0.7*** | ***3,440*** | ***2,330*** | ***0.3*** | ***1.3*** | ***NA*** | ***NA*** | ***108*** | ***225*** | ***NA*** | ***NA*** | ***72*** | ***NA*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) Method Detection Limit.
(4) NA = Not Applicable.

## Table 5-5

## Soil pH, Water-Soluble Pb, and Contaminants of Concern at Site 129-3 Prior to Adding Soil Amendments to 1998 Corn

| Grid No. | pH | | Water-Soluble Pb, mg/kg | | Pb[1], mg/kg | | Mn[1,2], mg/kg | | Sb[1,2], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 4 | 7.0 | 7.3 | 0.6 | 0.5 | 21 | 191 | 226 | 254 | <40[3] | <40[3] |
| 8 | 7.4 | 7.8 | 1.0 | 0.4 | 55 | 2 | 368 | 1,190 | <40 | <40 |
| 12 | 7.7 | 7.8 | 0.4 | <0.2[3] | 93 | 334 | 228 | 374 | <40 | <40 |
| 16 | 7.7 | 7.7 | <0.2[3] | 0.4 | 54 | 10 | 203 | 197 | <40 | <40 |
| 20 | 8.0 | 8.0 | 0.3 | <0.2 | 22 | 2 | 209 | 409 | <40 | <40 |
| 24 | 8.0 | 7.6 | <0.2 | <0.2 | 67 | 2 | 198 | 197 | <40 | <40 |
| 28 | 7.8 | 7.6 | 0.4 | <0.2 | 230 | 35 | 206 | 288 | <40 | <40 |
| 32 | 8.0 | 8.0 | <0.2 | <0.2 | 28 | 2 | 188 | 178 | <40 | <40 |
| 36 | 8.0 | 8.0 | 0.5 | <0.2 | 52 | 10 | 288 | 439 | <40 | <40 |
| | | | | | | | | | | |
| **Mean** | ***7.7*** | ***7.7*** | ***0.4*** | ***<0.1*** | ***69*** | ***65*** | ***235*** | ***392*** | ***<40*** | ***<40*** |
| **Std. Dev.** | ***0.3*** | ***0.2*** | ***0.4*** | ***0.2*** | ***65*** | ***118*** | ***58*** | ***315*** | ***NA[4]*** | ***NA*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) Method Detection Limit.
(4) NA = Not Applicable.

Thallium occurred in soil at Site C in localized, isolated areas (Table 5-4). However, the extent of thallium contamination was not determined for every grid since only every fourth grid was sampled. Concentrations were highest in the top 12 inches of soil and, in some cases, greatly exceeded the cleanup level stipulated for Site C by the ROD. Concentrations in the 12- to 24-inch depth were less than the detection limit, which may indicate limited mobility and migration of the element in soil. The normal thallium concentration range is from 0.02 to 2.8 mg/kg in surface soils of the U.S.[Ref. 29] The element is highly associated with K and other basic cations and may be incorporated into soil minerals during weathering. If in a soluble form, it is readily mobilized and transported together with the alkaline metals.[Ref. 30] Thus, in soluble form, the element is readily leached from sandy soils, particularly in the presence of basic cations such as K and Ca. Thallium uptake by plants is greatly affected by the presence of K. Thallium can replace K in several enzyme systems with deleterious effects on plants.[Refs. 31, 32] Soil levels from 2.1 mg/kg to 8.5 mg/kg may adversely affect plants with severe damage occurring at the higher concentration.[Ref. 32] Toxicity is greatest in soils of low fertility. Thus, the conditions at Site C could be conducive to thallium toxicity in crops grown there. Since accumulation in plants seems to be a function of thallium concentration in soil, a significant accumulation in the crops grown at Site C could occur should plants remain sufficiently viable for active uptake of thallium to occur.

#### 5.2.2.2 Post-Amendment Soil Sampling - 1998 Corn Crop

Soil amendment additions (acidifier and chelate) to corn at Site C and Site 129-3 were completed the week of July 20, 1998, after pre-amendment sampling. Soil amendment (acetic acid and EDTA) formulation, mixing, and application were done in cooperation with Lynn Sinness, Manager, ConAgra, Inc., 7632 Highway 101, Shakopee, Minnesota 55379, (612) 445-6570.

Soil amendment additions were as follows:

Acetic acid was applied to acidify the soil to a pH of 5.5 and a depth of two feet. The amount of acetic acid needed was calculated from buffer curves determined on bulk soil collected from the sites. The application rate of acetic acid at both Site C and at Site 129-3 was 4,018 pounds per plot. The acetic acid was hand-applied over a three-hour period at each site using a hose applicator connected to a 5,000-gallon tanker truck.

The EDTA was added to optimize the solubilization of lead in the first two feet of soil (root zone) with the application rate designed to provide an EDTA:lead molar ratio of 1:1, based on the lead soil concentrations found in the bulk soil samples (Table 5-3). The EDTA application rate at Site C was 6,750 pounds; the application rate at Site 129-3 was 850 pounds. The lower rate at 129-3 resulted from the lower average soil lead concentration at that site. Application was made with the equipment used for application of acetic acid. Application time was 5 hours at Site C and 3 hours at Site 129-3.

These loading rates were not considered excessive and were applied in a controlled manner. Far higher amounts of EDTA are released to the environment through essentially uncontrolled industrial processes every year. For example, one report documents the release of 60 tons of EDTA into the Ruhr River annually, while 1,080 tons or more of EDTA were released into the Rhine River over a 3-year period.[Ref. 33] Concentrations of EDTA in German rivers thus range up

to 60 μg/L. Concentrations in American rivers and tributaries are somewhat lower, averaging about 30 μg/L.[Ref. 34] Nonetheless, this represents significant input of EDTA, thus making EDTA one of the most abundant organic contaminants in natural waters of the U.S.

By July 27, 1998, the treated corn was bleached and dead. Stalks were collapsed and touching the ground at both sites. Untreated areas of the plots (a border row on each side of the plot) appeared to be in a normal growth state for corn plants and were upright and green. Appropriate care was used to obtain clean, soil-free plant samples from collapsed stalks.

To obtain post-amendment soil samples, the soil samples were taken three to four days after soil amendment application. These samples were obtained to determine the concentrations of EDTA and COCs in the soil and the effect of the application on soil pH.

After the addition of EDTA, the soil pH increased slightly at both sites (Tables 5-6 and 5-7). The initial drop in pH caused by the acetic acid was only temporary, as determined in the SFAAP greenhouse studies. The pH of the EDTA solution was approximately 7.5. The increase over indigenous soil pH may be due to solubilization, complexation, and concentration of calcium into the soil liquid phase by addition of EDTA to the soil.

Soil samples from half of the grids (every other grid) were analyzed for EDTA concentration. Concentrations were quite variable, but tended to be higher in the top 12 inches of soil (Tables 5-6 and 5-7). EDTA did not appear to move with the applied solution. Factors which may have influenced and reduced initial EDTA movement were: (1) a highly varied infiltration rate at both sites with reduced infiltration at the actual sampling point; (2) a wide range of soil types within the plot resulted in inaccurate estimation of soil field capacity, and additional solution would have been required for adequate wetting of the root zone; (3) adsorption of EDTA as a water-insoluble form on soil iron hydroxides and oxides and on the silt, clay, and organic matter fractions of the soil, as occurred in the SFAAP study. The silt and clay occurred as irregular, isolated pockets or “lenses” over the entire plot and this may have reduced EDTA mobility in some areas more than others. At Site C, particularly, the presence of a pan layer in part of the plot very close to the soil surface, within 6 inches in some areas, may have influenced depth of infiltration. As shown below in Tables 5-10 and 5-11 (see Section 5.2.3), a significant amount of EDTA was also removed from the soil by the plants.

Concentrations of water-soluble lead at Site C greatly increased after amendment application, averaging 455 mg/kg and 148 mg/kg for the 0- to 12-inch and 12- to 24-inch depths, respectively (Table 5-6). The large increase in water-soluble lead compared to the concentrations in the unamended soil provides an indication of treatment effectiveness in solubilizing lead in the soil. These concentrations were lower in the 12- to 24-inch depth, which coincided with the lower EDTA concentrations. The corresponding average concentrations of EDTA were 982 mg/kg and 323 mg/kg.

The variability in water-soluble lead concentrations among grids across the field was quite high at both depths, as indicated by the large standard deviations. The molar ratio of EDTA to water-soluble lead was approximately 1:1, which is similar to the ratio found for EDTA and lead in soil after amendment additions during the SFAAP greenhouse treatability study.[Ref. 2] The soils at Site C consist of an extreme range in texture (sand to clay), but encompass the soil types in the SFAAP study soils (i.e., silty clay, silt loam). Since the ratio of EDTA:Pb is fairly constant across these soil types, this finding may prove useful as a tool to predict the impact of chelate and acidifier additions on dissimilar soils. Average total lead concentrations across the field at Site C were very similar both before (Table 5-4) and after (Table 5-6) amendment addition, but levels within the same grid varied quite widely between the before and after samplings. Also, a change in total lead concentration did not always reflect a concomitant change in the concentrations of water-soluble lead.

A paired comparison t-test was used to test whether total soil lead had decreased after soil amendment addition and corn harvest for Site C (Model 2, Section 4.3.2.3.2). The same grids sampled before soil additions (Table 5-4) were used after corn harvest for the paired comparisons. Lead concentration differences before and after corn harvest were not significant at both the 0- to 12-inch depth (probability>T of 0.9320) and the 12- to 24-inch depth (probability>T of 0.3973), indicating that a decrease in lead concentration at Site C could not be detected. However, the large variability in lead concentrations observed in different samplings, as discussed in Section 5.2.2.1, precludes detecting differences in lead concentrations after one harvest.

At Site 129-3, average EDTA concentrations were 262 and 103 mg/kg for the 0- to 12-inch and 12- to 24-inch depths, respectively, and the corresponding water-soluble lead concentrations were 47 mg/kg and 20 mg/kg (Table 5-7). These concentrations represent a molar ratio of EDTA to lead of 3:1, as compared with the 1:1 ratio found at Site C. The reasons for this are unclear, but may be due to differences in the mineralogy at Site C. The presence of aluminum hydroxides at Site 129-3 would result in less adsorption of EDTA, with more in soluble form, as is observed here.

Results of a paired t-test (Model 2, Section 4.3.2.3.2) for Site 129-3 indicate that soil lead concentrations were not significantly changed by lead uptake in the corn at the 0- to 12-inch depth (probability>T of 0.3375) and the 12- to 24-inch depth (probability>T of 0.5350).

Arsenic concentrations at Site C were somewhat higher than the pre-amendment concentrations, but were within the statistical limits of the standard deviations of the pre- and post-amendment sampling (Tables 5-4 and 5-6). As with lead, there were isolated instances in localized areas where arsenic concentrations greatly exceeded the mean concentration. However, unlike lead which exists principally as the divalent cation (although a shift to the $Pb^{4+}$ state may occur at higher pH, usually >10), arsenic may be present in several valence states, ranging from -3 to +5. This influences arsenic behavior in soil and availability to plants. The +3 and the +5 states exist under higher redox and pH conditions such as those at TCAAP. The highest oxidation state limits bioavailability. Thus, when assessing potential environmental effects, the total arsenic

## Table 5-6

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site C After Soil Amendment Additions to 1998 Corn

| Grid No. | pH[1] | | EDTA as $Na_2EDTA$[1], mg/kg | | EDTA as EDTA[1], mg/kg | | Water-Soluble Pb, mg/kg | | Pb[2,3], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | NS[4] | NS[4] | NS[4] | NS[4] | NS[4] | NS[4] | 268 | 90 | 15,000 | 8,950 |
| 2 | 8.3 | 8.0 | 251 | 130 | 218 | 113 | 150 | 97 | 2,870 | 2,210 |
| 3 | NS | NS | NS | NS | NS | NS | 293 | 114 | 4,550 | 11,800 |
| 4 | 8.4 | 8.2 | 363 | 1,540 | 316 | 1,340 | 185 | 700 | 5,000 | 3,820 |
| 5 | NS | NS | NS | NS | NS | NS | 780 | 429 | 2,780 | 3,360 |
| 6 | 8.2 | 8.5 | 1,834 | 172 | 1,590 | 150 | 656 | 122 | 5,800 | 11,300 |
| 7 | NS | NS | NS | NS | NS | NS | 451 | 33 | 627 | 1,500 |
| 8 | 8.3 | 8.5 | 655 | 61 | 569 | 53 | 295 | 74 | 4,870 | 8,240 |
| 9 | NS | NS | NS | NS | NS | NS | 138 | 64 | 2,660 | 2,940 |
| 10 | 8.3 | 8.4 | 27 | 380 | 23 | 330 | 36 | 207 | 732 | 1,810 |
| 11 | NS | NS | NS | NS | NS | NS | 306 | 13 | 2,100 | 1,290 |
| 12 | 8.3 | 8.5 | 5,740 | 198 | 4,990 | 172 | 1,270 | 116 | 2,670 | 2,080 |
| 13 | NS | NS | NS | NS | NS | NS | 92 | 56 | 5,450 | 1,710 |
| 14 | 8.3 | 8.1 | 543 | 469 | 472 | 408 | 256 | 209 | 3,060 | 2,240 |
| 15 | NS | NS | NS | NS | NS | NS | 449 | 208 | 5,090 | 6,550 |
| 16 | 8.2 | 8.4 | 743 | 1,020 | 646 | 887 | 359 | 506 | 4,680 | 4,880 |
| 17 | NS | NS | NS | NS | NS | NS | 811 | 137 | 2,370 | 5,470 |
| 18 | 8.2 | 8.5 | 2,380 | 551 | 2,070 | 479 | 761 | 100 | 2,340 | 1,100 |
| 19 | NS | NS | NS | NS | NS | NS | 54 | 51 | 3,490 | 4,860 |
| 20 | 8.4 | 8.5 | 1,280 | 517 | 1,110 | 449 | 563 | 179 | 2,870 | 5,570 |
| 21 | NS | NS | NS | NS | NS | NS | 496 | 58 | 3,390 | 3,620 |
| 22 | 8.3 | 8.3 | 235 | 19 | 204 | 17 | 129 | 44 | 3,980 | 3,130 |
| 23 | NS | NS | NS | NS | NS | NS | 1,280 | 196 | 3,320 | 3,730 |
| 24 | 8.1 | 8.4 | 1,180 | 42 | 1,030 | 37 | 448 | 25 | 2,370 | 1,480 |
| 25 | NS | NS | NS | NS | NS | NS | 371 | 538 | 6,270 | 2,550 |
| 26 | 8.3 | 8.3 | 1,660 | 37 | 1,440 | 32 | 652 | 64 | 9,180 | 6,460 |
| 27 | NS | NS | NS | NS | NS | NS | 259 | 73 | 3,870 | 3,880 |
| 28 | 8.3 | 8.3 | 314 | 265 | 273 | 230 | 127 | 108 | 4,570 | 4,940 |
| 29 | NS | NS | NS | NS | NS | NS | 1,900 | 92 | 3,710 | 3,860 |
| 30 | 8.0 | 8.5 | 867 | 296 | 754 | 257 | 400 | 127 | 1,740 | 2,870 |
| 31 | NS | NS | NS | NS | NS | NS | 670 | 44 | 4,660 | 6,380 |
| 32 | 8.4 | 8.5 | 1,170 | 602 | 1,020 | 523 | 477 | 199 | 5,970 | 7,700 |
| 33 | NS | NS | NS | NS | NS | NS | 181 | 49 | 2,750 | 3,440 |
| 34 | 8.4 | 8.7 | 809 | 380 | 703 | 330 | 277 | 121 | 5,020 | 5,630 |
| 35 | NS | NS | NS | NS | NS | NS | 416 | 35 | 2,870 | 1,750 |
| 36 | 8.1 | 8.7 | 305 | 24 | 265 | 21 | 136 | 41 | 2,100 | 1,650 |
| | | | | | | | | | | |
| **Mean** | ***8.3*** | ***8.4*** | ***1,130*** | ***372*** | ***982*** | ***323*** | ***455*** | ***148*** | ***4,020*** | ***4,300*** |
| **Std. Dev.** | ***0.1*** | ***0.2*** | ***1,310*** | ***392*** | ***1,140*** | ***341*** | ***388*** | ***156*** | ***2,520*** | ***2,730*** |

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-6 (Continued)

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site C After Soil Amendment Additions to 1998 Corn

| Grid No. | As[2,3], mg/kg | | Be[2,3], mg/kg | | Mn[2,3], mg/kg | | Sb[2,3], mg/kg | | Tl[2,3], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | 6.2 | 3.2 | 1.2 | 1.2 | 249 | 275 | <40[5] | <40[5] | 92 | 74 |
| 2 | 3.2 | 2.6 | 1.2 | 1.2 | 281 | 210 | <40 | <40 | 99 | 74 |
| 3 | 2.3 | 2.9 | 1.2 | 1.2 | 288 | 204 | 63 | <40 | <50[5] | 89 |
| 4 | 2.7 | 2.3 | 1.2 | 1.1 | 240 | 186 | <40 | <40 | <50 | <50[5] |
| 5 | 5.1 | 3.7 | 1.3 | 1.4 | 324 | 357 | <40 | 20 | 123 | 106 |
| 6 | 3.9 | 3.8 | 1.3 | 1.2 | 283 | 287 | <40 | <40 | 106 | 94 |
| 7 | 2.2 | 1.9 | 1.2 | 1.2 | 231 | 202 | <40 | <40 | <50 | 64 |
| 8 | 2.8 | 3.2 | 1.2 | 1.2 | 225 | 216 | <40 | <40 | <50 | 71 |
| 9 | 2.4 | 9.9 | 1.1 | 1.1 | 187 | 209 | <40 | <40 | 63 | 74 |
| 10 | 1.9 | 2.0 | 1.1 | 1.1 | 174 | 194 | <40 | <40 | 56 | 61 |
| 11 | 11.8 | 16.3 | 1.5 | 1.6 | 550 | 826 | <40 | <40 | 241 | 470 |
| 12 | 3.7 | 3.3 | 1.2 | 1.3 | 361 | 278 | <40 | <40 | 115 | 102 |
| 13 | 2.4 | 2.6 | 1.1 | 1.2 | 198 | 251 | <40 | <40 | <50 | 71 |
| 14 | 2.8 | 2.7 | 1.2 | 1.2 | 218 | 445 | <40 | <40 | 96 | 66 |
| 15 | 2.6 | 2.7 | <0.5[5] | <0.5[5] | 211 | 299 | <40 | <40 | 64 | 62 |
| 16 | 2.5 | 2.9 | <0.5 | <0.5 | 214 | 170 | <40 | <40 | 66 | 80 |
| 17 | 9.4 | 9.6 | <0.5 | <0.5 | 517 | 528 | <40 | <40 | 188 | 196 |
| 18 | 4.6 | 3.8 | <0.5 | <0.5 | 267 | 307 | <40 | <40 | 107 | 107 |
| 19 | 2.4 | 2.5 | <0.5 | <0.5 | 179 | 379 | <40 | <40 | <50 | 53 |
| 20 | 2.2 | 3.3 | <0.5 | <0.5 | 182 | 215 | <40 | <40 | <50 | 64 |
| 21 | 2.6 | 4.1 | <0.5 | <0.5 | 210 | 319 | <40 | <40 | 58 | 64 |
| 22 | 3.5 | 2.5 | <0.5 | <0.5 | 421 | 241 | <40 | <40 | 71 | 60 |
| 23 | 3.3 | 3.0 | <0.5 | <0.5 | 252 | 276 | <40 | <40 | 67 | 83 |
| 24 | 3.2 | 3.1 | <0.5 | <0.5 | 209 | 212 | <40 | <40 | 62 | 75 |
| 25 | 1.9 | 2.4 | <0.5 | <0.5 | 181 | 208 | <40 | <40 | 57 | 71 |
| 26 | 3.0 | 2.9 | <0.5 | <0.5 | 230 | 189 | 107 | <40 | 64 | 61 |
| 27 | 2.3 | 2.4 | <0.5 | <0.5 | 238 | 513 | <40 | <40 | 51 | 57 |
| 28 | 2.6 | 2.2 | <0.5 | <0.5 | 337 | 151 | <40 | <40 | 58 | <50 |
| 29 | 3.7 | 3.2 | <0.5 | <0.5 | 264 | 311 | 139 | <40 | 64 | <50 |
| 30 | 1.9 | 2.0 | <0.5 | <0.5 | 242 | 164 | <40 | <40 | <50 | <50 |
| 31 | 2.4 | 3.0 | <0.5 | <0.5 | 192 | 179 | <40 | <40 | <50 | <50 |
| 32 | 2.3 | 2.3 | <0.5 | <0.5 | 205 | 172 | 3.2 | <40 | <50 | <50 |
| 33 | 2.1 | 1.8 | <0.5 | <0.5 | 233 | 196 | <40 | <40 | <50 | <50 |
| 34 | 2.2 | 2.6 | <0.5 | <0.5 | 181 | 206 | <40 | 19.6 | <50 | <50 |
| 35 | 7.3 | 3.2 | <0.5 | <0.5 | 640 | 339 | <40 | <40 | 159 | 92 |
| 36 | 1.9 | 2.0 | <0.5 | <0.5 | 191 | 192 | <40 | <40 | <50 | <50 |
| | | | | | | | | | | |
| **Mean** | ***3.4*** | ***3.6*** | ***0.5*** | ***0.5*** | ***267*** | ***275*** | ***8.6*** | ***1.1*** | ***59*** | ***59*** |
| **Std. Dev.** | ***2.2*** | ***2.8*** | ***0.6*** | ***0.6*** | ***108*** | ***132*** | ***30.2*** | ***4.6*** | ***59*** | ***85*** |

(1) Half (18) of the grids were sampled for pH and EDTA analysis.
(2) Concentrations were determined by acid digestion.
(3) Contaminant of Concern for this site.
(4) NS = Not sampled.
(5) Method Detection Limit.

## Table 5-7

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site 129-3 After Soil Amendment Additions to 1998 Corn

| Grid No. | pH[1] | | EDTA as $Na_2EDTA$[1], mg/kg | | EDTA as EDTA[1], mg/kg | | Water-Soluble Pb, mg/kg | | Pb[2,3], mg/kg | | Mn[2,3], mg/kg | | Sb[2,3], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | NS[4] | NS[4] | NS[4] | NS[4] | NS[4] | NS[4] | 29 | 44 | 233 | 265 | 222 | 258 | <40[5] | <40[5] |
| 2 | 8.5 | 8.6 | 237 | 89 | 206 | 77 | 96 | 44 | 301 | 258 | 229 | 223 | <40 | <40 |
| 3 | NS | NS | NS | NS | NS | NS | 121 | 61 | 305 | 230 | 281 | 216 | <40 | <40 |
| 4 | 8.6 | 8.4 | 296 | 62 | 257 | 54 | 132 | 39 | 363 | 403 | 227 | 191 | <40 | <40 |
| 5 | NS | NS | NS | NS | NS | NS | 43 | 11 | 161 | 123 | 281 | 324 | <40 | <40 |
| 6 | 8.2 | 8.6 | 296 | 38 | 257 | 33 | 23 | 4 | 114 | 57 | 244 | 208 | <40 | <40 |
| 7 | NS | NS | NS | NS | NS | NS | 15 | 11 | 49 | 57 | 209 | 196 | <40 | <40 |
| 8 | 8.5 | 8.9 | 341 | 319 | 296 | 277 | 38 | 17 | 88 | 78 | 257 | 689 | <40 | <40 |
| 9 | NS | NS | NS | NS | NS | NS | 45 | 14 | 99 | 65 | 262 | 217 | <40 | <40 |
| 10 | 8.7 | 8.7 | 73 | 18 | 63 | 16 | 3 | <1.0[5] | 30 | 23 | 245 | 274 | <40 | <40 |
| 11 | NS | NS | NS | NS | NS | NS | 3 | <1.0 | 32 | 26 | 276 | 241 | <40 | <40 |
| 12 | 8.4 | 8.6 | 69 | 36 | 60 | 31 | 2 | <1.0 | 25 | 17 | 226 | 204 | <40 | <40 |
| 13 | NS | NS | NS | NS | NS | NS | 3 | 6 | 29 | 32 | 224 | 220 | <40 | <40 |
| 14 | 8.4 | 8.7 | 346 | 246 | 301 | 214 | 30 | 21 | 89 | 140 | 236 | 330 | <40 | <40 |
| 15 | NS | NS | NS | NS | NS | NS | 49 | 25 | 361 | 140 | 272 | 285 | <40 | <40 |
| 16 | 8.5 | 8.3 | 966 | 69 | 840 | 60 | 35 | 2 | 83 | 36 | 297 | 307 | <40 | <40 |
| 17 | NS | NS | NS | NS | NS | NS | 6 | 3 | 36 | 104 | 286 | 279 | <40 | <40 |
| 18 | 8.1 | 8.2 | 451 | 282 | 392 | 245 | 47 | 12 | 105 | 52 | 278 | 244 | <40 | <40 |
| 19 | NS | NS | NS | NS | NS | NS | 63 | 54 | 376 | 447 | 228 | 225 | <40 | <40 |
| 20 | 8.6 | 8.6 | 70 | 31 | 61 | 27 | 34 | 14 | 226 | 143 | 183 | 277 | <40 | <40 |
| 21 | NS | NS | NS | NS | NS | NS | 38 | 2 | 74 | 32 | 230 | 304 | <40 | <40 |
| 22 | 8.2 | 8.7 | 16 | 5 | 14 | 4 | 2 | <1.0 | 37 | 42 | 255 | 322 | <40 | <40 |
| 23 | NS | NS | NS | NS | NS | NS | 11 | 9 | 45 | 42 | 238 | 244 | <40 | <40 |
| 24 | 8.4 | 8.6 | 321 | 130 | 279 | 113 | 15 | 11 | 54 | 46 | 229 | 268 | <40 | <40 |
| 25 | NS | NS | NS | NS | NS | NS | 210 | 116 | 795 | 600 | 317 | 265 | <40 | 73 |

## Table 5-7 (Continued)

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site 129-3 After Soil Amendment Additions to 1998 Corn

| Grid No. | pH[1] | | EDTA as $Na_2EDTA$[1], mg/kg | | EDTA as EDTA[1], mg/kg | | Water-Soluble Pb, mg/kg | | Pb[2,3], mg/kg | | Mn[2,3], mg/kg | | Sb[2,3], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 26 | 8.6 | 8.7 | 672 | 166 | 584 | 144 | 227 | 65 | 563 | 246 | 231 | 265 | <40 | <40 |
| 27 | NS | NS | NS | NS | NS | NS | 102 | 44 | 540 | 235 | 189 | 249 | <40 | <40 |
| 28 | 8.5 | 8.4 | 116 | 100 | 101 | 87 | 12 | 11 | 35 | 46 | 209 | 210 | <40 | <40 |
| 29 | NS | NS | NS | NS | NS | NS | 22 | 7 | 84 | 40 | 228 | 215 | <40 | <40 |
| 30 | 8.4 | 8.5 | 125 | 182 | 109 | 158 | 5 | 14 | 33 | 49 | 272 | 280 | <40 | <40 |
| 31 | NS | NS | NS | NS | NS | NS | 23 | 18 | 41 | 48 | 189 | 209 | <40 | <40 |
| 32 | 8.8 | 8.7 | 561 | 200 | 488 | 174 | 32 | 19 | 83 | 62 | 240 | 212 | <40 | <40 |
| 33 | NS | NS | NS | NS | NS | NS | 31 | 5 | 117 | 49 | 279 | 231 | <40 | <40 |
| 34 | 8.4 | 8.6 | 43 | 8 | 37 | 7 | 25 | 15 | 171 | 211 | 216 | 221 | <40 | <40 |
| 35 | NS | NS | NS | NS | NS | NS | 106 | 12 | 2,130 | 144 | 269 | 216 | <40 | <40 |
| 36 | 8.4 | 8.7 | 429 | 139 | 373 | 121 | 25 | 8 | 135 | 40 | 255 | 215 | <40 | <40 |
| | | | | | | | | | | | | | | |
| **Mean** | ***8.5*** | ***8.6*** | ***302*** | ***118*** | ***262*** | ***103*** | ***47*** | ***20*** | ***223*** | ***128*** | ***245*** | ***259*** | ***<40*** | ***<40*** |
| **Std. Dev.** | ***0.2*** | ***0.2*** | ***250*** | ***97*** | ***217*** | ***84*** | ***54*** | ***24*** | ***372*** | ***134*** | ***32*** | ***83*** | ***NA[6]*** | ***NA[6]*** |

(1) Half (18) of the grids were sampled for pH and EDTA analysis.
(2) Concentrations were determined by acid digestion.
(3) Contaminant of Concern for this site.
(4) NS = Not Sampled.
(5) Method Detection Limit.
(6) NA = Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

content of the soil, as well as the chemical form of arsenic, should be considered. However, a determination of arsenic speciation was beyond the scope of this study and, in any event, arsenic concentrations were so low as not to generate concern. Arsenic was not a Contaminant of Concern at Site 129-3.

Antimony concentrations at both Sites C and 129-3 were below the analytical Method Detection Limit (MDL) (Tables 5-6 and 5-7). This may indicate a very limited occurrence of antimony in these areas, which may diminish the importance of antimony as a primary COCs.

Thallium was detected in two-thirds of the soil samples collected after amendment addition at Site C (Table 5-6). The distribution was fairly uniform over the entire demonstration area, both at the 0- to 12-inch depth and the 12- to 24-inch depth. In only two instances were thallium not found at the 12- to 24-inch depth, which reflects the propensity for thallium leaching in sandy soils. Thallium concentrations averaged 59 mg/kg and ranged from <50 to 241 mg/kg in the top 12 inches of soil. Concentrations in the 12- to 24-inch depth also averaged 59 mg/kg, but the range of concentrations was higher at <50 to 470 mg/kg. These concentrations are considerably higher than found in the pre-amendment sampling (Table 5-4), but this is likely a function of the greater number of samples collected during the post-amendment sampling period. Since 2.1-8.5 mg/kg of thallium in soil can adversely affect plants,[Ref. 30] thallium present at Site C may be a significant factor in any remediation effort at this site.

### 5.2.3 Plant Sampling - 1998 Corn Crop

#### 5.2.3.1 Plant Growth - 1998 Corn Crop

The marginal levels of soil phosphorus at Site C (see Section 5.2.1) resulted in the development of a P deficiency, evidenced by stunted plants with a purple coloration of stems and leaves, early in the growing corn. The high lead concentrations at the site may have additionally reduced available P to the crop. In this situation, large amounts of P would have been needed to prevent the problem. However, over-applications of P could have caused complexion of lead as insoluble Pb-phosphates which would have hindered chelate efficiency. Only a small amount of additional P fertilizer had been added at Site C. To correct the deficiency, two foliar applications of a 0.5% P solution were made to the affected plants. This treatment resulted in the disappearance of visual deficiency symptoms. The initial inadequate P nutrition nonetheless resulted in less vigorous plants. A nutritional imbalance and deficiency of iron (Fe) and nitrogen subsequently developed. The affected plants were treated with a foliar application of a 2% solution of ferrous ammonium sulfate, which appeared to correct the Fe and N deficiency. However, the plants did not achieve maximum growth and yields were reduced. Corn at Site 129-3 appeared to grow normally during the season.

#### 5.2.3.2 Pre-Amendment Plant Sampling - 1998 Corn Crop

Lead concentrations in corn plants grown on Site C averaged 30 mg/kg before soil amendment addition (Table 5-8). Of the other COCs, only manganese accumulated in appreciable amounts in the tissue, averaging 34 mg/kg. Concentrations of arsenic, beryllium, and antimony were originally low in the soil. Consequently, little uptake of these elements occurred. Normal plant tissue concentrations are 1 to 1.7 for arsenic, <1 to 7 for beryllium, 7 to 50 for antimony, and <1 mg/kg for thallium.[Ref. 32] Arsenic, antimony, and thallium were present in corn tissue at concentrations below the lower limit of these ranges or at the detection limit of the analytical method; beryllium was found at slightly higher concentrations in plants from several of the grids.

Although soil concentrations of thallium were quite high, little thallium was found in the plant. Apparently, thallium was present in a form which had only limited availability to plants. The manganese concentrations observed in corn at Site C were within the commonly reported sufficiency level of 20 to 300 mg/kg for most plants, and well below the most commonly reported toxicity level of 500 mg/kg.[Ref. 32]

Lead concentrations in corn plants at Site 129-3 were much lower than at Site C, primarily due to the much lower lead content of the soil at this location (Table 5-9). Manganese levels in corn from Site 129-3 were comparable to levels found in plants at Site C.

Overall, there was nothing remarkable about the concentrations of COCs found in corn at both sites before soil amendment application. Arsenic and antimony (and beryllium except in a small area at Site C) were present in the tissue below toxic levels to the plant or were present in such low concentrations as to likely preclude contamination of the food chain if the plant tissues were consumed. Since thallium was found to be below the Method Detection Limit, there is uncertainty as to the potential impact of this element.

**Table 5-8**

**Contaminants of Concern in 1998 Corn from Site C Prior to Adding Soil Amendments**

| Grid No. | Pb, mg/kg | As[1], mg/kg | Be[1], mg/kg | Mn[1], mg/kg | Sb[1], mg/kg | Tl[1], mg/kg |
|---|---|---|---|---|---|---|
| 4 | 34 | <0.2[2] | <0.6[2] | 37 | <40[2] | <50[2] |
| 8 | 33 | <0.2 | 2.2 | 41 | <40 | <50 |
| 12 | 14 | <0.2 | <0.6 | 25 | <40 | <50 |
| 16 | 44 | <0.2 | 3.5 | 39 | 3 | <50 |
| 20 | 36 | <0.2 | <0.6 | 35 | <40 | <50 |
| 24 | 30 | <0.2 | 2.2 | 34 | <40 | <50 |
| 28 | 35 | <0.2 | <0.6 | 37 | <40 | <50 |
| 32 | 17 | <0.2 | <0.6 | 29 | <40 | <50 |
| 36 | 31 | <0.2 | <0.6 | 32 | <40 | <50 |
| | | | | | | |
| **Mean** | ***30*** | ***<0.2*** | ***0.9*** | ***34*** | ***<40*** | ***<50*** |
| **Std. Dev.** | ***10*** | ***NA[3]*** | ***1.4*** | ***5*** | ***NA*** | ***NA*** |

(1) Contaminant of Concern for this site.
(2) Method Detection Limit.
(3) NA = Not Applicable.

#### 5.2.3.3 Post-Amendment Plant Sampling - 1998 Corn Crop

The total yield of corn plant material at Site C (dry weight basis) was 850 pounds for the 0.2-acre area. On a per-acre basis, this was 4,250 lb/acre. The average lead concentration in plants was 6,460 mg/kg (0.65%) [see Table 5-10]. The amount of lead removed from the soil was calculated by the following:

4,250 lb/acre x 0.0065 = 27.6 lb lead/acre removed

The total yield of corn plant material at Site 129-3 (dry weight basis) was 1,431 pounds for the 0.2-acre area. On a per-acre basis, this was 7,155 lb/acre. The average lead concentration in plants was 1,300 mg/kg (0.13%) [see Table 5-11]. The amount of lead removed from the soil was calculated by the following:

7,155 lb/acre x 0.0013 = 9.3 lb lead/acre removed

These biomass yields were lower than those reported in the literature. The values in the literature were likely for reproductively mature plants, i.e., full-grown plants with mature ears, which would explain the discrepancy.

The EDTA content of post-amendment corn samples at Site C (Table 5-10) averaged 4.3% (43,000 mg/kg) and ranged from 2.3% (23,000 mg/kg) up to 7.2% (72,000 mg/kg). Values attained with corn in the previous greenhouse study[Ref. 2] were approximately 11%, but the corn plants were confined in pots and root exploration of the soil was at a maximum. However, the concentrations found in corn in the TCAAP demonstration are sufficiently high as to be considered significant as a removal mechanism of EDTA from the soil. The EDTA was present in corn tissue at an average ratio of EDTA to lead of 3.6 at Site C and 2.9 at Site 129-3.

Lead concentrations in corn at Site C averaged 6,460 mg/kg (0.65%) after amendment additions and ranged from 3,300 mg/kg (0.33%) up to 11,300 mg/kg (1.1%) [see Table 5-10]. These lead concentrations were very similar to concentrations attained in corn in the SFAAP greenhouse pot study.[Ref. 2] Soils in that study differed in chemical and physical properties from soils at TCAAP, but had a similar lead content as the soil at Site C. These results indicates that the technology is applicable across differing soil types if the soil types being treated are fairly homogeneous. There was considerable variation in plant tissue lead content because of the variability across the field, but generally, uptake of lead increased with increasing amounts of lead in the soil. Lead concentrations in corn across the plots were analyzed statistically using Model 1 in Section 4.3.2.3.1. Variability across rows was not significant (Appendix E, Table E-2). Variability across columns was significant at the 0.1 level of probability, indicating variable uptake of lead by corn across the field. The variable concentrations of soil lead across the plot was expected to affect the amount of uptake by the plants and this is indicated by these statistics. The comparisons of column means using the Least Significant Difference t-test is given in Appendix E, Table E-2A.

**Table 5-9**

**Contaminants of Concern in 1998 Corn from Site 129-3**
**Prior to Adding Soil Amendments**

| Grid No. | Pb, mg/kg | Mn[1], mg/kg | Sb[1], mg/kg |
|---|---|---|---|
| 4 | <1[2] | 27 | <40[2] |
| 8 | 4 | 29 | <40 |
| 12 | 9 | 28 | <40 |
| 16 | 8 | 31 | <40 |
| 20 | 9 | 33 | <40 |
| 24 | 7 | 34 | <40 |
| 28 | 13 | 36 | <40 |
| 32 | 7 | 36 | <40 |
| 36 | 27 | 36 | <40 |
| | | | |
| **Mean** | ***9*** | ***32*** | ***<40*** |
| **Std. Dev.** | ***7*** | ***4*** | ***NA[3]*** |

(1) Contaminant of Concern for this site.
(2) Method Detection Limit.
(3) NA = Not Applicable.

## Table 5-10
## EDTA and Contaminants of Concern in 1998 Corn from Site C
## After Soil Amendment Additions

| Grid No. | EDTA as $Na_2EDTA$[1], mg/kg | EDTA as EDTA[1], mg/kg | Pb[2], mg/kg | As[2,3], mg/kg | Be[2,3] mg/kg | Mn[2,3], mg/kg | Sb[2,3], mg/kg | Tl[2,3], mg/kg |
|---|---|---|---|---|---|---|---|---|
| 1 | NS[4] | NS[4] | 4,510 | 0.2 | 2.5 | 802 | <40[5] | <50[5] |
| 2 | NS | NS | 7,170 | 0.3 | 3.1 | 589 | <40 | <50 |
| 3 | NS | NS | 7,800 | 0.2 | <0.6[5] | 580 | <40 | <50 |
| 4 | 26,000 | 23,000 | 6,240 | 0.2 | <0.6 | 420 | <40 | <50 |
| 5 | NS | NS | 4,940 | 0.2 | <0.6 | 358 | <40 | <50 |
| 6 | NS | NS | 5,680 | <0.16[5] | <0.6 | 392 | <40 | <50 |
| 7 | NS | NS | 5,740 | 0.2 | <0.6 | 851 | <40 | <50 |
| 8 | 43,000 | 37,000 | 6,330 | 0.2 | <0.6 | 560 | <40 | <50 |
| 9 | NS | NS | 7,380 | 0.2 | 8.0 | 669 | <40 | <50 |
| 10 | NS | NS | 5,090 | 0.4 | <0.6 | 530 | <40 | <50 |
| 11 | NS | NS | 4,730 | <0.16 | 2.9 | 414 | <40 | <50 |
| 12 | 43,000 | 37,000 | 4,020 | <0.16 | <0.6 | 433 | <40 | <50 |
| 13 | NS | NS | 7,520 | <016 | <0.6 | 764 | <40 | <50 |
| 14 | NS | NS | 8,300 | <0.16 | <0.6 | 661 | <40 | <50 |
| 15 | NS | NS | 5,590 | <0.16 | <0.6 | 593 | <40 | <50 |
| 16 | 49,000 | 43,000 | 9,700 | <0.16 | <0.6 | 446 | <40 | <50 |
| 17 | NS | NS | 3,970 | 0.2 | 1.6 | 385 | <40 | <50 |
| 18 | NS | NS | 5,630 | <0.16 | <0.6 | 520 | <40 | <50 |
| 19 | NS | NS | 8,390 | 0.2 | <0.6 | 641 | <40 | <50 |
| 20 | 75,000 | 65,000 | 9,040 | 0.2 | <0.6 | 576 | <40 | <50 |
| 21 | NS | NS | 5,130 | 0.2 | <0.6 | 601 | <40 | <50 |
| 22 | NS | NS | 11,300 | 0.2 | 0.7 | 504 | <40 | <50 |
| 23 | NS | NS | 5,090 | <0.16 | <0.6 | 407 | <40 | <50 |
| 24 | 39,000 | 34,000 | 6,290 | <0.16 | <0.6 | 431 | <40 | <50 |
| 25 | NS | NS | 6,590 | <016 | <0.6 | 576 | <40 | <50 |
| 26 | NS | NS | 8,970 | 0.3 | <0.6 | 563 | <40 | <50 |
| 27 | NS | NS | 3,300 | <0.16 | <0.6 | 634 | <40 | <50 |
| 28 | 40,000 | 35,000 | 8,270 | <0.16 | <0.6 | 456 | <40 | <50 |
| 29 | NS | NS | 6,910 | <016 | <0.6 | 335 | <40 | <50 |
| 30 | NS | NS | 7,600 | <0.16 | <0.6 | 593 | <40 | <50 |
| 31 | NS | NS | 5,870 | <016 | 1.0 | 642 | <40 | <50 |
| 32 | 83,000 | 72,000 | 5,630 | 0.2 | <0.6 | 591 | <40 | <50 |
| 33 | NS | NS | 3,720 | <0.16 | <0.6 | 562 | <40 | <50 |
| 34 | NS | NS | 6,200 | <016 | <0.6 | 453 | <40 | <50 |
| 35 | NS | NS | 8,620 | <0.16 | <0.6 | 424 | <40 | <50 |
| 36 | 52,000 | 45,000 | 5,440 | <016 | 0.9 | 507 | <40 | <50 |
| | | - | | | | | | |
| **Mean** | ***50,000*** | ***43,000*** | ***6,460*** | ***<0.16*** | ***<0.6*** | ***541*** | ***<40*** | ***<50*** |
| **Std. Dev.** | ***18,000*** | ***16,000*** | ***1,830*** | ***NA[6]*** | ***NA[6]*** | ***123*** | ***NA[6]*** | ***NA[6]*** |

(1) Nine of 36 grids sampled for EDTA analysis.
(2) Concentrations were determined by acid digestion
(3) Contaminant of Concern for this site.
(4) NS = Not sampled.
(5) Method Detection Limit.
(6) NA = Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-11
## EDTA and Contaminants of Concern in 1998 Corn from Site 129-3 After Soil Amendment Additions

| Grid No. | EDTA as $Na_2EDTA$[1], mg/kg | EDTA as EDTA[1], mg/kg | Pb[2], mg/kg | Mn[2,3], mg/kg | Sb[2,3], mg/kg |
|---|---|---|---|---|---|
| 1 | NS[4] | NS[4] | 1,110 | 521 | <40[5] |
| 2 | NS | NS | 2,090 | 799 | <40 |
| 3 | NS | NS | 1,700 | 838 | <40 |
| 4 | 4,000 | 3,000 | 1,440 | 773 | <40 |
| 5 | NS | NS | 1,140 | 739 | <40 |
| 6 | NS | NS | 106 | 61 | <40 |
| 7 | NS | NS | 608 | 877 | <40 |
| 8 | 5,000 | 4,000 | 1,000 | 971 | <40 |
| 9 | NS | NS | 1,190 | 865 | <40 |
| 10 | NS | NS | 901 | 771 | <40 |
| 11 | NS | NS | 391 | 565 | <40 |
| 12 | 1,000 | 900 | 9 | 27 | 6 |
| 13 | NS | NS | 822 | 783 | <40 |
| 14 | NS | NS | 984 | 607 | <40 |
| 15 | NS | NS | 2,230 | 531 | <40 |
| 16 | 8,000 | 7,000 | 643 | 659 | <40 |
| 17 | NS | NS | 147 | 642 | <40 |
| 18 | NS | NS | 153 | 321 | <40 |
| 19 | NS | NS | 3,220 | 449 | 26 |
| 20 | 10,000 | 9,000 | 4,380 | 486 | 16 |
| 21 | NS | NS | 859 | 520 | <40 |
| 22 | NS | NS | 425 | 647 | <40 |
| 23 | NS | NS | 465 | 812 | <40 |
| 24 | 13,000 | 11,000 | 381 | 504 | <40 |
| 25 | NS | NS | 3,200 | 396 | 8 |
| 26 | NS | NS | 2,990 | 546 | <40 |
| 27 | NS | NS | 4,130 | 725 | <40 |
| 28 | 13,000 | 11,000 | 1,230 | 504 | <40 |
| 29 | NS | NS | 1,670 | 799 | <40 |
| 30 | NS | NS | 372 | 516 | 4 |
| 31 | NS | NS | 1,590 | 614 | <40 |
| 32 | 11,000 | 10,000 | 972 | 612 | <40 |
| 33 | NS | NS | 1,270 | 723 | <40 |
| 34 | NS | NS | 1,180 | 653 | <40 |
| 35 | NS | NS | 1,550 | 763 | <40 |
| 36 | 8,000 | 7,000 | 308 | 295 | <40 |
| | | | | | |
| **Mean** | ***8,000*** | ***7,000*** | ***1,300*** | ***609*** | ***1.7*** |
| **Std. Dev.** | ***4,000*** | ***3,000*** | ***1,100*** | ***211*** | ***5.2*** |

(1) Nine of 36 grids sampled for EDTA analysis.
(2) Concentrations were determined by acid digestion.
(3) Contaminant of Concern for this site.
(4) NS = Not Sampled.
(5) Method Detection Limit.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

Lead concentrations in corn at Site 129-3 were much lower than at Site C (Table 5-11) and reflect the much lower soil lead content at Site 129-3 (Table 5-4). Lead concentrations in the corn averaged 1,300 mg/kg (0.13%) at Site 129-3 and ranged from a low of 9 mg/kg (<0.001%) to a high of 4,380 mg/kg (0.44%).

Variability analysis for grid rows and columns using Model 1 in Section 4.3.2.3.1 indicated variable uptake of lead by the corn across the plots (Appendix E, Table E-3), as shown by significance at the 0.05 level of probability for both rows and columns. No discernible pattern is apparent for the row means (Appendix E, Table E-3A); however, the lowest means are found for columns 4, 5, and 6 (Appendix E, Table E-3B). Soil lead concentrations were also lowest for these columns, although variability analysis was not significant for columns (Section 5.2.1 and Appendix E, Table E-1). These results indicate a lower level of lead contamination in the eastern side of the plot.

Given that the objective of the demonstration at Site 129-3 was to determine the effect of low soil lead concentrations on treatment effectiveness, a level of 0.44% in the plants may be significant for removing lead from a low-level contaminated site. What is notable is that similar EDTA-to-lead ratios in tissue were observed at both sites, as discussed in the section above, indicating that a similar uptake mechanism may occur at either low or high soil lead concentrations. However, phytoremediation may be more applicable to sites with low soil lead concentrations, since remediation time would be far less than for sites with higher concentrations.

Concentrations of arsenic in plants growing on uncontaminated soils normally range from 1 to 1.7 mg/kg and may be found at levels of 20 mg/kg under contaminated conditions. As such, the low levels reported for corn after amendment addition at Site C (<0.16 to 0.4 mg/kg, Table 5-10) are likely insignificant from an environmental standpoint.

Beryllium concentrations in the corn at Site C were generally below the detection limit of 0.6 mg/kg for the analytical method employed, with the highest concentration being 8.0 mg/kg (Table 5-10). The higher values occurred at isolated areas within the plot. These values are below the reported toxicity level of 10 to 50 mg/kg manifested in mature leaves.

The average manganese concentrations in corn were 541 mg/kg for Site C and 609 at Site 129-3 (Tables 5-10 and 5-11), which were 15- to 20-fold greater than in corn sampled before amendment application (Tables 5-8 and 5-9). This indicated solubilization of manganese and subsequent uptake by the plants. However, the lower concentrations of manganese in the plants relative to lead are most likely due to EDTA specificity for lead rather than manganese. The low concentrations of manganese in the soil relative to lead may have also been a factor in the lower uptake of manganese, as the amount of metals uptake induced by EDTA application to the soil is usually a function of the metal concentration in the soil.

Antimony concentrations in corn from Site C and at Site 129-3 were below the detection limit of the analytical method employed (Tables 5-10 and 5-11).

Thallium concentrations in corn from Site C also were below Method Detection Limits. This indicates that either the chemical form of thallium in the soil was unchanged by amendment application or that the corn did not accumulate appreciable amounts of thallium.

Overall, lead and manganese were the only COCs that accumulated in significant concentrations in the corn at either site. Other COCs were, for the most part, present at very low concentrations in the soil and, consequently, little or no plant uptake occurred.

Regression analyses were conducted to discern whether the level of a measured parameter, such as soil lead concentration, could be used to predict the level of another parameter, such as uptake of lead by the crop (Appendix E, Table E-4). For Site C, only the regression of corn lead concentration on the initial total soil lead concentration was significant. The regression of corn lead concentrations on total soil lead concentrations at 0-12 inches and 12-24 inches, and concentrations averaged using the values at 0-12 inches and 12-24 inches, were not significant. The regressions of corn lead concentrations on water-soluble lead concentrations were not significant, and the regressions of water-soluble lead on total soil lead also were not significant. This is evident from the data in Table 5-6 which, for any given sample, shows wide variability between the total lead content of the soil and the water-soluble lead and no consistent ratio between the two.

Regressions for Site 129-3 were all significant. These results indicate that plant lead uptake increased with an increase in the lead concentration of the soil. As would be expected, plant lead uptake also increases with an increase in water-soluble lead in the soil. However, the R-square values for these regressions are low, which indicates that while soil lead concentrations affect plant lead uptake, the ability to predict plant lead uptake from soil lead concentrations is low.

#### 5.2.3.4 Ancillary Plant Sampling

Browning and loss of foliage from cottonwood trees located adjacent to the demonstration plots was observed shortly after amendment addition at Site C. Inspection at Site C revealed more extensive browning and loss of leaves in trees adjacent to the downhill side (extreme northwestern corner) of the demonstration plot after amendment addition for corn. In addition, a trail of dead grass following an old, compacted gravel roadbed led away from the plot exclusion fence into a nearby field. One small cottonwood located about 90 feet from the fence, but only 20 feet from the trail, was also affected. A willow tree about the same distance from the trail as the small cottonwood was not affected, nor was a wetlands area in the vicinity.

Leaf samples were taken from affected branches from the trees adjacent to the exclusion fence, from the small tree 90 feet from the fence, and from an unaffected tree some distance from the plot on the uphill (southern) side of the demonstration plot. Samples were placed in separate plastic bags and labeled. These samples were delivered to ATK staff for further packaging and transport to an overnight delivery service and, from there, to the TVA Analytical Laboratory in Muscle Shoals, Alabama. Analysis of the leaf tissue showed a concentration of 1,300 ppm lead in the impacted trees and 10 ppm in non-impacted trees. The leaves of apparently unaffected trees immediately adjacent to the affected trees were not analyzed.

It was determined that runoff of acetic acid had occurred from a limited portion of Site C, which resulted in vegetation kill and may have enhanced lead uptake by these plants. It was also determined that only a small quantity of EDTA, if any, was in the runoff since the problem was detected immediately after acetic acid addition. Although this runoff affected adjacent vegetation and trees, roots of the impacted plants were found growing well into the plot area, which exposed the plants to lead in a plant-available form. Thus, these plants would have been impacted regardless of contact with the runoff.

To prevent dispersion of lead in wind-blown leaves outside the immediate area at both sites, and to prevent a recurrence of this event, trees within 100 feet of the plot fences were removed, regardless of whether or not they had been affected by runoff. To formulate disposal options of the cut trees, tree trunk sections were analyzed for lead content. Results showed an average lead content of 99 mg/kg in both affected and unaffected trees. The slope of the land was so slight that a runoff was not anticipated. However, this slope, in conjunction with restricted infiltration in some areas of the plot due to the varying soil texture, and the hardpan road bed which channeled the solution, did result in some runoff. Therefore, pro-active construction of dikes and berms around potential runoff areas at both Site C and at Site 129-3 was undertaken and completed to prevent future occurrences. After harvest of the corn, deeper tillage was conducted within the plot in areas of preferential flow before planting of the white mustard crop to improve infiltration of amendment solutions.

Samples of bark, trunk, and branches from cottonwood trees growing on Site A were also collected by ATK personnel and analyzed by the TVA Analytical Laboratory for total lead content. Site A (Figure 3-2) is another of the source area sites at TCAAP that has shallow soil lead contamination and is being excavated as part of the Superfund cleanup. The results were compared with lead concentrations in cottonwood trees from Site C affected by runoff during amendment application for corn. Lead concentrations in trees from Site A (average - 276 mg/kg) were two to three times higher than lead concentrations in trees from Site C (average - 99 mg/kg). The higher concentrations may have been due to the spatial variability of the soil lead within each contaminated area, natural variations within the soil body, the type of waste at each site, or the proximity of trees to the contamination source. Thus, while exposure to runoff at Site C may have resulted in elevated lead concentrations in the trees, it is also possible that random variation in lead could have accounted for a significant amount of the increase in tissue lead.

### 5.2.4 Soil Sampling - 1998 White Mustard Crop

#### 5.2.4.1 Pre-Amendment Soil Sampling - 1998 White Mustard Crop

Prior to planting the white mustard crop (August 17, 1998), a drip delivery system was installed on Site C and on Site 129-3. The system at Site C consisted of a 90-foot-long main header across the south end of the field with 90-foot-long strips of drip tubing attached every two feet along the length of the header. These strips extended northerly across the entire field and provided the means for chelate delivery for the white mustard. The system was the same at Site 129-3, except that the header was placed on the north end of the field and drip tubing extended from it across the demonstration area in a southerly direction.

Sampling and amendment addition activities for the white mustard crop commenced on October 7, 1998. Pre-amendment plant and soil sampling for Site C was completed on October 7, 1998, and for Site 129-3 on October 8, 1998. At this time, at Site C, essentially all of the white mustard had bolted and was in full bloom. About 10%-15% of the plants had shed blooms and had initiated seed pod formation. At Site 129-3, the plants were in various stages of bloom and bolt. The full blossom stage had not been reached in about 25% of the plants. Blooming was about 75% complete in these plants. About 15% of the plants had not bolted.

The average pH at Site C changed very little for white mustard (Table 5-12) from the post-amendment soil sampling after corn harvest (Table 5-6). At Site 129-3, soil pH decreased slightly from 8.5 to 8.1 for the 0- to 12-inch depth and from 8.6 to 8.1 for the 12- to 24-inch depth. In this case, the tendency of EDTA to increase soil pH was negated to an extent by the tillage/irrigation cycle conducted before the white mustard was planted. As discussed in Section 5.2.2.1, tilling of soil tends to cause a decrease in soil pH. Thus, the increase in soil pH caused by release of ammonia during degradation of EDTA was offset somewhat by tillage. However, degradation of ferric-EDTA (and possibly other cation-EDTA complexes such as Ca- or Mg-EDTA) has been shown to be inhibited above pH 8.0, and this may have resulted in essentially no net change in pH.[Ref. 35] Less EDTA was added at Site 129-3 than at Site C, so the effect on pH would not be as large.

At Site C, the average EDTA concentration in the 0- to 12-inch depth decreased from 982 mg/kg after adding the soil amendments to corn (Table 5-6) to 360 mg/kg (Table 5-12) ten weeks later at pre-amendment sampling for white mustard. The decrease in EDTA most likely was due to a combination of (1) adsorption onto soil minerals, e.g., iron oxides and hydroxides; (2) some degradation of EDTA due to tillage/irrigation discussed above, and (3) downward movement of EDTA. Downward movement in the rooting zone of EDTA apparently did occur since concentrations in the 12- to 24-inch depth increased from 323 mg/kg in the post-amendment soil samples for corn (Table 5-6) to 887 mg/kg in the pre-amendment samples for white mustard (Table 5-12).

At Site C, higher concentrations of water-soluble Pb were generally found at the 12- to 24-inch level (Table 5-12); whereas, with post-amendment soil samples for corn, the higher concentrations were observed in the 0- to 12-inch level (Table 5-6). This indicated that water-soluble lead may have moved downward in the soil, similar to EDTA. Some of the reduction might be attributed to removal by the crop, although biomass production was insufficient to account for a significant portion of this lead. The inherent variability in soil lead concentration and the difficulties in sampling also made an accounting difficult.

A decrease in water-soluble Pb, particularly in the 0- to 12-inch level, may also have been due to some degradation of EDTA from the tillage/irrigation cycles, or displacement of Pb from the EDTA complex by other cations. This would release complexed lead, which then would react with soil to revert to an insoluble form. This might readily occur if EDTA was complexed with iron or other nutrient cations such as Ca, Mg, and Mn. Lauff *et al* [Ref. 35] found high degradation rates of ferric-EDTA (up to 24mM/day), which was an order of magnitude greater than previously reported rates of EDTA and its metal chelates. Nortemann [Ref. 33] reported rapid and

complete biodegradation of Ca, Mg, and Mn complexes of EDTA by a mixed microbial population. These metals are of low toxicity and are essential micronutrients which serve as a food source to microbes, which would result in an enhanced microbial population capable of degrading EDTA. The resulting degradation products would have lower affinity for lead than the parent EDTA compound, and lead released from the complex would remain bound as insoluble forms in the soil. Also, sorption could simply remove the lead-EDTA complex from solution.

The average concentration for water-soluble lead in the top 24 inches of soil at Site C after amendment additions to corn was 301 mg/kg and for pre-amendment samples for white mustard, the average concentration was 255 mg/kg (where the 24-inch average is the average of the concentrations of 0-12 inches and 12-24 inches). Therefore, *ten weeks after adding EDTA to the soil, the majority of water-soluble lead (84.7%) remained in the top two feet*, which is considered the rooting zone of the plant.

At Site 129-3, very little EDTA remained in the 0- to 12-inch or the 12- to 24-inch soil levels (6 and 16 mg/kg, respectively, Table 5-13), as compared to levels found in post-amendment soil samples for corn of 262 and 103 mg/kg (Table 5-7). Similarly, very little water-soluble lead remained in the top 24 inches (Tables 5-7 and 5-13). EDTA appears to have also moved downward at this site, as concentrations at the 12- to 24-inch level were higher than at the 0- to 12-inch depth. Apparently, a large portion of the water-soluble lead and EDTA moved downward in the top 24 inches within the ten weeks between the corn harvest and pre-amendment soil sampling for white mustard. A high concentration of EDTA in the soil solution three weeks after soil amendments were applied for corn on August 6, 1998 (Section 5.2.6, Table 5-22) may have been indicative of downward movement of EDTA. However, sorption of EDTA in the top 12 inches by iron oxides in the top 12 inches would also have reduced the concentrations of extractable EDTA.

At Site C, the average total lead concentration was 5,430 mg/kg at the 0- to 12-inch depth (Table 5-12), which was higher than the level measured in post-amendment soil samples taken for the corn crop; however, if the concentration of 50,900 mg/kg for grid 20 was discounted, then the average total lead concentration would be 2,760 mg/kg, which is very similar to the average total lead concentration of 2,730 mg/kg found in the initial soil characterization (Table 5-1). The average total lead concentration of 2,930 mg/kg for the 12- to 24-inch depth at Site C is much lower than the post-amendment concentration for corn of 4,300 mg/kg (compare Tables 5-12 and 5-6). Again, this variation in average lead concentration for both soil levels was due to the non-uniform distribution of lead across the plot.

There appeared to be some reductions in total lead concentrations at Site 129-3 (Table 5-13), compared to total lead concentrations for post-amendment samples for the corn crop (Table 5-7), but the variation at this site also was too large to distinguish whether an actual reduction occurred.

## Table 5-12

## Soil pH, EDTA, Water-Soluble Pb, and Other Contaminants of Concern in Soil at Site C Prior to Adding Soil Amendments to 1998 White Mustard

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb mg/kg | | Pb[1,2] mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | 8.5 | 8.6 | 4 | 11 | 3 | 10 | 70 | 56 | 2,739 | 4,170 |
| 3 | 8.6 | 8.6 | <0.3[3] | 8 | <0.3[3] | 7 | 4 | 79 | 131 | 2,710 |
| 5 | 8.8 | 8.3 | 3 | 7 | 3 | 6 | 5 | 1 | 661 | 752 |
| 8 | 8.5 | 8.1 | 6 | 98 | 5 | 85 | 33 | 66 | 13,500 | 4,020 |
| 10 | 9.1 | 8.7 | <0.3 | 53 | <0.3 | 46 | 12 | 23 | 346 | 222 |
| 12 | 8.4 | 8.0 | <0.3 | 20 | <0.3 | 17 | 3 | 6 | 381 | 348 |
| 13 | 7.9 | 8.2 | 297 | 1,660 | 258 | 1,440 | 137 | 693 | 2,460 | 1,380 |
| 15 | NS[4] | NS[4] | NS[4] | NS4 | NS[4] | NS[4] | 13 | 860 | 263 | 4,463 |
| 17 | 8.1 | 7.9 | 2,090 | 3,440 | 1,817 | 2,990 | 592 | 305 | 4,696 | 2,340 |
| 20 | 9.0 | 8.8 | 21 | 165 | 18 | 143 | 102 | 28 | 50,900 | 6,040 |
| 22 | NS | NS | NS | NS | NS | NS | 80 | 939 | 4,590 | 2,080 |
| 24 | 9.1 | 7.9 | 43 | 1,540 | 37 | 1,340 | 33 | 691 | 8,930 | 3,280 |
| 25 | 8.6 | 8.2 | 397 | 2,880 | 345 | 2,500 | 110 | 1,100 | 3,860 | 1,360 |
| 27 | NS | NS | NS | NS | NS | NS | 96 | 1,730 | 524 | 4,190 |
| 29 | 8.3 | 8.1 | 1,280 | 3,180 | 1,113 | 2,760 | 252 | 464 | 2,000 | 3,740 |
| 32 | NS | NS | NS | NS | NS | NS | 49 | 77 | 850 | 9,820 |
| 34 | NS | NS | NS | NS | NS | NS | 88 | 293 | 762 | 1,320 |
| 36 | 8.2 | 8.0 | 3 | 210 | 3 | 183 | 4 | 98 | 162 | 466 |
| | | | | | - | - | | | | |
| **Mean** | ***8.5*** | ***8.3*** | ***414*** | ***1,020*** | ***360*** | ***887*** | ***93*** | ***417*** | ***5,430*** | ***2,930*** |
| **Std. Dev.** | ***0.4*** | ***0.3*** | ***710*** | ***1,350*** | ***617*** | ***1,170*** | ***140*** | ***490*** | ***11,880*** | ***2,400*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) Method Detection Limit.
(4) NS = Not sampled.
(5) NA = Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-12 (Continued)**

**Soil pH, EDTA, Water-Soluble Pb, and Other Contaminants of Concern in Soil at Site C Prior to Adding Soil Amendments to 1998 White Mustard**

| Grid No. | As[1,2] mg/kg | | Be[1,2] mg/kg | | Mn[1,2] mg/kg | | Sb[1,2] mg/kg | | Tl[1,2] mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | <5[3] | <5[3] | <0.4[3] | <0.4[3] | 183 | 201 | <40[3] | <40[3] | <50[3] | <50[3] |
| 3 | <5 | <5 | <0.4 | <0.4 | 81 | 143 | <40 | <40 | <50 | <50 |
| 5 | 9 | 5 | <0.4 | <0.4 | 329 | 272 | <40 | <40 | 150 | 111 |
| 8 | <5 | <5 | <0.4 | <0.4 | 173 | 348 | <40 | <40 | 63 | 57 |
| 10 | <5 | <5 | <0.4 | <0.4 | 91 | 120 | <40 | <40 | 86 | 70 |
| 12 | <5 | <5 | <0.4 | <0.4 | 169 | 134 | <40 | <40 | <50 | <50 |
| 13 | <5 | <5 | <0.4 | <0.4 | 223 | 352 | <40 | <40 | <50 | <50 |
| 15 | <5 | <5 | <0.4 | <0.4 | 88 | 169 | <40 | <40 | 92 | <50 |
| 17 | 8 | 12 | <0.4 | <0.4 | 976 | 649 | <40 | <40 | 163 | 263 |
| 20 | <5 | <5 | <0.4 | <0.4 | 166 | 200 | <40 | <40 | 103 | 62 |
| 22 | <5 | <5 | <0.4 | <0.4 | 147 | 178 | <40 | <40 | 60 | <50 |
| 24 | <5 | <5 | <0.4 | <0.4 | 161 | 246 | <40 | <40 | 77 | 60 |
| 25 | <5 | <5 | <0.4 | <0.4 | 226 | 260 | <40 | <40 | 68 | 64 |
| 27 | <5 | <5 | <0.4 | <0.4 | 95 | 362 | <40 | <40 | 72 | <50 |
| 29 | 6 | 18 | <0.4 | <0.4 | 405 | 727 | <40 | <40 | 92 | 286 |
| 32 | <5 | <5 | <0.4 | <0.4 | 125 | 206 | <40 | <40 | 89 | 65 |
| 34 | <5 | <5 | <0.4 | <0.4 | 227 | 599 | <40 | <40 | 51 | <50 |
| 36 | <5 | <5 | <0.4 | <0.4 | 73 | 174 | <40 | <40 | <50 | <50 |
| | | | | | | | | | | |
| **Mean** | ***1.3*** | ***1.9*** | ***<0.4*** | ***<0.4*** | ***219*** | ***297*** | ***<40*** | ***<40*** | ***55*** | ***50*** |
| **Std. Dev.** | ***4.7*** | ***4.9*** | ***NA[5]*** | ***NA[5]*** | ***208*** | ***183*** | ***NA[5]*** | ***NA[5]*** | ***53*** | ***88*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) Method Detection Limit.
(4) NS = Not sampled.
(5) NA = Not Applicable.

Concentrations of the other COCs at either site, with the exception of thallium at Site C, were only slightly affected by treatments (Tables 5-12 and 5-13). Arsenic was found in isolated, localized areas within the plot. There did not appear to be a significant decrease in manganese concentrations from those found in post-amendment soil samples for corn. Beryllium and antimony were below the analytical Method Detection Limit. Thallium was present in several areas of Site C at concentrations which would be toxic to plants (Table 5-12). These concentrations were similar to those found in the previous soil samplings. In almost all cases, where thallium was present in the soil, plant growth was severely inhibited (Section 5.2.5.1, Table 5-16).

#### 5.2.4.2 Post-Amendment Soil Sampling - 1998 White Mustard

Soil amendment additions (EDTA only) were made to the white mustard crop at Site C on October 9, 1998, and to white mustard at Site 129-3 on October 10, 1998. EDTA formulation, mixing, and application was done in cooperation with Lynn Sinness, Manager, ConAgra, Shakopee, Minnesota. The EDTA was applied through the drip delivery system. Application time for Site C was approximately 7 hours and for Site 129-3 about 4 hours.

The EDTA was added to optimize the solubilization of lead in the first two feet of soil (root zone). Since only half the plot area at Site C was populated with plants, the EDTA application rate there was reduced from the originally planned 6,750 pounds to 3,375 pounds of EDTA. Only the grids with growing plants received the chelate application. The reduced application was achieved by selectively blocking the sections of the drip tubing which extended across bare areas in the plot. The application rate at Site 129-3 was 850 pounds, the same amount as applied for the 1998 corn crop. The lower rate at 129-3 was selected due to the lower average soil lead concentration at that site. Adjustments were made in the sampling activities at Site C due to the reduced plant stand and, as such, a reduced number of both plant and soil samples was collected.

There was little change in soil pH at Site C after EDTA application for white mustard (Table 5-14).

EDTA concentrations in the soil at Site C were much higher in the 0- to 12-inch depth than in the 12- to 24-inch depth for most grids (Table 5-14). Also, EDTA concentrations were approximately five times higher in post-amendment soil samples for white mustard than in post-amendment soil samples for corn. Soil sampling was not done directly beneath the drip lines in order to avoid sampling in a zone of high EDTA concentration. A drip delivery system was used to apply EDTA to the soil over a 7-hour period. The slower application rate allowed the EDTA to infiltrate into the soil slowly, thus minimizing runoff, compared to the hose application method used for corn, which applied the solution rapidly so that amendments ran down the slight slope. The corn crop removed 42.5 pounds of EDTA at Site C and 11.5 pounds at Site 129-3. White mustard removed 70.6 pounds of EDTA at Site C and 39.3 pounds at Site 129-3. These amounts alone cannot account for the difference in EDTA concentrations in soil for Site C for the post-amendment soil samples for corn and white mustard. However, sampling was done seven days after application for corn, but two days afterward for white mustard. The EDTA,

## Table 5-13

## Soil pH, EDTA, Water-Soluble Pb, and Other Contaminants of Concern in Soil at Site 129-3 Prior to Adding Soil Amendments to 1998 White Mustard

| Grid No. | pH | | EDTA as $Na_2EDTA$ mg/kg | | EDTA as EDTA mg/kg | | Water-Soluble Pb mg/kg | | Pb[1,2] mg/kg | | Mn[1,2] mg/kg | | Sb[1,2] mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | 8.1 | 8.0 | <0.3[3] | 2 | <0.3[3] | 2 | 2 | 2 | 114 | 130 | 225 | 178 | <40[3] | <40[3] |
| 3 | 7.8 | 7.7 | <0.3 | 4 | <0.3 | 3 | <0.3[3] | <0.3[3] | 52 | 63 | 153 | 161 | <40 | <40 |
| 5 | 8.3 | 8.1 | 7 | 3 | 6 | 3 | <0.3 | 1 | 71 | 146 | 176 | 262 | <40 | <40 |
| 8 | 8.4 | 8.5 | <0.3 | 3 | <0.3 | 3 | <0.3 | <0.3 | 28 | 23 | 120 | 199 | <40 | <40 |
| 10 | 7.1 | 7.9 | <0.3 | <0.3[3] | <0.3 | <0.3[3] | <0.3 | <0.3 | 64 | 56 | 186 | 241 | <40 | <40 |
| 12 | 7.8 | 8.1 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | 25 | 20 | 295 | 263 | <40 | <40 |
| 13 | 8.0 | 7.9 | <0.3 | 87 | <0.3 | 76 | <0.3 | <0.3 | 54 | 27 | 357 | 289 | <40 | <40 |
| 15 | 8.0 | 8.2 | 3 | 16 | 3 | 14 | 6 | 13 | 352 | 255 | 186 | 230 | <40 | <40 |
| 17 | 8.3 | 8.3 | 3 | 4 | 3 | 3 | <0.3 | <0.3 | 24 | 22 | 155 | 326 | <40 | <40 |
| 20 | 7.9 | 8.0 | 13 | 28 | 11 | 24 | 47 | 26 | 1,336 | 353 | 227 | 167 | <40 | <40 |
| 22 | 8.2 | 8.2 | 4 | 4 | 3 | 3 | <0.3 | <0.3 | 49 | 80 | 175 | 193 | <40 | <40 |
| 24 | 8.4 | 8.3 | 3 | <0.3 | 3 | <0.3 | <0.3 | <0.3 | 20 | 42 | 244 | 261 | <40 | <40 |
| 25 | 8.2 | 8.0 | 2 | 3 | 2 | 3 | 12 | 3 | 440 | 207 | 188 | 225 | <40 | <40 |
| 27 | 8.2 | 8.3 | 16 | 94 | 14 | 82 | 25 | 57 | 423 | 215 | 218 | 247 | <40 | <40 |
| 29 | 8.1 | 8.0 | 2 | 3 | 2 | 3 | 1 | <0.3 | 74 | 112 | 146 | 345 | <40 | <40 |
| 32 | 8.2 | 8.4 | 3 | 4 | 3 | 3 | <0.3 | <0.3 | 31 | 14 | 262 | 222 | <40 | <40 |
| 34 | 8.3 | 7.8 | 19 | <0.3 | 17 | <0.3 | 1 | <0.3 | 93 | 44 | 177 | 208 | <40 | <40 |
| 36 | 8.0 | 8.4 | <0.3 | 1 | <0.3 | 1 | <0.3 | <0.3 | 63 | 46 | 183 | 288 | <40 | <40 |
| | | | | | | | | | | | | | | |
| **Mean** | ***8.1*** | ***8.1*** | ***7*** | ***18*** | ***6*** | ***16*** | ***5.2*** | ***5.6*** | ***184*** | ***96*** | ***204*** | ***239*** | **<40** | **<40** |
| **Std. Dev.** | ***0.3*** | ***0.2*** | ***6*** | ***31*** | ***5*** | ***27*** | ***12.2*** | ***14.4*** | ***318*** | ***96*** | ***58*** | ***52*** | ***NA[4]*** | ***NA[4]*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) Method Detection Limit.
(4) NA = Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

thus, may have moved downward to a greater extent with the corn crop. Adsorption of EDTA onto various soil fractions could not be measured, but this mechanism likely played a major role in the decrease of EDTA. The time difference between sampling events after chelate application would have allowed more adsorption to occur for the corn crop soils.

Water-soluble lead in the soil at Site C increased significantly after chelate addition to white mustard (Table 5-14). The concentrations were higher with white mustard than with the corn (Table 5-6), but, again, the soil for corn was sampled after a longer time interval.

At Site 129-3, there was a slight increase in pH associated with the application of EDTA (Table 5-15). Most grids showed very low concentrations of EDTA, apparently due to the slow rate of delivery by the drip delivery system and consequent limited lateral movement away from the drip lines. Soil sampling was not done directly beneath the drip lines in order to avoid sampling in a zone of high EDTA concentration. The average concentration for the 0- to 12-inch depth was 311 mg/kg, but the high concentrations in grids 30 and 32 skewed this value upwards. Water-soluble lead concentrations were also low, likely due to the low concentrations of EDTA in the areas sampled. In a number of the grids, concentrations of water-soluble lead were non-detectable. However, the low concentration of lead and the amount of variability confounded the interpretation of these results.

At Site C, the average total lead concentration of 2,320 mg/kg at the 0- to 12-inch depth was slightly lower than values found in the previous soil samplings for both corn and white mustard (Tables 5-1, 5-4, 5-6, and 5-12); the value of 2,320 mg/kg was within the standard deviation of the means of all previous samplings. This could mean either that a decrease in soil lead occurred due to uptake by plants, that lead moved out of the top 12 inches of soil due to EDTA complexation, or simply that the variability in soil lead concentration was too great to determine if the change was real. At the 12- to 24-inch depth, the average lead concentration was within the range of values found in previous samplings (Tables 5-4, 5-6, and 5-12).

For Site 129-3, average lead concentrations were also within ranges found in previous sampling for both 0- to 12-inch and 12- to 24-inch soil levels (Tables 5-2, 5-5, 5-7, and 5-13).

At Site C, there was very little change in the average manganese concentration as a result of chelate application (Tables 5-12 and 5-14). At Site 129-3, the average manganese concentration did not change at the 0- to 12-inch depth (Tables 5-13 and 5-15); there appeared to be an increase at the 12-to 24-inch depth, but this is probably due to variation across the demonstration plot and is within the standard deviation of the means.

Arsenic was found at detectable concentrations in soil at Site C in only three grids (Table 5-14). Antimony concentrations were all below the Method Detection Limit. Thallium was again found in significant concentrations across the field area at Site C. Although thallium concentrations in the post-amendment soil samples varied somewhat from the concentrations in samples taken before amendment application, the areas where thallium was found essentially corresponded to areas of poor plant growth.

## Table 5-14

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern in Soil at Site C After Soil Amendment Additions to 1998 White Mustard

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb mg/kg | | Pb[1,2] mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | 8.0 | 8.2 | 3,650 | 1,620 | 3,170 | 1,410 | 773 | 488 | 759 | 3,470 |
| 2 | 8.4 | 7.9 | 3,500 | 1,050 | 3,040 | 910 | 1,700 | 434 | 1,440 | 2,280 |
| 5 | 8.3 | 7.9 | 11,800 | 2,840 | 10,300 | 2,470 | 918 | 488 | 1,610 | 1,710 |
| 6 | 8.6 | 8.5 | 4,360 | 2,080 | 3,790 | 1,810 | 907 | 941 | 10,300 | 9,490 |
| 7 | 8.2 | 8.2 | 6,070 | 431 | 5,280 | 370 | 633 | 146 | 702 | 479 |
| 8 | 8.1 | 8.6 | 5,380 | 963 | 4,680 | 840 | 865 | 430 | 895 | 3,190 |
| 12 | 8.4 | 8.1 | 8,900 | 1,450 | 7,740 | 1,260 | 1,320 | 764 | 1,620 | 2,780 |
| 13 | 8.0 | 8.3 | 9,240 | 502 | 8,030 | 440 | 821 | 205 | 1,720 | 469 |
| 14 | 8.3 | 8.5 | 760 | 1,520 | 660 | 1,320 | 274 | 463 | 745 | 5,910 |
| 15 | NS[3] | NS[3] | NS[3] | NS[3] | NS[3] | NS[3] | 172 | 1,140 | 2,210 | 10,300 |
| 18 | 8.4 | 7.9 | 2,770 | 2,090 | 2,410 | 1,820 | 1,200 | 1,000 | 1,800 | 2,300 |
| 19 | 8.9 | 8.6 | 4,820 | 811 | 4,190 | 700 | 1,650 | 419 | 4,440 | 1,310 |
| 20 | 9.0 | 8.5 | 1,130 | 1,770 | 980 | 1,540 | 609 | 969 | 2,860 | 5,400 |
| 21 | NS | NS | NS | NS | NS | NS | 517 | 2,120 | 659 | 4,210 |
| 24 | 8.8 | 8.4 | 3,970 | 1,050 | 3,450 | 910 | 1,370 | 502 | 1,860 | 3,910 |
| 25 | 8.8 | 8.4 | 2,740 | 1,470 | 2,380 | 1,280 | 1,240 | 748 | 4,800 | 4,140 |
| 26 | 8.8 | 8.1 | 1,000 | 2,510 | 870 | 2,180 | 444 | 885 | 5,850 | 9,600 |
| 27 | NS | NS | NS | NS | NS | NS | 346 | 1,290 | 1,110 | 6,790 |
| 29 | 8.6 | 8.3 | 7,960 | 8,190 | 6,920 | 7,120 | 671 | 1,130 | 867 | 2,180 |
| 30 | 8.6 | 8.0 | 2,390 | 1,220 | 2,080 | 1,060 | 532 | 254 | 2,900 | 428 |
| 35 | 8.4 | 8.0 | 7,210 | 1,530 | 6,270 | 1,330 | 928 | 432 | 1,140 | 3,280 |
| 36 | 8.7 | 8.5 | 12,600 | 1,650 | 11,000 | 1,430 | 672 | 803 | 691 | 1,330 |
| | | | | | | | | | | |
| **Mean** | ***8.5*** | ***8.2*** | ***5,280*** | ***1,830*** | ***4,590*** | ***1,590*** | ***844*** | ***730*** | ***2,320*** | ***3,860*** |
| **Std. Dev.** | ***0.3*** | ***0.2*** | ***3,510*** | ***1,660*** | ***3,050*** | ***1,440*** | ***422*** | ***449*** | ***2,290*** | ***2,960*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) Method Detection Limited.
(4) NS = Not sampled.
(5) NA = Not applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-14 (Continued)

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern in Soil at Site C After Soil Amendment Additions to 1998 White Mustard

| Grid No. | As[1,2] mg/kg | | Be[1,2] mg/kg | | Mn[1,2] mg/kg | | Sb[1,2] mg/kg | | Tl[1,2] mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | <5[3] | <5[3] | 11 | <0.4[3] | 172 | 246 | <40[3] | <40[3] | <50[3] | <50[3] |
| 2 | <5 | <5 | 4 | <0.4 | 232 | 259 | <40 | <40 | 250 | 265 |
| 5 | 5.2 | 6 | <0.4[3] | <0.4 | 278 | 407 | <40 | <40 | 305 | 368 |
| 6 | <5 | <5 | <0.4 | <0.4 | 268 | 482 | <40 | <40 | 293 | 244 |
| 7 | <5 | <5 | 26 | <0.4 | 125 | 231 | <40 | <40 | 79 | 53 |
| 8 | <5 | <5 | <0.4 | <0.4 | 149 | 248 | <40 | <40 | <50 | <50 |
| 12 | <5 | <5 | <0.4 | <0.4 | 172 | 185 | <40 | <40 | <50 | <50 |
| 13 | <5 | <5 | <0.4 | <0.4 | 152 | 182 | <40 | <40 | <50 | <50 |
| 14 | <5 | <5 | <0.4 | <0.4 | 132 | 232 | <40 | <40 | <50 | <50 |
| 15 | <5 | <5 | <0.4 | <0.4 | 98.3 | 284 | <40 | <40 | 70 | 77 |
| 18 | <5 | <5 | <0.4 | <0.4 | 144 | 246 | <40 | <40 | <50 | <50 |
| 19 | <5 | <5 | <0.4 | <0.4 | 1,140 | 140 | <40 | <40 | <50 | <50 |
| 20 | <5 | <5 | <0.4 | <0.4 | 159 | 198 | <40 | <40 | 84 | 56 |
| 21 | 17.3 | <5 | <0.4 | <0.4 | 166 | 326 | <40 | <40 | 55 | 58 |
| 24 | <5 | <5 | <0.4 | <0.4 | 246 | 153 | <40 | <40 | 64 | 53 |
| 25 | <5 | <5 | <0.4 | <0.4 | 155 | 250 | <40 | <40 | 51 | 62 |
| 26 | <5 | <5 | <0.4 | <0.4 | 187 | 318 | <40 | <40 | 62 | 54 |
| 27 | <5 | <5 | <0.4 | <0.4 | 164 | 250 | <40 | <40 | <50 | <50 |
| 29 | <5 | 6 | <0.4 | <0.4 | 152 | 486 | <40 | <40 | 68 | 161 |
| 30 | <5 | <5 | <0.4 | <0.4 | 134 | 179 | <40 | <40 | 52 | <50 |
| 35 | <5 | <5 | <0.4 | <0.4 | 219 | 327 | <40 | <40 | 89 | 89 |
| 36 | <5 | <5 | <0.4 | <0.4 | 146 | 241 | <40 | <40 | 75 | 63 |
| | | | | | | | | | | |
| **Mean** | ***1.2*** | ***0.8*** | ***2.7*** | ***<0.4*** | ***218*** | ***267*** | ***<40*** | ***<40*** | ***76*** | ***73*** |
| **Std. Dev.** | ***4.2*** | ***2.0*** | ***6.5*** | ***NA[5]*** | ***211*** | ***94*** | ***NA[5]*** | ***NA[5]*** | ***93*** | ***100*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) Method Detection Limit.
(4) NS = Not sampled.
(5) NA = Not Applicable.

## Table 5-15

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern in Soil at Site 129-3 After Soil Amendment Additions to 1998 White Mustard

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb, mg/kg | | Pb[1,2] mg/kg | | Mn[1,2] mg/kg | | Sb[1,2] mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 1 | NS[3] | NS[3] | NS[3] | NS[3] | NS[3] | NS[3] | <0.3[4] | <0.3[4] | 314 | 330 | 212 | 267 | <40[4] | <40[4] |
| 2 | 8.2 | 8.0 | 3 | 2 | 3 | 2 | <0.3 | 2 | 266 | 305 | 192 | 221 | <40 | <40 |
| 3 | NS | NS | NS | NS | NS | NS | 3 | <0.3 | 288 | 274 | 198 | 231 | <40 | <40 |
| 4 | 8.2 | 8.1 | 3 | 3 | 3 | 3 | <0.3 | <0.3 | 219 | 248 | 208 | 219 | <40 | <40 |
| 5 | NS | NS | NS | NS | NS | NS | 6 | 6 | 97 | 130 | 218 | 242 | <40 | <40 |
| 6 | 8.3 | 8.6 | <0.3[4] | <0.3[4] | <0.3[4] | <0.3[4] | 2 | 2 | 73 | 71 | 476 | 300 | <40 | <40 |
| 7 | NS | NS | NS | NS | NS | NS | <0.3 | <0.3 | 27 | 18 | 276 | 211 | <40 | <40 |
| 8 | 8.5 | 8.5 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | 28 | 27 | 223 | 259 | <40 | <40 |
| 9 | NS | NS | NS | NS | NS | NS | 5 | 9 | 123 | 91 | 168 | 276 | <40 | <40 |
| 10 | 8.3 | 8.7 | 3 | 2 | 3 | 2 | 7 | 4 | 55 | 35 | 168 | 233 | <40 | <40 |
| 11 | NS | NS | NS | NS | NS | NS | 4 | 2 | 37 | 35 | 206 | 606 | <40 | <40 |
| 12 | 8.3 | 8.6 | <0.3 | <0.3 | <0.3 | <0.3 | 3 | 3 | 23 | 25 | 268 | 314 | <40 | <40 |
| 13 | NS | NS | NS | NS | NS | NS | 160 | 4 | 314 | 37 | 208 | 266 | <40 | <40 |
| 14 | 8.3 | 8.5 | 209 | 57 | 182 | 50 | 119 | 14 | 351 | 76 | 217 | 311 | <40 | <40 |
| 15 | NS | NS | NS | NS | NS | NS | 10 | 2 | 259 | 74 | 175 | 458 | <40 | <40 |
| 16 | 8.2 | 8.4 | <0.3 | 3 | <0.3 | 3 | <0.3 | <0.3 | 68 | 40 | 197 | 350 | <40 | <40 |
| 17 | NS | NS | NS | NS | NS | NS | <0.3 | <0.3 | 21 | 27 | 208 | 491 | <40 | <40 |
| 18 | 8.3 | 8.2 | <0.3 | 5 | <0.3 | 4 | <0.3 | <0.3 | 26 | 39 | 190 | 274 | <40 | <40 |
| 19 | NS | NS | NS | NS | NS | NS | 348 | 104 | 1240 | 669 | 241 | 196 | <40 | <40 |
| 20 | 8.3 | 8.5 | 128 | 78 | 111 | 68 | 100 | 19 | 1380 | 80 | 185 | 178 | <40 | <40 |
| 21 | NS | NS | NS | NS | NS | NS | <0.3 | <0.3 | 43 | 26 | 165 | 236 | <40 | <40 |
| 22 | 8.3 | 8.4 | 5 | 2 | 4 | 2 | 2 | <0.3 | 62 | 60 | 188 | 231 | <40 | <40 |
| 23 | NS | NS | NS | NS | NS | NS | 8 | 1 | 24 | 73 | 188 | 190 | <40 | <40 |

## Table 5-15 (Continued)

## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern in Soil at Site 129-3 After Soil Amendment Additions to 1998 White Mustard

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb, mg/kg | | Pb[1,2] mg/kg | | Mn[1,2] mg/kg | | Sb[1,2] mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 24 | 8.4 | 8.7 | <0.3 | 2 | <0.3 | 2 | <0.3 | <0.3 | 18 | 142 | 213 | 302 | <40 | <40 |
| 25 | NS | NS | NS | NS | NS | NS | 15 | 23 | 499 | 187 | 209 | 212 | <40 | <40 |
| 26 | 8.5 | 8.4 | 2 | 32 | 2 | 28 | 4 | 74 | 234 | 471 | 226 | 250 | <40 | <40 |
| 27 | NS | NS | NS | NS | NS | NS | 260 | 116 | 797 | 374 | 225 | 238 | <40 | <40 |
| 28 | 8.4 | 8.5 | 12 | 4 | 10 | 3 | 5 | 3 | 145 | 64 | 226 | 266 | <40 | <40 |
| 29 | NS | NS | NS | NS | NS | NS | <0.3 | <0.3 | 81 | 9 | 191 | 196 | <40 | <40 |
| 30 | 8.3 | 8.3 | 985 | 3 | 856 | 3 | 14 | <0.3 | 10 | 12 | 176 | 314 | <40 | <40 |
| 31 | NS | NS | NS | NS | NS | NS | <0.3 | <0.3 | 11 | 9 | 198 | 207 | <40 | <40 |
| 32 | 7.7 | 8.2 | 2940 | 187 | 2,560 | 163 | 34 | 7 | 12 | 9 | 130 | 1560 | <40 | <40 |
| 33 | NS | NS | NS | NS | NS | NS | <0.3 | 1 | 11 | 8 | 230 | 321 | <40 | <40 |
| 34 | 8.3 | 8.3 | 2 | 2 | 2 | 2 | 1 | 1 | 14 | 9 | 193 | 232 | <40 | <40 |
| 35 | NS | NS | NS | NS | NS | NS | 1 | 2 | 11 | 3 | 187 | 254 | <40 | <40 |
| 36 | 8.4 | 8.5 | 3 | 3 | 3 | 3 | 1 | <0.3 | 12 | 7 | 146 | 230 | <40 | <40 |
| | | | | | | | | | | | | | | |
| **Mean** | ***8.3*** | ***8.4*** | ***358*** | ***21*** | ***311*** | ***18*** | ***31*** | ***11*** | ***200*** | ***114*** | ***209*** | ***309*** | ***<40*** | ***<40*** |
| **Std. Dev.** | ***0.2*** | ***0.2*** | ***713*** | ***47*** | ***620*** | ***41*** | ***77*** | ***28*** | ***321*** | ***152*** | ***54*** | ***231*** | ***NA[5]*** | ***NA[5]*** |

(1) Concentrations were determined by acid digestion.
(2) Contaminant of Concern for this site.
(3) NS = Not Sampled.
(4) Method Detection Limit.
(5) NA = Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

### 5.2.5 Plant Sampling - 1998 White Mustard Crop

#### 5.2.5.1 Plant Growth - 1998 White Mustard Crop

The white mustard crop was broadcast seeded on August 20, 1998. However, poor stand establishment (approximately 50% at Site C and 70% at Site 129-3) necessitated replanting after two weeks. This was done by broadcast seeding over the existing crop. A final stand establishment of about 50% at Site C and 90% at Site 129-3 was achieved. Many of the plants at Site C were stunted and coverage within individual plots varied considerably (Table 5-16). Coverage and plant size at Site 129-3 was more uniform and consistent (Table 5-17). However, examination of plants excavated from the soil at both sites revealed a very shallow and sparse root system, approximately 6 inches in spread, which penetrated the soil for only about 3 to 4 inches deep. A more typical spread would be 1 foot, with penetration down to 2 to 3 feet.

#### 5.2.5.2 Pre-Amendment Plant Sampling - 1998 White Mustard Crop

At Site C, the average lead concentration of white mustard plants before soil amendment addition was 47 mg/kg (Table 5-18). This is slightly more than the value of 30 mg/kg observed in corn before soil amendment additions (Table 5-8). Manganese was the only other COCs that accumulated to detectable levels and this was in the same range as observed with corn before soil amendment application. The low concentrations of lead and manganese in the white mustard plants indicate that the EDTA remaining in the soil from the application to the corn crop, which was measured immediately before soil amendment application to white mustard (Table 5-12), did not significantly enhance uptake of lead and manganese during the growth of the white mustard crop over that expected from a contaminated soil without soil amendments. However, no analysis was conducted for EDTA in plant tissue before soil amendments to white mustard. Possibly the effect on mustard during the growing season of residual EDTA from the previous application to corn could have caused reduced lead uptake (discussed in Section 5.2.5.3) when EDTA was applied to mustard. In addition, factors such as other contaminants in the soil, the poor agronomic conditions at the site, and excess rainfall likely contributed to diminished plant function and lead uptake was reduced as a result.

For Site 129-3 also, lead accumulated only in low concentrations in the white mustard during the growing season (Table 5-19). There was less lead accumulation in these plants than at Site C due to the lower concentration of lead in the soil at Site 129-3. Lead concentrations in white mustard were only slightly higher than concentrations seen in corn (Table 5-9) before EDTA application (18 and 9 mg/kg for white mustard and corn, respectively). Manganese accumulated in low amounts in concentrations similar to those observed in corn (Table 5-9) before chelate application. The low lead and manganese concentrations in white mustard were not unexpected, since at Site 129-3, very little EDTA and water-soluble lead remained in the soil from the previous amendment application to corn (Table 5-13).

**Table 5-16**
**1998 White Mustard Crop Characteristics at Site C**
**Before Soil Amendment Application**

| Site | Grid No. | Percent of Grid Covered by Plants | Relative Plant Size[1] |
|---|---|---|---|
| C | 1 | 100 | L |
| | 2 | 75 | S, L |
| | 3 | 20 | S |
| | 4 | 50 | S |
| | 5 | 50 | S, M |
| | 6 | 90 | L |
| | 7 | 100 | L |
| | 8 | 60 | L |
| | 9 | 0 | NA |
| | 10 | 10 | VS |
| | 11 | 30 | M |
| | 12 | 90 | L |
| | 13 | 100 | M, L |
| | 14 | 75 | M, L |
| | 15 | 0 | NA |
| | 16 | 0 | NA |
| | 17 | 10 | S, M |
| | 18 | 85 | M, L |
| | 19 | 100 | M, L |
| | 20 | 50 | S, M |
| | 21 | 0 | NA |
| | 22 | 0 | NA |
| | 23 | 5 | VS |
| | 24 | 90 | S, M, L |
| | 25 | 45 | L |
| | 26 | 50 | M, L |
| | 27 | 0 | NA |
| | 28 | 0 | NA |
| | 29 | 35 | S, M |
| | 30 | 100 | L |
| | 31 | 5 | S |
| | 32 | 5 | S |
| | 33 | 0 | NA |
| | 34 | 10 | VS |
| | 35 | 50 | S, M |
| | 36 | 90 | L |

(1) VS - Very small plants, <6 inches tall.
S - Small plants, 6-12 inches tall.
M - Medium plants, 12-24 inches tall.
L - Large plants, 24-36 inches.
NA - Not Applicable.
Note: More than one designation indicates equal distribution of plants among categories.

**Table 5-17**
**1998 White Mustard Crop Characteristics at Site 129-3**
**Before Soil Amendment Application**

| Site | Grid No. | Percent of Grid Covered by Plants | Relative Plant Size[1] |
|---|---|---|---|
| 129-3 | 1 | 100 | M, L |
| | 2 | 75 | M, L |
| | 3 | 70 | S, M |
| | 4 | 80 | S, M, L |
| | 5 | 100 | VL |
| | 6 | 100 | VL |
| | 7 | 50 | S, M |
| | 8 | 50 | S, M |
| | 9 | 80 | S, M, L |
| | 10 | 80 | S, M |
| | 11 | 95 | VL |
| | 12 | 90 | VL |
| | 13 | 85 | S (10%), M, L |
| | 14 | 95 | VL |
| | 15 | 95 | M, VL |
| | 16 | 90 | M, L, VL |
| | 17 | 95 | VL |
| | 18 | 100 | VL |
| | 19 | 95 | M, L |
| | 20 | 100 | VL |
| | 21 | 100 | VL |
| | 22 | 90 | S(10%), M(30%), VL |
| | 23 | 95 | VL |
| | 24 | 80 | S(10%), VL |
| | 25 | 95 | VL |
| | 26 | 100 | VL |
| | 27 | 90 | S, M |
| | 28 | 90 | S, M, VL |
| | 29 | 100 | VL |
| | 30 | 75 | L |
| | 31 | 100 | VL |
| | 32 | 100 | VL |
| | 33 | 100 | VL |
| | 34 | 90 | M,VL |
| | 35 | 100 | VL |
| | 36 | 70 | L |

(1) VS - Very small plants, <6 inches tall.
S - Small plants, 6-12 inches tall.
M - Medium plants, 12-24 inches tall.
L - Large plants, 24-36 inches.
VL - Very large plants, >36 inches tall.
Note: Unless otherwise noted, more than one designation indicates equal distribution of plants among categories. Numbers in parentheses indicate percent of plants populated by the given plant size.

## Table 5-18

## Contaminants of Concern in 1998 White Mustard from Site C Prior to Adding Soil Amendments

| Grid No. | Pb, mg/kg | As[1], mg/kg | Be[1], mg/kg | Mn[1], mg/kg | Sb[1], mg/kg | Tl[1], mg/kg |
|---|---|---|---|---|---|---|
| 1 | 27 | <4.4[2] | <0.34[2] | 21 | <40[2] | <50[2] |
| 3 | 62 | <4.4 | <0.34 | 18 | <40 | <50 |
| 5 | 27 | <4.4 | <0.34 | 20 | <40 | <50 |
| 8 | 20 | <4.4 | <0.34 | 65 | <40 | <50 |
| 10 | 94 | <4.4 | <0.34 | 23 | <40 | <50 |
| 12 | 21 | <4.4 | <0.34 | 36 | <40 | <50 |
| 13 | 40 | <4.4 | <0.34 | 13 | <40 | <50 |
| 17 | 21 | <4.4 | <0.34 | 24 | <40 | <50 |
| 20 | 124 | <4.4 | <0.34 | 38 | <40 | <50 |
| 24 | 95 | <4.4 | <0.34 | 44 | <40 | <50 |
| 25 | 47 | <4.4 | <0.34 | 19 | <40 | <50 |
| 29 | 20 | <4.4 | <0.34 | 19 | <40 | <50 |
| 36 | 14 | <4.4 | <0.34 | 25 | <40 | <50 |
| | | | | | | |
| **Mean** | ***47*** | ***<4.4*** | ***<0.34*** | ***28*** | ***<40*** | ***<50*** |
| **Std. Dev.** | ***36*** | ***NA[3]*** | ***NA*** | ***14*** | ***NA*** | ***NA*** |

(1) Contaminant of Concern for this site.
(2) Method Detection Limit.
(3) NA = Not Applicable.

#### 5.2.5.3 Post-Amendment Plant Sampling - 1998 White Mustard Crop

Post-harvest soil and plant sampling was done at Site C on October 11, 1998, and at Site 129-3 on October 12, 1998. Plant sampling at both sites was performed at or shortly after the prescribed 48-hour period determined to be optimal during the SFAAP Treatability Study conducted at TVA.[Ref. 2] At this time, the treated white mustard was observed to be mostly green, but wilted, although some bleaching of leaves had occurred with drooping flower heads and leaves. The plants had not dried out. Stalks were upright with leaves still attached. Plants directly adjacent to the drip delivery lines were wilted to a greater extent than plants in between the lines. The plants between the lines were wilting, but at a slower rate. As the plants were wilted, but were not desiccated and brittle, this facilitated the subsequent harvest. This operation was performed with no shattering and wind dispersal of plant tissue and the material was easily bundled for removal from the field and transport to the smelter. At a small untreated area at each site, the plants appeared to be in a normal growth state for white mustard plants, i.e., upright and green. However, the root system for the plants appeared to be diminutive and shallow. Appropriate care was used to obtain clean, soil-free plant samples from sampled stalks.

Harvesting of the crop was completed on October 13, 1998, and the crop was transported to the smelter on October 28, 1998, after appropriate samples were taken to determine final moisture content for yields. Yields of white mustard at both sites were determined by delineating several 2.8-square-foot areas within each plot, then harvesting plants within that area by cutting the stem 1 inch above the soil surface and extrapolating the plant biomass in the areas to obtain the biomass of the whole plot.

The total yield of white mustard at Site C (dry weight basis) was 377 pounds for the 0.2-acre area at 44% plant coverage. However, assuming 100% coverage, this was 4,280 lb/acre on a per-acre basis. The total yield of white mustard at Site 129-3 (dry weight basis) was 700 pounds for the 0.2-acre area at 89% plant coverage. Assuming 100% coverage, this was 3,890 lb/acre.

Lead uptake by white mustard after soil amendment application was lower than expected at both Site C and Site 129-3 (Tables 5-20 and 5-21). The average lead concentration in white mustard for Site C was 829 mg/kg and for Site 129-3, 338 mg/kg. This compares to average concentrations of 6,460 mg/kg and 1,300 mg/kg for corn (Tables 5-10 and 5-11). The average lead concentrations found for white mustard in the SFAAP greenhouse studies were 15,000 mg/kg.[Ref. 2] The average EDTA concentrations in white mustard at Site C and Site 129-3 of 77,200 mg/kg and 47,300 mg/kg, respectively, were higher than concentrations of 40,000 mg/kg observed in white mustard in the SFAAP greenhouse study.

Several factors may have contributed to the low uptake of lead by white mustard. The rooting system of the white mustard on the demonstration plots was shallow and limited, whereas corn roots were deep and extensive. The limited rooting pattern of the white mustard may have been due to carry-over EDTA and water-soluble lead from the amendment application to corn, or may have resulted from the poor soil conditions and excess rainfall. The greenhouse studies of white

**Table 5-19**
**Contaminants of Concern in 1998 White Mustard from Site 129-3 Prior to Adding Soil Amendments**

| Grid No. | Pb, mg/kg | Mn[1], mg/kg | Sb[1], mg/kg |
|---|---|---|---|
| 1 | 7 | 25 | <40[2] |
| 3 | 17 | 39 | <40 |
| 5 | 7 | 33 | <40 |
| 8 | 16 | 38 | <40 |
| 10 | 9 | 38 | <40 |
| 12 | 3 | 35 | <40 |
| 13 | 10 | 55 | <40 |
| 15 | 54 | 34 | <40 |
| 17 | 6 | 40 | <40 |
| 20 | 25 | 30 | <40 |
| 22 | 13 | 34 | <40 |
| 24 | <1.5[2] | 27 | <40 |
| 25 | 35 | 31 | <40 |
| 27 | 61 | 61 | <40 |
| 29 | 15 | 38 | <40 |
| 32 | 6 | 41 | <40 |
| 34 | 20 | 37 | <40 |
| 36 | 10 | 25 | <40 |
| | | | |
| **Mean** | ***18*** | ***37*** | ***<40*** |
| **Std. Dev.** | ***17*** | ***9*** | ***NA[3]*** |

(1) Contaminant of Concern for this site.
(2) Method Detection Limit.
(3) NA = Not Applicable.

mustard grown in pots did not indicate the type of rooting that occurred at TCAAP. Lead may have moved downward to varying extents in the soil, after the corn crop was harvested, due to solubilization by EDTA and subsequent tillage/irrigation cycles before white mustard was planted. A large portion of the lead could have moved below the shallow rooting zone of the white mustard, but still be present in significant concentrations in the top 24 inches of soil, as shown in Tables 5-12 and 5-13.

The drip delivery system used for application of EDTA to the white mustard crop did not rapidly saturate the soil and required an extensive time for application, up to seven hours at Site C. The plant could take up lead in the vicinity of its roots as it was solubilized by EDTA, but as the soil was not quickly saturated, an aqueous medium did not exist for the constant movement of water-soluble lead to the plant roots. However, the plants were continuously exposed to EDTA by the slow application of the drip delivery system, which would allow the plants to take up large amounts of EDTA without concomitant accumulation of lead (Tables 5-20 and 5-21). Prolonged exposure of white mustard to EDTA may have killed the plants before they could take up significant amounts of lead.

### 5.2.6 1998 Soil Solution Data for Sites C and 129-3

Soil solution sample collection was attempted three weeks prior to amendment application in accordance with the procedures outlined in the Technology Demonstration Plan. The first sample that could be collected was on July 20, 1998, immediately following soil amendment applications to corn and ceased on October 19, 1998, two weeks after chelate application to white mustard. Lead and manganese were the only COCs present in detectable concentrations in soil solution samples collected from Site C and from Site 129-3 (Table 5-22). The sample solutions were also analyzed for EDTA to monitor movement of the chelate down through the soil (Table 5-22). Samples could not be obtained during corn growth apparently because the soil was too dry from water use by the dense rooting system of corn which prevented water from moving below the rooting zone.

Lead, EDTA, and manganese were detected in the soil solution at Site C beginning on August 1, 1998, about two weeks after amendment addition and harvest of the corn. The concentration of EDTA and lead at Site C reached a maximum of 2,170 mg/L and 900 mg/L, respectively, on October 2, 1998. However, these concentrations represented the contribution from only one lysimeter (#4) of the twelve that were installed, and these values radically skewed the averaged results (Table 5-23). When this lysimeter was collecting soil moisture, the average concentrations of lead and EDTA in the composite samples of soil solution increased. When this lysimeter did not collect solution, the average concentration of lead and EDTA in the composite sample decreased dramatically.

The lysimeter was installed correctly according to the manufacturer's instructions, and was effective in collecting the soil solution, although the amounts collected from week to week were somewhat erratic (Table 5-23). However, the lysimeter was installed in the area of the 1962 Pit, an area of the plot where extensive alteration to the native soil occurred due to dumping, burning, and soil excavation and replacement. Quite likely, the decomposing debris in the pit left channels and voids in the soil through which water from the surface could channel and collect.

**Table 5-20**
**EDTA and Contaminants of Concern in 1998 White Mustard from Site C After Soil Amendment Additions**

| Grid No. | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg | Pb, mg/kg | As[1], mg/kg | Be[1], mg/kg | Mn[1], mg/kg | Sb[1], mg/kg | Tl[1], mg/kg |
|---|---|---|---|---|---|---|---|---|
| 1 | NS[2] | NS[2] | 629 | <4.5[3] | 0.4 | 152 | <40[3] | <50[3] |
| 2 | 80,000 | 69,500 | 627 | <4.5 | 0.7 | 121 | <40 | <50 |
| 5 | NS | NS | 651 | <4.5 | <0.35[2] | 127 | <40 | <50 |
| 6 | 100,000 | 86,900 | 811 | <4.5 | <0.35 | 93 | <40 | <50 |
| 7 | NS | NS | 356 | <4.5 | <0.35 | 88 | <40 | <50 |
| 8 | 80,800 | 70,200 | 934 | <4.5 | <0.35 | 131 | <40 | <50 |
| 12 | NS | NS | 602 | <4.5 | <0.35 | 99 | <40 | <50 |
| 13 | 105,000 | 91,300 | 582 | <4.5 | <0.35 | 87 | <40 | <50 |
| 14 | NS | NS | 1,030 | <4.5 | <0.35 | 82 | <40 | <50 |
| 18 | 78,900 | 68,600 | 937 | <4.5 | <0.35 | 129 | <40 | <50 |
| 19 | 98,200 | 85,400 | 824 | <4.5 | <0.35 | 85 | <40 | <50 |
| 20 | NS | NS | 1,960 | <4.5 | <0.35 | 110 | <40 | <50 |
| 24 | NS | NS | 1,240 | <4.5 | <0.35 | 148 | <40 | <50 |
| 25 | NS | NS | 636 | <4.5 | <0.35 | 85 | <40 | <50 |
| 26 | 84,800 | 73,700 | 1,440 | <4.5 | <0.35 | 131 | <40 | <50 |
| 29 | 82,800 | 72,000 | 597 | <4.5 | <0.35 | 78 | <40 | <50 |
| 30 | NS | NS | 589 | <4.5 | <0.35 | 81 | <40 | <50 |
| 35 | NS | NS | 787 | <4.5 | <0.35 | 94 | <40 | <50 |
| 36 | 89,100 | 77,400 | 514 | <4.5 | <0.35 | 93 | <40 | <50 |
| | | - | | | | | | |
| **Mean** | ***88,800*** | ***77,200*** | ***829*** | ***<4.5*** | ***<0.35*** | ***106*** | ***<40*** | ***<50*** |
| **Std. Dev.** | ***9,800*** | ***8,500*** | ***379*** | ***NA[4]*** | ***0.2*** | ***24*** | ***NA*** | ***NA*** |

(1) Contaminant of Concern for this site.
(2) NS = Not sampled.
(3) Method Detection Limit.
(4) NA = Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-21**
**EDTA and Contaminants of Concern in 1998 White Mustard from Site 129-3 After Soil Amendment Additions**

| Grid No. | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg | Pb, mg/kg | Mn[1], mg/kg | Sb[1], mg/kg |
|---|---|---|---|---|---|
| 1 | NS[2] | NS[2] | 108 | 143 | <40[3] |
| 2 | NS | NS | 76 | 133 | <40 |
| 3 | NS | NS | 128 | 197 | <40 |
| 4 | 40,200 | 34,900 | 95 | 231 | <40 |
| 5 | NS | NS | 159 | 301 | <40 |
| 6 | NS | NS | 216 | 481 | <40 |
| 7 | NS | NS | 59 | 145 | <40 |
| 8 | 31,500 | 27,400 | 129 | 201 | <40 |
| 9 | NS | NS | 238 | 254 | <40 |
| 10 | NS | NS | 105 | 348 | <40 |
| 11 | NS | NS | 76 | 324 | <40 |
| 12 | 57,900 | 50,300 | 47 | 613 | <40 |
| 13 | NS | NS | 238 | 850 | <40 |
| 14 | NS | NS | 236 | 220 | <40 |
| 15 | NS | NS | 1,530 | 419 | <40 |
| 16 | 67,900 | 59,000 | 101 | 335 | <40 |
| 17 | NS | NS | 90 | 432 | <40 |
| 18 | NS | NS | 108 | 478 | <40 |
| 19 | NS | NS | 1,530 | 124 | <40 |
| 20 | 36,300 | 31,600 | 719 | 274 | <40 |
| 21 | NS | NS | 239 | 189 | <40 |
| 22 | NS | NS | 88 | 261 | <40 |
| 23 | NS | NS | 87 | 222 | <40 |
| 24 | 53,700 | 46,700 | 44 | 368 | <40 |
| 25 | NS | NS | 1,080 | 377 | <40 |
| 26 | NS | NS | 532 | 347 | <40 |
| 27 | NS | NS | 1,730 | 331 | <40 |
| 28 | 73,100 | 63,500 | 261 | 359 | <40 |
| 29 | NS | NS | 226 | 301 | <40 |
| 30 | NS | NS | 83 | 275 | <40 |
| 31 | NS | NS | 274 | 247 | <40 |
| 32 | 64,700 | 56,200 | 308 | 309 | <40 |
| 33 | NS | NS | 411 | 331 | <40 |
| 34 | NS | NS | 439 | 322 | <40 |
| 35 | NS | NS | 151 | 362 | <40 |
| 36 | 64,200 | 55,800 | 232 | 343 | <40 |
| | | - | | | |
| **Mean** | ***54,400*** | ***47,300*** | ***338*** | ***318*** | ***<40*** |
| **Std. Dev.** | ***15,000*** | ***13,000*** | ***437*** | ***139*** | ***NA[4]*** |

(1) Contaminant of Concern for this site.
(2) NS = Not sampled.
(3) Method Detection Limit.
(4) Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-22
## EDTA and Contaminants of Concern in Soil Solution from Lysimeters (1998)

| Date | Site | Sample Event | EDTA as $Na_2EDTA$, mg/L | EDTA as EDTA, mg/L | Pb, mg/L | As[1], mg/L | Be[1], mg/L | Mn[1], mg/L | Sb[1], mg/L | Tl[1], mg/L |
|---|---|---|---|---|---|---|---|---|---|---|
| 07/20/98 | C | Pre-Amendment Corn | <0.1[2] | <0.1[2] | <0.1[2] | <0.3[2] | <0.01[2] | 1 | <0.6[2] | <1.0[2] |
| 08/01/98 | C | Post-Amendment Corn | 40 | 35 | 10 | <0.3 | <0.01 | 2 | <0.6 | <1.0 |
| 08/06/98 | C | Post-Amendment Corn | 54 | 47 | 7 | <0.3 | <0.01 | 2 | <0.6 | <1.0 |
| 08/11/98 | C | Post-Amendment Corn | 40 | 35 | 10 | <0.3 | <0.01 | 2 | <0.6 | <1.0 |
| 08/25/98 | C | Growing-Season Mustard | 516 | 449 | 131 | <0.3 | <0.01 | 16 | <0.6 | <1.0 |
| 09/04/98 | C | Growing-Season Mustard | 488 | 424 | 260 | <0.3 | <0.01 | 21 | <0.6 | <1.0 |
| 09/11/98 | C | Growing-Season Mustard | 1,890 | 1,640 | 270 | <0.3 | <0.01 | 19 | <0.6 | <1.0 |
| 09/18/98 | C | Growing-Season Mustard | 73 | 63 | 17 | <0.3 | <0.01 | 1 | <0.6 | <1.0 |
| 09/25/98 | C | Growing-Season Mustard | 2,170 | 1,890 | 644 | <0.3 | <0.01 | 24 | <0.6 | <1.0 |
| 10/02/98 | C | Growing-Season Mustard | 2,500 | 2,170 | 900 | <0.3 | <0.01 | 32 | <0.6 | <1.0 |
| 10/19/98 | C | Post-Amendment Mustard | 1,946 | 1,690 | 783 | <0.3 | <0.01 | 34 | <0.6 | <1.0 |
| | | | | | | | | | | |
| 08/06/98 | 129-3 | Post-Amendment Corn | 1,430 | 1,240 | 14 | <0.3 | <0.01 | 10 | <0.6 | NA |
| 09/04/98 | 129-3 | Growing-Season Mustard | 380 | 330 | 155 | NA[3] | NA | 16 | <0.6 | NA |
| 09/18/98 | 129-3 | Growing-Season Mustard | 5 | 4 | 2 | NA | NA | <0.01 | <0.6 | NA |

(1) Contaminant of Concern for this site.
(2) Method Detection Limit.
(3) NA = Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

The porous cup may have been inserted into a void, and lead and EDTA-contaminated water from the treated upper soil layer may have pooled around the cup, thus accounting for the elevated concentrations of lead and EDTA in the solution. Alternately, a leakage could have occurred in the bentonite clay seal around the neck of the lysimeter at the soil surface, and leakage would have allowed channeling from the surface. Such a break would not have been obvious to an observer, since tilling operations normally covered the clay cap.

This lysimeter was located in the southeast corner of Site C, which was part of the 1962 Pit, a large area (60 ft x 20 ft x 30 ft) where equipment was decontaminated by drenching with fuel oil and burning. The equipment was removed, but a considerable amount of metal scrap, wood, and concrete debris was subsequently disposed of in the pit, and soil of diverse type was used as fill and cover. The soil of Unit 1 was shallow in this part of the field and the underlying clay of Unit 2 may have created an impermeable "bowl" which trapped a pool of contaminated water which bathed the porous cup of the lysimeter. Samples could not be obtained from lysimeters at Site 129-3 until August 6, 1998 (Table 5-24). EDTA and lead were also detected in lysimeter samples at Site 129-3 beginning on August 6, 1998.

**Table 5-23**
**Summary of Soil Solution Collection in Lysimeters at Site C in 1998**
**(Milliliters)**

| Lys. No. | 8/01 | 8/06 | 8/11 | 8/25 | 9/04 | 9/11 | 9/18 | 9/25 | 10/02 | 10/19 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ---- | 776 | 64 | 434 | 149 | ---- | ---- | ---- | ---- | ---- |
| 2 | ---- | 927 | 10 | 290 | 94 | ---- | ---- | ---- | ---- | ---- |
| 3 | ---- | 508 | 64 | 206 | 72 | ---- | ---- | ---- | ---- | ---- |
| 4 | ---- | 1017 | 100 | 120 | 728 | 531 | ---- | 528 | 360 | 500 |
| 5 | ---- | 684 | 96 | 526 | 230 | 40 | ---- | ---- | ---- | 210 |
| 6 | ---- | 1060 | 376 | 714 | 410 | 185 | 54 | 82 | 4 | ---- |
| 7 | ---- | --- | ---- | 24 | ---- | ---- | ---- | ---- | ---- | ---- |
| 8 | ---- | 898 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| 9 | 125 | 80 | 130 | 317 | 268 | 150 | 24 | ---- | ---- | ---- |
| 10 | ---- | 798 | ---- | 214 | ---- | ---- | ---- | ---- | ---- | ---- |
| 11 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| 12 | ---- | 418 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |

**Table 5-24**
**Summary of Soil Solution Collection in Lysimeters at Site 129-3 in 1998**
**(Milliliters)**

| Lys. No. | 8/01 | 8/06 | 8/11 | 8/25 | 9/04 | 9/11 | 9/18 | 9/25 | 10/02 | 10/19 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ---- | 1086 | ---- | ---- | 1071 | ---- | ---- | ---- | ---- | ---- |
| 2 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| 3 | ---- | ---- | ---- | ---- | 965 | ---- | ---- | ---- | ---- | ---- |
| 4 | ---- | 547 | ---- | ---- | 606 | ---- | ---- | ---- | ---- | ---- |
| 5 | ---- | 213 | ---- | ---- | 536 | ---- | ---- | ---- | ---- | ---- |
| 6 | ---- | 937 | ---- | ---- | 1156 | ---- | ---- | ---- | ---- | ---- |
| 7 | ---- | 204 | ---- | ---- | 614 | ---- | ---- | ---- | ---- | ---- |
| 8 | ---- | 468 | ---- | ---- | 775 | ---- | ---- | ---- | ---- | ---- |
| 9 | 125 | 123 | ---- | ---- | 610 | ---- | 270 | ---- | ---- | ---- |
| 10 | ---- | 485 | ---- | ---- | 380 | ---- | ---- | ---- | ---- | ---- |
| 11 | ---- | ---- | ---- | ---- | 168 | ---- | ---- | ---- | ---- | ---- |
| 12 | ---- | ---- | ---- | ---- | 900 | ---- | ---- | ---- | ---- | ---- |

A sample collected from the lysimeter in the northwest corner of Site C (lysimeter #9) on August 25, 1998, exhibited a blue color. This blue color prompted an analysis for cobalt and copper, since these elements may form complexes which, in solution, are blue in color, e.g., sulfates, amines, etc.

Blue-colored soil solution samples showed copper concentrations ranging from 3 ppm up to 267 ppm over the 8-week period in which they were collected (Table 5-25). A soil solution sample taken immediately prior to amendment addition showed a copper concentration of <0.004 ppm. The presence of copper in the solutions likely was the result of a reaction between acetic acid and EDTA with copper particulate (copper-jacketed projectiles, copper scrap metal, wire, etc.) which have been observed in the soil. It is likely there was a localized copper source in the soil in the immediate vicinity of the lysimeter collecting the solution. This episode seemed to be an isolated event from a single source and the reduction in concentration at subsequent sampling events (Table 5-25) indicated that copper persistence in the soil solution would probably diminish with time.

**Table 5-25**
**Results of Copper Analysis on Water Collected from Lysimeter at Site C (1998)**

| Sample | Date | Copper, mg/L |
|---|---|---|
| 1 | 7/20/98[1] | <0.004[2] |
| 2 | 8/6/98 | 8 |
| 3 | 8/11/98 | 3 |
| 4 | 8/25/98 | 12 |
| 5 | 9/4/98 | 57 |
| 6 | 9/11/98 | 253 |
| 7 | 9/18/98 | 11 |
| 8 | 9/25/98 | 267 |
| 9 | 10/2/98 | 190 |
| 10 | 10/19/98 | 77 |

(1) Pre-amendment addition sample; however, a single sample may not be indicative of true baseline copper concentrations.
(2) Method Detection Limit.

### 5.2.7 Soil Sampling - 1999 Corn Crop

#### 5.2.7.1 Pre-Amendment Soil Sampling - 1999 Corn Crop

At Site C, the EDTA in the soil was present at very low concentrations in samples taken immediately before soil amendment application for the 1999 corn crop (Table 5-26). The most recent application of EDTA before this sampling was in October 1998 for the white mustard crop (Table 5-14). At that time soil samples taken 2 to 3 days after EDTA was added to the mustard showed EDTA concentrations of 4,590 mg/kg at the 0- to 12-inch depth and 1,590 at the 12 to 24-inch depth (Table 5-14). Over the winter and during the following spring and summer growing season, EDTA concentrations decreased to those shown in Table 5-26. This could be due to degradation of EDTA, adsorption of EDTA onto organic matter and soil minerals (e.g., iron oxides and hydroxides), or movement of EDTA to soil depths below the sampling zone of 2 feet, but is likely a combination of all these factors.

Water-soluble lead concentrations, as shown in Table 5-26, were also low, compared to 1998 values following the EDTA application to the white mustard crop (Table 5-14). This would be expected from the low concentrations of EDTA. Adsorption of EDTA onto hydrous oxide fractions, or degradation of EDTA and re-precipitation of lead into less soluble forms in the soil, could account for the large decrease in soluble lead concentrations in the top 24 inches of soil.

Downward movement of lead could also have occurred. As with EDTA, this would likely have been promoted by the heterogeneous physical nature of the site.

Overall, total lead concentrations were lower at both sampling depths (Table 5-26) than observed in the 1998 growing season after amendment application to white mustard (Table 5-14). Since there was lead uptake by the corn crop in 1998, this decrease in soil lead concentration was partly attributed to phytoextraction by the crop. The mean for total lead at the 12- to 24-inch depth (1,281 mg/kg) was slightly lower than in the upper layer. However, the variability in lead

concentrations from grid to grid and at different sampling periods prevents a conclusive determination of the dynamics of lead in the soil. There was one outlier value in the data (54,300 mg/kg in grid 36) which may be artificially high due to contamination of the sample by particulate lead.

Of the other COCs in pre-amendment soil samples, manganese concentrations were similar to values found in the 1998 demonstration. Concentrations of antimony, arsenic, and beryllium were essentially below the method detection limit at both soil depths. Thallium was found at high levels only in grid 11.

At Site 129-3, inadequate plant growth throughout the plot area precluded sampling any grids except grids 1 and 2. However, total lead concentrations in these grids (Table 5-27) were similar to values obtained for soil samples taken throughout the 1998 growing season (Tables 5-5, 5-7, 5-13, 5-15). Both EDTA and water-soluble lead were found at very low concentrations. The concentrations of manganese and antimony found in 1999 in one of the two grids was similar to 1998 values.

#### 5.2.7.2 Post-Amendment Soil Sampling - 1999 Corn Crop

For Site C, EDTA concentrations in soil (Table 5-28) tended to be quite variable and localized primarily in the top 12 inches of soil. Although a sufficient volume of EDTA solution was applied to wet the top 24 inches of soil, the concentration of EDTA this year was reduced by one-third from the concentration applied in 1998 to reflect an application based on the frequency of occurrence of a given lead concentration within the grids across the field. Adsorption of the majority of EDTA on the organic matter and hydrous oxides in the soil likely occurred in the top 12 inches at the time of application. Therefore less of the EDTA was found at the lower depth. Higher concentrations of water-soluble lead were found at the 0- to12-inch than at 12- to 24-inch depth, corresponding to the higher concentration of EDTA in the upper layer. Total lead concentrations were highly variable, and no discernible patterns of lead distribution in the soil were observed.

None of the other COCs showed significantly altered concentrations in the soil after amendment application (Table 5-26 *vs* Table 5-28).

At Site 129-3, EDTA concentrations in soil at the 0- to 12-inch depth in the two grids sampled (Table 5-29) averaged about the same as the average concentration found after amendment additions for corn in the 1998 demonstration (Table 5-7). Very little EDTA was found at the 12- to 24-inch depth.

Water-soluble lead concentrations were a reflection of the amount of EDTA found in the soil. Detectable levels of water-soluble lead were found only in grid 1 at the 0- to 12-inch depth, which corresponds to a high concentration of EDTA in the soil (Table 5-29).

Total lead concentrations were quite variable (Table 5-29), but were generally somewhat lower in grid 1 than found in the 1998 demonstration. Grid 2 values varied widely from values found after amendment application to mustard (Table 5-15), most likely due to the high variability of lead in the soil.

Antimony concentrations were below detection limits; manganese concentrations were relatively unchanged from the 1998 values.

In order to determine if lateral movement of amendments occurred, samples (designated as A, B, C, and D in Table 5-30) were taken from locations in grids 4, 10, 16, and 22 at Site C that were immediately adjacent to the treated areas. There was a possibility that some lateral movement of EDTA occurred, but this was minimal, since EDTA concentrations observed in the treated areas (Table 5-28) were higher than concentrations observed in the adjacent areas. Similarly, concentrations of water-soluble lead in the treated areas were much higher than in the non-treated areas. The limited data collected for Site 129-3 from grids 3 and 7 (samples A and B in Table 5-30) adjacent to the sampled grids 1 and 2 did not indicate lateral movement of EDTA at this site.

**Table 5-26**
**Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site C in 1999 Prior to Soil Amendment Additions to Corn**

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb, mg/kg | | Pb, mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 5 | 8.8 | 8.7 | 7.9 | 9.1 | 6.9 | 7.9 | 29.8 | 13.3 | 956 | 1,740 |
| 6 | 8.6 | 8.7 | 3.2 | 5.7 | 2.8 | 5.0 | 48.9 | 93.6 | 3,220 | 3,410 |
| 11 | 8.7 | 8.5 | 13.1 | 7.0 | 11.4 | 6.1 | 14.3 | 2.6 | 686 | 813 |
| 12 | 8.6 | 8.8 | 3.3 | 2.3 | 2.9 | 2.0 | 27.6 | 5.9 | 826 | 382 |
| 17 | 8.5 | 8.6 | 4.1 | 13.6 | 3.6 | 11.8 | 2.9 | 1.4 | 382 | 861 |
| 18 | 8.5 | 8.7 | 4.1 | 4.7 | 3.6 | 4.1 | 54.0 | 2.5 | 3,540 | 595 |
| 23 | 8.0 | 8.2 | 7.6 | 14.2 | 6.6 | 12.3 | 6.6 | <0.96[2] | 774 | 1,660 |
| 24 | 8.5 | 8.5 | 4.6 | 6.1 | 4.0 | 5.3 | 41.4 | 29.5 | 1,500 | 1,110 |
| 29 | 8.6 | 8.4 | 5.6 | 7.5 | 4.9 | 6.5 | 31.3 | 24.5 | 755 | 1,340 |
| 30 | 8.6 | 8.7 | <0.3[2] | 3.4 | <0.3[2] | 3.0 | 16.4 | 3.8 | 903 | 315 |
| 35 | 8.6 | 8.7 | 2.6 | 4.1 | 2.3 | 3.6 | 20.8 | 40.6 | 3,200 | 1,870 |
| 36 | 8.4 | 8.7 | <0.3[2] | <0.3[2] | <0.3[2] | <0.3[2] | <0.87[2] | 14.8 | 1,260 | (54,300)[3] |
| | | | | | | | | | | |
| **Mean** | ***8.5*** | ***8.6*** | ***4.7*** | ***6.5*** | ***4.1*** | ***5.6*** | ***24.5*** | ***19.4*** | ***1,500*** | ***1,280*** |
| **Std. Dev.** | ***0.2*** | ***0.2*** | ***3.6*** | ***4.2*** | ***3.1*** | ***3.7*** | ***17.6*** | ***26.7*** | ***1,135*** | ***887*** |

(1) Contaminant of Concern for this site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied.
For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) 54,300 is an outlier, probably caused by particulate lead. This result was excluded from the statistical analysis.
(4) Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-26 (Continued)
## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site C in 1999 Prior to Soil Amendment Additions to Corn

| Grid No. | As[1], mg/kg | | Be[1], mg/kg | | Mn[1], mg/kg | | Sb[1], mg/kg | | Tl[1], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| | | | | | | | | | | |
| 5 | <1.02[3] | <1.14[3] | <0.05[3] | <0.06[3] | 355 | 652 | <1.53[3] | <1.71[3] | <2.54[3] | <2.86[3] |
| 6 | <0.92 | <0.76 | <0.05 | <0.04 | 171 | 193 | <1.38 | <1.15 | <2.30 | <1.91 |
| 11 | <1.11 | <1.23 | 0.4 | 0.1 | 539 | 684 | <1.67 | <1.85 | 96.9 | 32.8 |
| 12 | <1.08 | <0.97 | 0.1 | 0.3 | 198 | 276 | <1.62 | <1.45 | <2.71 | <2.42 |
| 17 | <0.95 | <0.94 | 0.3 | 0.3 | 445 | 736 | <1.42 | <1.41 | <2.37 | 10.6 |
| 18 | <0.84 | <1.01 | 0.1 | 0.1 | 265 | 254 | <1.26 | <1.51 | 4.03 | <2.51 |
| 23 | <0.91 | <0.77 | 0.1 | 3.9 | 235 | 274 | <1.37 | <1.15 | <2.28 | 4.67 |
| 24 | <0.80 | <0.75 | 0.5 | 0.2 | 190 | 237 | <1.20 | <1.13 | <2.01 | <1.88 |
| 29 | <0.95 | <0.99 | 0.5 | 5.4 | 259 | 295 | <1.43 | <1.49 | <2.38 | <2.48 |
| 30 | <0.95 | <1.10 | 0.7 | 0.3 | 170 | 169 | <1.42 | <1.65 | <2.37 | <2.75 |
| 35 | <1.01 | <0.88 | 0.1 | 0.0 | 196 | 274 | <1.52 | <1.32 | <2.53 | <2.21 |
| 36 | <1.07 | <0.67 | 0.1 | 0.1 | 221 | 212 | <1.61 | 852 | <2.68 | <1.68 |
| | | | | | | | | | | |
| **Mean** | ***<MDL[3]*** | ***<MDL[3]*** | ***0.2*** | ***0.9*** | ***270*** | ***355*** | ***<MDL[3]*** | ***71.0*** | ***9.4*** | ***4.9*** |
| **Std. Dev.** | ***NA[4]*** | ***NA[4]*** | ***0.2*** | ***1.8*** | ***117*** | ***207*** | ***NA[4]*** | ***NA[4]*** | ***27.6*** | ***9.2*** |

(1) Contaminant of Concern for this site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) 54,300 is an outlier, probably caused by particulate lead. This result was excluded from the statistical analysis.
(4) Not Applicable.

## Table 5-27
## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site 129-3 in 1999 Prior to Soil Amendment Additions to Corn

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb, mg/kg | | Pb, mg/kg | | Mn[1], mg/kg | | Sb[1], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| | | | | | | | | | | | | | | |
| 1 | 7.8 | 8.1 | 1.9 | 1.6 | 1.7 | 1.4 | 6.0 | 2.8 | 27 | 117 | 262 | 315 | <1.35[2] | <1.44[2] |
| 2 | 7.5 | 8.1 | <0.3[2] | 1.3 | <0.3[2] | 1.1 | <0.87[2] | 4.1 | 60 | 216 | 1,230 | 206 | <1.18 | <1.61 |
| | | | | | | | | | | | | | | |
| **Mean** | ***7.7*** | ***8.1*** | ***1.0*** | ***1.4*** | ***0.9*** | ***1.2*** | ***3.2*** | ***3.4*** | ***44*** | ***167*** | ***746*** | ***261*** | ***<MDL[2]*** | ***<MDL[2]*** |
| **Std. Dev.** | ***0.3*** | ***0.1*** | ***NA[3]*** | ***0.2*** | ***NA[3]*** | ***0.2*** | ***NA[3]*** | ***0.9*** | ***23*** | ***70*** | ***684*** | ***77*** | ***NA[3]*** | ***NA[3]*** |

(1) Contaminant of Concern for this site.
(2) Method Detection Limit. Where one datum point was equal to or less than the MDL, one-half the value of the MDL was substituted for this number when calculating the mean and standard deviation.
(3) Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-28
## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site C in 1999 after Soil Amendment Additions to Corn

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb, mg/kg | | Pb, mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 5 | 8.9 | 8.8 | 26 | 6 | 23 | 5 | 13 | 2 | 553 | 1,510 |
| 6 | 9.3 | 9.5 | 238 | 47 | 207 | 41 | 200 | 80 | 3,120 | 12,900 |
| 11 | 8.7 | 8.8 | 3,760 | 13 | 3,270 | 11 | 182 | <1.05[2] | 953 | 2,320 |
| 12 | 9.3 | 9.4 | 794 | 158 | 690 | 137 | 314 | 162 | 2,100 | 2,840 |
| 17 | 8.8 | 8.6 | 6,290 | 15 | 5,470 | 13 | 192 | 3 | 551 | 732 |
| 18 | 8.7 | 9.1 | 377 | 135 | 328 | 117 | 190 | 121 | 1,310 | 2,030 |
| 23 | 8.9 | 8.5 | 2,390 | 21 | 2,080 | 18 | 138 | <1.08 | 469 | 1,240 |
| 24 | 8.6 | 9.3 | 1,390 | 569 | 1,210 | 495 | 747 | 340 | 4,030 | 3,900 |
| 29 | 9.1 | 8.7 | 12 | 38 | 10 | 33 | 15 | 31 | 991 | 4,200 |
| 30 | 9.1 | 9.4 | 2,740 | 5 | 2,380 | 4 | 469 | 34 | 542 | 256 |
| 35 | 9.2 | 8.9 | 1,210 | 135 | 1,050 | 117 | 217 | 83 | 1,070 | 1,660 |
| 36 | 9.4 | 9.3 | 1,020 | 396 | 887 | 344 | 492 | 258 | 797 | 5,160 |
| | | | | | | | | | | |
| **Mean** | ***9.0*** | ***9.0*** | ***1,660*** | ***179*** | ***1,440*** | ***156*** | ***264*** | ***93*** | ***1,370*** | ***3,230*** |
| **Std. Dev.** | ***0.3*** | ***0.3*** | ***943*** | ***199*** | ***820*** | ***173*** | ***212*** | ***111*** | ***1,138*** | ***3,378*** |

(1) Contaminant of Concern for this Site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-28 (Continued)**
**Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site C in 1999 after Soil Amendment Additions to Corn**

| Grid No. | As[1], mg/kg | | Be[1], mg/kg | | Mn[1], mg/kg | | Sb[1], mg/kg | | Tl[1], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| 5 | <0.95[2] | <0.82[2] | <0.05[2] | <0.04[2] | 1100 | 305 | <1.43[2] | <1.23[2] | <2.39[2] | <2.04[2] |
| 6 | <0.78 | <0.96 | <0.04 | <0.05 | 258 | 166 | <1.17 | <1.27 | <1.95 | <2.39 |
| 11 | <0.97 | <1.03 | <0.05 | <0.05 | 232 | 766 | <1.46 | <1.55 | <2.43 | 47.3 |
| 12 | <0.68 | <1.03 | 1.69 | 0.23 | 240 | 217 | <1.02 | <1.55 | <1.70 | <2.58 |
| 17 | <0.83 | <1.01 | <0.04 | <0.05 | 371 | 564 | <1.24 | <1.52 | <2.07 | <2.53 |
| 18 | <0.99 | <0.74 | <0.05 | <0.04 | 187 | 294 | <1.49 | <1.10 | <2.48 | <1.84 |
| 23 | <0.70 | <1.18 | <0.04 | <0.06 | 222 | 438 | <1.06 | <1.77 | <1.76 | <2.95 |
| 24 | <0.79 | <0.73 | <0.04 | 2.68 | 190 | 341 | <1.18 | <1.10 | <1.97 | <1.83 |
| 29 | <1.00 | <0.70 | <0.05 | <0.04 | 235 | 313 | <1.50 | <1.05 | <2.49 | <1.75 |
| 30 | <0.73 | <0.66 | 4.06 | 0.39 | 223 | 200 | <1.09 | <1.00 | <1.82 | <1.66 |
| 35 | <0.91 | <0.98 | 0.09 | <0.05 | 234 | 354 | <1.36 | <1.47 | <2.27 | <2.45 |
| 36 | <0.88 | <0.80 | <0.04 | 3.15 | 147 | 169 | <1.32 | <1.21 | <2.20 | <2.01 |
| | | | | | | | | | | |
| **Mean** | ***<MDL[2]*** | ***<MDL[2]*** | ***0.5*** | ***0.4*** | ***303*** | ***344*** | ***<MDL[2]*** | ***<MDL[2]*** | ***<MDL[2]*** | ***11.0*** |
| **Std. Dev.** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** | ***257*** | ***176*** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** |

(1) Contaminant of Concern for this Site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) Not Applicable.

## Table 5-29
## Soil pH, EDTA, Water-Soluble Pb, and Contaminants of Concern at Site 129-3 in 1999 After Soil Amendment Additions to Corn

| Grid No. | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb, mg/kg | | Pb, mg/kg | | Mn[1], mg/kg | | Sb[1], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Depth, inches | | | | | | | | | | | | | |
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| | | | | | | | | | | | | | | |
| 1 | 8.2 | 8.6 | 665 | 2.6 | 578 | 2.3 | 19.6 | <0.96[2] | 63 | 105 | 212 | 187 | <1.19[2] | <1.16[2] |
| 2 | 8.4 | 8.3 | 6 | 2.8 | 5 | 2.4 | <0.97[2] | <0.92 | 556 | 69 | 234 | 214 | <1.48 | <1.22 |
| | | | | | | | | | | | | | | |
| **Mean** | ***8.3*** | ***8.4*** | ***336*** | ***2.7*** | ***292*** | ***2.3*** | ***9.8*** | ***<MDL[2]*** | ***310*** | ***87*** | ***223*** | ***201*** | ***<MDL*** | ***<MDL*** |
| **Std. Dev.** | ***0.1*** | ***0.1*** | ***466*** | ***0.1*** | ***405*** | ***0.1*** | ***13.9*** | ***NA[3]*** | ***349*** | ***25*** | ***16*** | ***19*** | ***NA*** | ***NA*** |

(1) Contaminant of Concern for this site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) Not Applicable.

**NOTE**: Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-30**
**Analyses of Soil Samples Taken in 1999 from**
**Grids Adjacent to Areas Receiving Soil Amendments**

| Sample | pH | | EDTA as $Na_2EDTA$, mg/kg | | EDTA as EDTA, mg/kg | | Water-Soluble Pb[1], mg/kg | | Pb[1], mg/kg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 | 0-12 | 12-24 |
| **Site C** | | | | | | | | | | |
| A | 8.7 | 9.0 | 28 | 44 | 24 | 38 | 129 | 74.1 | 4,940 | 14,200 |
| B | 8.8 | 8.7 | <0.3[2] | 11 | <0.3[2] | 10 | 40 | 61 | 1,350 | 1,720 |
| C | 8.7 | 8.6 | 75 | 33 | 65 | 29 | 92 | 147 | 1,340 | 4,390 |
| D | 8.8 | 8.5 | 14 | 66 | 12 | 57 | 116 | 153 | 3,800 | 8,630 |
| **Mean** | ***8.8*** | ***8.6*** | ***29*** | ***39*** | ***25*** | ***34*** | ***94*** | ***109*** | ***2,858*** | ***7,235*** |
| **Std. Dev.** | ***0.1*** | ***0.1*** | ***33*** | ***23*** | ***29*** | ***20*** | ***39*** | ***48*** | ***1,807*** | ***5,446*** |
| | | | | | | | | | | |
| **Site 129-3** | | | | | | | | | | |
| A | 8.5 | 8.6 | <0.3 | 3.4 | <0.3 | 3.0 | <0.93[2] | <0.96[2] | 127 | 11 |
| B | 8.2 | 8.4 | <0.3 | <0.3[2] | <0.3 | <0.3[2] | 48.9 | 13.4 | 2,280 | 356 |
| **Mean** | ***8.4*** | ***8.5*** | ***<MDL[2]*** | ***1.8*** | ***<MDL[2]*** | ***1.6*** | ***25*** | ***7*** | ***1,203*** | ***184*** |
| **Std. Dev.** | ***0.2*** | ***0.1*** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** | ***NA[3]*** | ***1,522*** | ***244*** |

(1) Contaminant of Concern for this site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) Not Applicable.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

### 5.2.8 Plant Sampling - 1999 Corn Crop

#### 5.2.8.1 Plant Growth

Three changes in the corn crop were implemented in the 1999 season: (1) use of a silage variety of corn planted at twice the density of the 1998 crop; (2) a higher rate of nitrogen fertilizer than used in 1998 was applied during the growing season to meet N requirements of the silage corn; and (3) additional phosphate was applied at planting.

The silage variety of corn rather than a seed variety was chosen for use in 1999 based on recommendations from plant breeders and growers in the Minnesota/North Dakota region for a deeper rooting, higher yielding strain. The additional N fertilizer was required for the additional biomass production by the silage corn variety. Additional P was band-applied along the seed row to prevent a recurrence of P deficiency in the corn that was observed in 1998. Although there is the potential for binding of some soil lead by phosphate into insoluble forms, application of additional P was deemed acceptable since not all of the soil lead will be complexed with phosphate. There are several Pb-$PO_4$ compounds which can exist in soil, depending on pH and halogen (Br-, Cl-, F-) content. The most soluble and most plant-available of these (i.e., $Pb(H_2PO_4)_2$, $PbHPO_4$, and to a much lesser extent, $Pb_4O(PO_4)_2$) form soon after fertilizer addition. EDTA is a sufficiently strong chelate to break the Pb-$PO_4$ complex and form the EDTA-Pb complex that is taken up into the plant. The most recent P addition doesn't react to fully complex Pb into the most insoluble $PO_4$ complex (chloropyromorphite). Cerrusite ($PbCO_3$) is the compound which will most strongly control lead solubility in this type soil, regardless of the amount of P added. Therefore, the supplemental P would have minimal effect on lead solubility. For Site C, cooler temperatures and continued rainfall after planting and seedling emergence resulted in stunted growth and symptoms of nitrogen deficiency (yellowing of leaves from the leaf tip in a "V" shape back toward the stalk). Extensive bird damage to the emerging seedlings necessitated several replantings over many areas of the plot, which resulted in various stages of plant development across the plot. On many areas within the plot, the plant population was very sparse or barren altogether. Coverage on individual grids ranged from 8% - 42% of the potential maximum population of 180 plants/grid (Table 4-4). In the eastern third of the plot, where sampling and amendment application activities were conducted, the maximum plant height was 6 ft, the average height was 5 ft, and the range was 3 to 6 ft (Table 4-4). Plants appeared generally healthy, except for sporadic necrotic spots on the leaves. Ear development was at the brown silk stage; kernels were at the milk stage, and very small. The average ear diameter was 1.5 inches.

The rooting depth for the Norvartis/Mycogen silage corn variety, according to plant breeders in the North Dakota/Minnesota region, was purported to be 6-8 ft in a sandy soil. However, excavated plants across the plot showed a fibrous root system of only about 8 inches across and 6 inches in length. The limited root development for plants throughout the plot shows the effect of excess rainfall, where roots stay close to the surface in the saturated zone and do not develop deeper into the soil. In addition, in the western part of the plot, a hard pan layer in the soil (visible underneath the plants) likely inhibited deeper root growth. Since the pan layer is not present in the eastern part of the plot, toxicity from one or more other contaminants in the soil could also have been a cause of root stunting in that area. Most of the debris that was deposited

at Site C (railroad ties, metal scrap, burned material, and broken concrete) is found in this eastern part of the plot, and this could be a source of some toxic components.

At Site 129-3, extensive bird damage and several replantings resulted in plants ranging in size from 2 to 7 ft (Table 4-5). The plant coverage on individual grids ranged from 2% to 42%. Fully mature plants were 7 ft tall and usually had two ears. Many of the ears showed abnormal development in that the shuck development was incomplete and bare kernels were showing for 1-3 inches from the tip of the ears. Ears were at the brown silk stage and had an average diameter in most mature plants of 2 inches. Kernels were at the milk stage. The bird damage affected the plant population to the extent that only grids 1 and 2 had a sufficient number of mature plants to justify amendment additions, in spite of several replantings. Other grids had 3 to 4 rows of mature plants, while some had almost a full complement of immature plants. None of these grids, however, had sufficiently uniform and mature growth to provide representative lead uptake. Excavated plants showed a root system of about 10 inches across and 15-18 inches in length which, as with Site C, was much less than the expected root length of 6 ft.

#### 5.2.8.2 Pre-Amendment Plant Sampling - 1999 Corn Crop

Lead concentrations in plants at Site C before adding soil amendments (Table 5-31) were as low or lower than observed for corn before soil amendment additions in 1998 (Table 5-8). EDTA concentrations in the 1999 plants were below the method detection limit. This indicates that there was no carry-over lead or EDTA from the previous year taken up into the plant. Concentrations of the other COCs, except for manganese, were low or below detection limit (Table 5-31).

Results at Site 129-3 were similar to those found at Site C and at Site 129-3 in 1998 (Table 5-9), i.e., lead concentrations were very low, and EDTA and antimony were below detection limits (Table 5-32). Concentrations of manganese were similar to that found in corn at Site C (Table 5-31).

#### 5.2.8.3 Post-Amendment Plant Sampling - 1999 Corn Crop

At Site C, the lead concentration in corn plants averaged 854 mg/kg, and ranged from 343 to 1,380 mg/kg (Table 5-33). These values were tenfold less than obtained in corn treated in 1998 (Table 5-10). Conditions in 1999 were not optimal for lead uptake, as the corn crop at this site exhibited several different growth stages, ranging from immature to mature plants with ears. In addition, corn plants exhibited a shallow rooting system at site C, with the majority of roots in the top 6 inches of soil. This top soil layer would be most susceptible to movement of lead down to lower layers due to EDTA applications in the previous year. The average for total lead in the top 0-12 inches was lower for measurements taken before soil amendments in 1999 (Table 5-26) than for measurements taken before and after amendment additions for white mustard at the end of the previous year (Tables 5-12 and 5-14). This suggests that the 6-inch rooting zone for corn most likely had lower lead concentrations than the previous year, so that efficient scavenging for lead by corn roots could not be achieved. However, as noted above in Section 3.2, the high degree of variability in lead concentrations from grid to grid makes a conclusive determination of soil lead dynamics difficult. EDTA concentrations in the corn averaged approximately 40% lower than found in the corn crop in 1998 (Table 5-9), but still averaged 26,200 mg/kg in 1999

(Table 5-33). This lower average concentration was probably a function of the overall poor growth of the corn and the application of less EDTA in 1999.

Arsenic, beryllium, and antimony were below concentration detection limits in plant tissue. The average manganese concentration was approximately fourfold higher than pre-amendment concentrations (Table 5-31), indicating that the soil amendments enhanced manganese uptake, similar to results in the 1998 corn crop (Table 5-9). Thallium, at low but detectable concentrations, was found in plants from 8 of the 12 grids sampled, whereas plant samples from just two grids contained detectable levels of thallium in the pre-amendment sampling. This indicated that, as with manganese, EDTA application enhanced thallium uptake.

**Table 5-31**
**Concentrations of EDTA and Contaminants of Concern in 1999**
**Demonstration Year Corn from Site C Prior to Adding Soil Amendments**

| Grid No. | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg | Pb,[1] mg/kg | As[1], mg/kg | Be[1], mg/kg | Mn[1], mg/kg | Sb[1], mg/kg | Tl[1], mg/kg |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| 5 | <3.7[2] | <3.2[2] | 12.3 | <0.49[2] | <0.02[2] | 32.8 | <0.74[2] | <1.24 [2] |
| 6 | <3.7 | <3.2 | 6.6 | <0.50 | <0.03 | 25.8 | <0.75 | <1.25 |
| 11 | <3.7 | <3.2 | 12.9 | <0.49 | <0.02 | 35.0 | <0.74 | <1.23 |
| 12 | <3.7 | <3.2 | 6.2 | <0.50 | 0.18 | 30.7 | <0.75 | <1.24 |
| 17 | <3.7 | <3.2 | 10.1 | <0.49 | <0.02 | 25.0 | <0.74 | <1.24 |
| 18 | <3.7 | <3.2 | 8.9 | <0.49 | <0.02 | 32.1 | <0.74 | <1.24 |
| 23 | <3.7 | <3.2 | 7.8 | 1.59 | 1.83 | 34.9 | 1.88 | 1.71 |
| 24 | <3.7 | <3.2 | 18.3 | <0.49 | <0.02 | 30.1 | <0.75 | <1.24 |
| 29 | <3.7 | <3.2 | 10.6 | 1.51 | 1.44 | 18.7 | 1.94 | 1.59 |
| 30 | <3.7 | <3.2 | 6.3 | <0.49 | <0.02 | 28.6 | <0.74 | <1.23 |
| 35 | <3.7 | <3.2 | 9.7 | <0.51 | <0.03 | 29.8 | <0.76 | <1.27 |
| 36 | <3.7 | <3.2 | 9.4 | <0.49 | <0.02 | 23.4 | <0.74 | <1.23 |
| | | | | | | | | |
| **Mean** | ***<MDL[2]*** | ***<MDL[2]*** | ***9.9*** | ***0.5*** | ***0.3*** | ***28.9*** | ***0.6*** | ***0.8*** |
| **Std. Dev.** | ***NA[3]*** | ***NA[3]*** | ***3.4*** | ***0.5*** | ***0.6*** | ***4.9*** | ***0.6*** | ***0.4*** |

(1) Contaminant of Concern for this Site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) NA = Not Applicable.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-32**
**Concentrations of EDTA and Contaminants of Concern in 1999 Demonstration Year Corn from Site 129-3 Prior to Adding Soil Amendments**

| Grid No. | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg | Pb[1], mg/kg | Mn[1], mg/kg | Sb[1], mg/kg |
|---|---|---|---|---|---|
| | | | | | |
| 1 | <3.7[2] | <3.2[2] | 6.2 | 29.2 | <0.65[2] |
| 2 | <3.7 | <3.2 | 5.8 | 53.8 | <0.73 |
| | | | | | |
| **Mean** | ***<MDL[2]*** | ***<MDL[2]*** | ***6.0*** | ***41.5*** | ***<MDL[2]*** |
| **Std. Dev.** | ***NA[3]*** | ***NA[3]*** | ***0.3*** | ***17.4*** | ***NA[3]*** |

(1) Contaminant of Concern for this Site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and deviation for a set of values, where data was standard equal to or less than the MDL, one-half the value of the MDL was used.
(3) NA = Not Applicable.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-33**
**Concentrations of EDTA and Contaminants of Concern in 1999 Demonstration Year Corn from Site C After Adding Soil Amendments**

| Grid No. | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg | Pb[1], mg/kg | As[1], mg/kg | Be[1], mg/kg | Mn[1], mg/kg | Sb[1], mg/kg | Tl[1], mg/kg |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| 5 | 19,900 | 17,300 | 496 | <0.48[2] | <0.02[2] | 122 | <0.72[2] | <1.20[2] |
| 6 | 25,600 | 22,300 | 714 | <0.49 | <0.02 | 113 | <0.73 | 1.98 |
| 11 | 25,600 | 22,300 | 439 | <0.50 | <0.02 | 113 | <0.75 | <1.25 |
| 12 | 37,600 | 32,700 | 1,120 | <0.51 | <0.03 | 152 | <0.77 | 2.16 |
| 17 | 26,400 | 22,900 | 343 | <0.49 | <0.02 | 101 | <0.74 | <1.23 |
| 18 | 39,000 | 33,900 | 1,320 | <0.50 | <0.02 | 203 | <0.75 | 2.03 |
| 23 | 27,900 | 24,300 | 660 | <0.50 | <0.02 | 105 | <0.75 | 1.3 |
| 24 | 42,400 | 36,900 | 1,380 | <0.50 | <0.02 | 197 | <0.75 | 1.93 |
| 29 | 20,800 | 18,100 | 885 | <0.48 | <0.02 | 107 | <0.72 | 1.64 |
| 30 | 27,200 | 23,600 | 875 | <0.50 | <0.02 | 139 | <0.75 | 1.4 |
| 35 | 30,400 | 26,400 | 1,000 | <0.48 | <0.02 | 124 | <0.72 | 1.98 |
| 36 | 39,700 | 34,500 | 1,010 | <0.46 | <0.02 | 160 | <0.69 | 2.31 |
| | | | | | | | | |
| **Mean** | ***30,200*** | ***26,200*** | ***854*** | ***<MDL[2]*** | ***<MDL[2]*** | ***136*** | ***<MDL[2]*** | ***1.55*** |
| **Std. Dev.** | ***7,610*** | ***6,610*** | ***334*** | ***NA[3]*** | ***NA[3]*** | ***35*** | ***NA[3]*** | ***0.63*** |

(1) Contaminant of Concern for this site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) NA = Not Applicable.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

Very little lead uptake occurred in the plants from the two grids sampled at Site 129-3 (Table 5-34), most likely due to the limited root system of the plants and low lead concentrations in the root zone. Concentrations of lead in the plants were ten-fold higher in the previous year. EDTA concentrations in the corn were similar to concentrations observed in the 1998 crop (Table 5-11). EDTA again enhanced uptake of manganese by sixfold for this site. Antimony concentrations in the corn tissue were below the method detection limit.

**Table 5-34**
**Concentration of EDTA and Contaminants of Concern in 1999 Demonstration Year Corn from Site 129-3 After Adding Soil Amendments**

| Grid No. | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg | Pb[1], mg/kg | Mn[1], mg/kg | Sb[1], mg/kg |
|---|---|---|---|---|---|
| | | | | | |
| 1 | 6,970 | 6,060 | 93.6 | 262 | <0.74[2] |
| 2 | 14,100 | 12,300 | 115.0 | 304 | <0.74 |
| | | | | | |
| **Mean** | ***10,500*** | ***9,130*** | ***104*** | ***283*** | ***<MDL[2]*** |
| **Std. Dev.** | ***5,040*** | ***4,380*** | ***15*** | ***30*** | ***NA[3]*** |

(1) Contaminant of Concern for this site.
(2) Values preceded by a less than sign "<" indicate that the results were less than the Method Detection Limit (MDL). The MDL varied for these results because the sample weights and/or the dilution factors used in the analyses varied. For calculating the mean and standard deviation for a set of values, where data was equal to or less than the MDL, one-half the value of the MDL was used.
(3) NA = Not Applicable.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

### 5.2.9 Soil Sequential Extraction Analysis

Basing EDTA applications on the total soil lead concentrations may result in excess amounts of EDTA being applied, since the metal is partitioned in soil in fractions of varying solubility and plant-availability. A sequential extraction analysis procedure uses progressively stronger extractants to differentiate and quantify that fraction of the total amount of a metal in soil that is available or potentially available to plants. The purpose for using the sequential extraction technique is to determine the percentage of total lead that is most plant-available. The molar ratio of EDTA-to-soil lead then can be equalized to match the plant-available fraction of soil lead, which will reduce the amount of chelate required to solubilize lead for plant uptake.

The results of the sequential extraction analyses are shown in Tables 5-35 through 5-38. It should be noted that the sum of the values for lead concentration in the individual fractions does not necessarily equal the value for the total lead concentration. This is because: (1) analyses for total and water-soluble lead and the sequential extraction were performed on soil from the same bulk field sample, but on two separate samples (i.e., the sequential analysis was done later on a

separate sample from the same batch of soil); and (2) the soil was not analyzed for two additional fractions, the lead that is bound to organic matter, and the "residual" fraction, or lead that is bound up in the soil mineral crystalline matrix, since lead in these two components is in a form that is not immediately plant-available. However, it should also be noted that, although lead in the Fe and Mn oxide fraction is considered a plant-available form, lead in this fraction is more tightly bound, and thus is more slowly available.

The amount of EDTA to be added could be determined from the plant-available lead concentration that is equal to or greater than the plant-available lead concentration in 75% of the grids, as determined by the frequency distribution for the grids (Figure 5-3). The bars in this figure indicate the frequency or number of grids that fall within each lead concentration range. The cumulative percentage line plot indicates the percentage of grids that have lead concentrations equal to or less than the concentration range at a given point on the line. From the cumulative percentage plot, 75% of the grids contain plant-available lead concentrations of 1000 mg/kg or less. This concentration of lead would be used to determine the molar amount of EDTA to be added.

Combining the 0- to 12-inch and the 12- to 24-inch results, the amount of plant-available lead at Site C before EDTA application was about 55% of the total lead concentration (Table 5-35). The sequential extraction method provides a better basis for calculating the amount of EDTA needed to solubilize a sufficient amount of lead for plant uptake. This practice would further reduce the amount of EDTA added to soil, thus reducing potential adverse environmental effects.

The effect of EDTA on increasing the pool of plant-available lead is clearly shown in Table 5-36, wherein the total plant-available lead pool increased at both soil depths. In the 0- to 12-inch soil layer, the water-soluble and exchangeable lead pool increased while the carbonate-bound pool showed an insignificant decrease. In the 12- to 24-inch depth, the water-soluble, exchangeable, and carbonate pools all increased, with the largest apparent increase being in the carbonate pool.

The lead concentration in the carbonate pool at the 12- to 24-inch depth was nearly threefold higher in the post-amendment samples than in pre-amendment soils. However, the percentages of lead in the plant-available pools at the 12- to 24-inch depth was the same for the pre- and post-amendment samples.

The increase in the carbonate pool at the 12- to 24-inch depth after EDTA application and the higher soil pH (9.0) were consistent with degradation of EDTA and production of $CO_2$ and ammonia. The $CO_2$ would have been converted to carbonate and the ammonia would have caused the rise in soil pH. Carbonate dissolution is dependent upon particle size and the type and percentage of the various carbonate minerals in the soil. Differential solubilization of the various carbonate minerals by acetic acid may have resulted in varying release of lead that was bound to carbonates. No conclusions could be drawn from the limited data obtained for Site 129-3 (Tables 5-37 and 5-38).

**Table 5-35**
**Sequential Fractionation Analysis of Soil from Site C Prior to Adding Soil Amendments in 1999**

| | | Sequential Fraction- Pb, mg/kg | | | | | |
|---|---|---|---|---|---|---|---|
| **Grid No.** | **Depth, inches** | **Total** | **(A) Water-soluble** | **(B) Exchange-able** | **(C) Carbonate** | **Fe+Mn Oxide** | **Total Plant-Available (A+B+C)** |
| | | | | | | | |
| 5 | 0-12 | 956 | 30 | 2 | 223 | 367 | 255 |
| 6 | 0-12 | 3,220 | 49 | 13 | 1,940 | 721 | 2,002 |
| 11 | 0-12 | 686 | 14 | 1 | 73 | 275 | 88 |
| 12 | 0-12 | 826 | 28 | 1 | 291 | 392 | 320 |
| 17 | 0-12 | 382 | 3 | 0 | 26 | 152 | 29 |
| 18 | 0-12 | 3,540 | 54 | 16 | 2,660 | 920 | 2,730 |
| 23 | 0-12 | 774 | 7 | 1 | 113 | 303 | 121 |
| 24 | 0-12 | 1,500 | 41 | 13 | 1,400 | 800 | 1,454 |
| 29 | 0-12 | 755 | 31 | 2 | 355 | 319 | 388 |
| 30 | 0-12 | 903 | 16 | 3 | 289 | 180 | 308 |
| 35 | 0-12 | 3,200 | 21 | 6 | 563 | 456 | 590 |
| 36 | 0-12 | 1,260 | 1 | 1 | 212 | 208 | 214 |
| | | | | | | | |
| **Mean** | ***0-12*** | ***1,500*** | ***25*** | ***5*** | ***679*** | ***424*** | ***708*** |
| **Std. Dev** | ***0-12*** | ***1,135*** | ***17*** | ***6*** | ***853*** | ***254*** | ***873*** |
| | | | | | | | |
| 5 | 12-24 | 1,740 | 13 | 2 | 271 | 538 | 286 |
| 6 | 12-24 | 3,410 | 94 | 16 | 3,080 | 683 | 3,190 |
| 11 | 12-24 | 813 | 3 | 1 | 103 | 371 | 107 |
| 12 | 12-24 | 382 | 6 | 1 | 858 | 349 | 865 |
| 17 | 12-24 | 861 | 1 | 1 | 105 | 252 | 107 |
| 18 | 12-24 | 595 | 3 | 5 | 412 | 224 | 420 |
| 23 | 12-24 | 1,660 | 1 | 2 | 184 | 565 | 187 |
| 24 | 12-24 | 1,110 | 30 | 6 | 637 | 273 | 673 |
| 29 | 12-24 | 1,340 | 25 | 5 | 612 | 595 | 642 |
| 30 | 12-24 | 315 | 4 | 2 | 1,370 | 394 | 1,376 |
| 35 | 12-24 | 1,870 | 41 | 15 | 1,590 | 623 | 1,646 |
| 36 | 12-24 | 1,200 | 15 | 3 | 293 | 192 | 1,703 |
| | | | | | | | |
| **Mean** | ***12-24*** | ***1,274*** | ***20*** | ***5*** | ***793*** | ***422*** | ***934*** |
| **Std. Dev.** | ***12-24*** | ***846*** | ***27*** | ***5*** | ***866*** | ***172*** | ***912*** |

**Table 5-36**
**Sequential Fractionation Analysis of Soil from Site C After Adding Soil Amendments in 1999**

| | | Sequential Fraction - Pb, mg/kg | | | | | |
|---|---|---|---|---|---|---|---|
| **Grid No.** | **Depth, inches** | **Total** | **(A) Water-soluble** | **(B) Exchange-able** | **(C) Carbonate** | **Fe+Mn Oxide** | **Total Plant-Available (A+B+C)** |
| | | | | | | | |
| 5 | 0-12 | 553 | 13 | 4 | 502 | 549 | 519 |
| 6 | 0-12 | 3,120 | 200 | 111 | 2,380 | 781 | 2,691 |
| 11 | 0-12 | 953 | 182 | 168 | 39 | 139 | 389 |
| 12 | 0-12 | 2,100 | 314 | 340 | 410 | 272 | 1,064 |
| 17 | 0-12 | 551 | 192 | 176 | 23 | 157 | 391 |
| 18 | 0-12 | 1,310 | 190 | 174 | 841 | 366 | 1,205 |
| 23 | 0-12 | 469 | 138 | 81 | 112 | 229 | 331 |
| 24 | 0-12 | 4,030 | 747 | 618 | 1,580 | 507 | 2,945 |
| 29 | 0-12 | 991 | 15 | 3 | 339 | 345 | 357 |
| 30 | 0-12 | 542 | 469 | 344 | 130 | 175 | 943 |
| 35 | 0-12 | 1,070 | 217 | 226 | 339 | 434 | 782 |
| 36 | 0-12 | 797 | 492 | 400 | 627 | 305 | 1,519 |
| | | | | | | | |
| **Mean** | ***0-12*** | ***1,374*** | ***264*** | ***220*** | ***610*** | ***355*** | ***1,095*** |
| **Std. Dev.** | ***0-12*** | ***1,138*** | ***212*** | ***179*** | ***705*** | ***189*** | ***891*** |
| | | | | | | | |
| 5 | 12-24 | 1,510 | 2 | 2 | 343 | 416 | 347 |
| 6 | 12-24 | 12,900 | 80 | 33 | 10,400 | 1,010 | 10,513 |
| 11 | 12-24 | 2,320 | 1 | 1 | 162 | 423 | 164 |
| 12 | 12-24 | 2,840 | 162 | 88 | 2,430 | 439 | 2,680 |
| 17 | 12-24 | 732 | 3 | 1 | 217 | 400 | 221 |
| 18 | 12-24 | 2,030 | 121 | 38 | 1,340 | 431 | 1,499 |
| 23 | 12-24 | 1,240 | 1 | 2 | 288 | 461 | 291 |
| 24 | 12-24 | 3,900 | 340 | 247 | 3,230 | 643 | 3,817 |
| 29 | 12-24 | 4,200 | 31 | 5 | 842 | 678 | 878 |
| 30 | 12-24 | 256 | 34 | 2 | 124 | 88 | 160 |
| 35 | 12-24 | 1,660 | 83 | 15 | 1,250 | 723 | 1,348 |
| 36 | 12-24 | 5,160 | 258 | 129 | 3,570 | 619 | 3,957 |
| | | | | | | | |
| **Mean** | ***12-24*** | ***3,229*** | ***93*** | ***47*** | ***2,016*** | ***528*** | ***2,156*** |
| **Std. Dev.** | ***12-24*** | ***3,378*** | ***111*** | ***75*** | ***2,905*** | ***228*** | ***2,974*** |

**Table 5-37**
**Sequential Fractionation Analysis of Soil from Site 129-3**
**Prior to Adding Soil Amendments in 1999**

| | | Sequential Fraction- Pb, mg/kg | | | | | |
|---|---|---|---|---|---|---|---|
| **Grid No.** | **Depth, inches** | **Total** | **(A) Water-soluble** | **(B) Exchange-able** | **(C) Carbonate** | **Fe+Mn Oxide** | **Total Plant-Available (A+B+C)** |
| | | | | | | | |
| 1 | 0-12 | 27 | 6 | 1 | 18 | 39 | 25 |
| 2 | 0-12 | 60 | 1 | 1 | 30 | 39 | 32 |
| | | | | | | | |
| **Mean** | ***0-12*** | ***43.5*** | ***3.5*** | ***1*** | ***24*** | ***39*** | ***29*** |
| **Std. Dev.** | ***0-12*** | ***23*** | ***4*** | ***0*** | ***8*** | ***0*** | ***5*** |
| | | | | | | | |
| 1 | 12-24 | 117 | 3 | 1 | 57 | 72 | 61 |
| 2 | 12-24 | 216 | 4 | 1 | 26 | 54 | 31 |
| | | | | | | | |
| **Mean** | ***12-24*** | ***167*** | ***4*** | ***1*** | ***42*** | ***63*** | ***46*** |
| **Std. Dev.** | ***12-24*** | ***70*** | ***1*** | ***0*** | ***22*** | ***13*** | ***21*** |

**Table 5-38**
**Sequential Fractionation Analysis of Soil from Site 129-3 After**
**Adding Soil Amendments in 1999**

| | | Sequential Fraction- Pb, mg/kg | | | | | |
|---|---|---|---|---|---|---|---|
| **Grid No.** | **Depth, inches** | **Total** | **(A) Water-soluble** | **(B) Exchange-able** | **(C) Carbonate** | **Fe+Mn Oxide** | **Total Plant-Available (A+B+C)** |
| | | | | | | | |
| 1 | 0-12 | 63 | 20 | 16 | 12 | 34 | 48 |
| 2 | 0-12 | 556 | 1 | 1 | 15 | 54 | 17 |
| | | | | | | | |
| **Mean** | ***0-12*** | ***310*** | ***11*** | ***9*** | ***14*** | ***44*** | ***33*** |
| **Std. Dev.** | ***0-12*** | ***349*** | ***13*** | ***11*** | ***2*** | ***14*** | ***22*** |
| | | | | | | | |
| 1 | 12-24 | 105 | 1 | 1 | 26 | 73 | 28 |
| 2 | 12-24 | 69 | 1 | 1 | 38 | 32 | 40 |
| | | | | | | | |
| **Mean** | ***12-24*** | ***87*** | ***1*** | ***1*** | ***32*** | ***53*** | ***34*** |
| **Std. Dev.** | ***12-24*** | ***25*** | ***0*** | ***0*** | ***8*** | ***29*** | ***8*** |

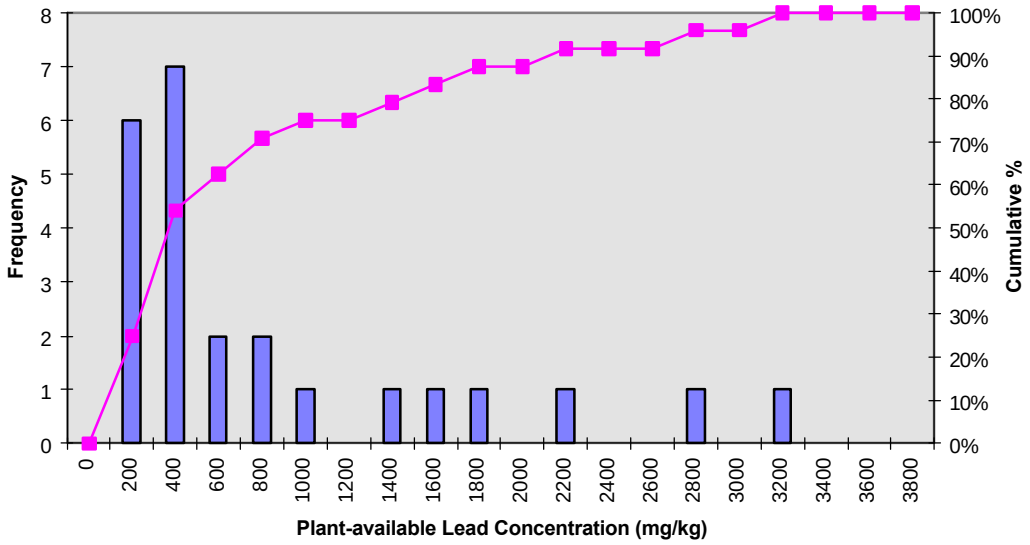



**Figure 5-3**
**Plant-Available Lead at**
**Site C Pre-Amendment**

Frequency distribution of grids for plant-available lead concentration ranges, and cumulative percentage of grids at each plant-available lead concentration range.

### 5.2.10 2000 Field Sampling Results

#### 5.2.10.1 Mechanisms Controlling Lead Solubility and EDTA Degradation at Site C and Site 129-3

A discussion of the primary mechanisms involved in the overall outcome of the demonstration is essential to understanding the final results of the 2000 field activities.

##### 5.2.10.1.1 Lead Solubility

In a phytoextraction scheme, lead may undergo several reactions (or pathways) in a soil following treatment with acetic acid and EDTA. These reactions involve both the dissolution of lead from the non-water-soluble solid phases into soluble forms which are available to plants and may be subject to leaching, as well as the subsequent re-precipitation of lead into *insoluble* forms which are unavailable to plants and which are less conducive to movement.

A summary of the three general processes lead will undergo in soil during a phytoextraction scheme is presented in Figure 5-4. These reactions are:

1. Dissolution of lead solid phases and complexation by EDTA, followed by uptake into plants.
2. Inactivation of EDTA through degradation or sorption on soil components with subsequent release and re-precipitation of lead in soil.
3. Displacement of lead from the EDTA complex by competing cations and subsequent reprecipitation of lead in soil.

An understanding of the first reaction of lead in the soil must be preceded by a discussion of the basic components of the system. The water-soluble and exchangeable forms are considered to be the most readily complexed by EDTA, while the carbonate form is less so. The availability to plants follows the same order. These forms of lead in soil may be grouped as follows:

1. Water-soluble
2. Exchangeable
3. Carbonate-bound
4. Iron and manganese oxide-bound
5. Organic-bound
6. Crystalline matrix-bound

The first three forms are considered to be the most potentially available to plants in the phytoextraction process. The water-soluble and exchangeable forms are considered to be most available to plants, while the carbonate form is less so. The ease of complexation by EDTA follows the same order. Harsh dissolution processes would be required to make lead in the oxide, organic, and crystalline matrix forms available to plants. In the TCAAP soils, the amount of lead that is potentially plant available (sum of the first three forms) is 55% of the total lead concentration in soil. This was determined by the sequential extraction procedure in Section 5.2.9.

Therefore, in the first reaction (i.e., dissolution and complexation) (Fig. 5-4) reduction of soil pH to 5.5 by acetic acid helps release lead from the most soluble solid phase forms into the soil

solution as the free lead ion ($Pb^{2+}$). The lead ion is then complexed by EDTA and maintained in a water-soluble form that is available to plants. The soil returns to its indigenous pH after a short time, but for a time, lead remains in a water-soluble form. Lead in this form may react with the soil to again become unavailable, it may be taken up into the plant, or it may remain in solution.

In the second reaction, several individual processes are at work simultaneously. Other cations in the soil, which are typically found at far greater concentrations in the soil than lead, compete with lead for complexation by EDTA. Also, as EDTA undergoes microbial degradation, (see Section 5.2.10.1.2, below, for a more detailed discussion of EDTA degradation in soil) lead may be released and re-precipitated in the soil as progressive degradation of EDTA produces compounds that are more selective for cations other than lead. If there is a sufficient amount of iron oxide present in the soil, EDTA may be sorbed onto these compounds, and the lead in the EDTA complex may be subject to reaction with soil. This usually involves the formation of a weak bond between EDTA and the oxide, so the oxide must be present at fairly high concentration for this reaction to be significant.

In the third reaction, other cations such as Ca, Mg, Fe, etc., compete with lead in soil micro-sites for complexation by EDTA. Lead is displaced from the complex by simple mass action (i.e., the abundance of other cations relative to lead "swamps" the system). The cation that will replace lead (1) will be determined by the system pH; (2) will follow metal-chelate selectivity coefficients (i.e., displacement series); and (3) is dependent on the cation concentration in the soil. The Ca-EDTA complex will ultimately predominate in alkaline soil, and Fe-EDTA will be the predominate form in acid to neutral soil. Once lead is displaced, the processes of ion exchange, adsorption, and precipitation on soil minerals and organic matter will eventually convert lead into insoluble forms, such as carbonates, phosphates, sulfates, and organic complexes. At higher soil pH, the solubility of lead in these complexes is low. The pH-dependent sorption of lead on hydrous oxides of aluminum, iron, and manganese will also occur, which will limit the activity of the lead ion in solution. Thus plant availability and the potential for leaching of lead is also low. This reversion process will take several decades before lead is as insoluble as it was before the phytoextraction process.[Ref. 9]

#### 5.2.10.1.2 EDTA Fate and Degradation in Soil

The aminopolycarboxylic acid chelate EDTA is produced in large quantities for a variety of uses ranging from cleaning solutions and detergents to food preservatives to decontamination of nuclear power plant equipment. EDTA sales in Europe in 1997 were 32,550 tons.[Ref. 36] No instances of EDTA toxicity to mammals have been reported at the concentrations found in aquatic environments, although annual loading rates in surface waters have in the past been quite high. For example, annual amounts of EDTA released into the Ruhr River, Germany, in 1984 were about 60 tons, and over 1,080 tons were released annually into the Rhine River, Germany, from 1985 to 1987.[Ref. 33] EDTA is persistent in the environment, and for many years was thought to be resistant to degradation.[Ref. 37,38] However, biodegradation of EDTA has been investigated from the perspective of many different researchers and EDTA is now recognized to

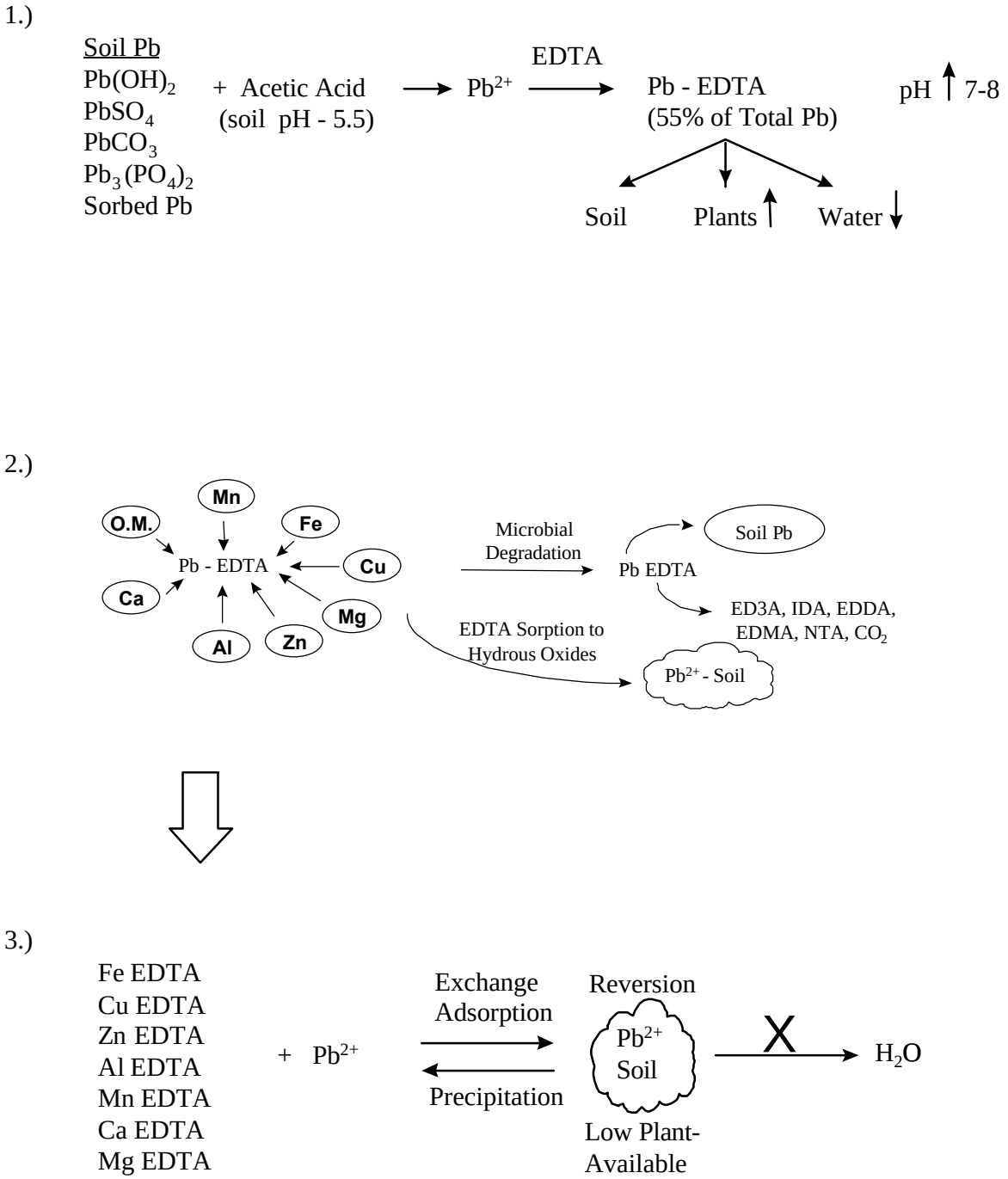



**Figure 5-4**
**Lead Pathways in Soil**

biodegrade through several various mechanisms.[Ref. 39] EDTA may react in soil systems to persist or to disappear entirely depending on the unique set of conditions that occur in different soils. Overall, in a typical soil, the fate of EDTA is governed by five mechanisms:

1. Reaction and complexation with soil cations
2. Microbial degradation
3. Adsorption onto iron hydrous oxide surfaces and soil organic matter
4. Binding to clay fractions
5. Leaching

The affinity of EDTA for metal cations varies with system pH and the displacement series for EDTA and metals. The displacement series is based on formation constants of EDTA-metal complexes (i.e., bonding energies) derived either experimentally or empirically. So, the displacement series is a measure of the strength of bonding of a given cation-EDTA complex. The series may be a function of the concentration of a given cation that can potentially bond with EDTA. Thus, a primary cation with a strong binding affinity for EDTA may be replaced by a secondary cation which has less affinity for EDTA, but which is present in far greater concentration. For example the primary cation, lead, may be replaced by secondary cations such as calcium, iron, or magnesium in an EDTA complex.

Direct degradation of EDTA is obviously an important mechanism for controlling the activity of EDTA in a soil. The rate and extent of EDTA microbial degradation is highly variable. [Ref. 40] Factors controlling and influencing degradation include:

- Aeration
- pH
- Temperature
- Appropriate microbial population in soil
- Organic matter content and fertility level of soil
- Resistance of EDTA to degradation
- EDTA concentration
- Metals that EDTA is complexed with

Overall, annual degradation rates of EDTA may range from <5% after 10 weeks in acidic soil to 50% - 75% after one year in alkaline soil. [Ref. 41] EDTA will normally be degraded by the indigenous soil microbial population. Ironically, EDTA may be degraded more rapidly in cold (i.e., freezing) temperatures than during warmer periods. [Ref. 41] An alkaline pH is more conducive to degradation, since the primary cation complexes of EDTA at higher pH are those with the nutrient cations, which tend to sustain the microbial population. The rate will vary depending on the cation with which the EDTA is complexed. Heavy metal complexes of EDTA, such as Cu-, Ni-, or Cd- which may be toxic to soil microbes, will degrade at a slower rate than EDTA complexes of low toxicity nutrient cations, such as Ca-, Fe-, or Mg-EDTA. [Ref. 42] Ferric iron complexes of EDTA potentially will degrade at higher rates than EDTA complexes with other nutrient cations.[Ref. 36] As EDTA degrades, heavy metals such as lead may be released into solution, where adsorption reactions may render the metal insoluble. Incorporation of an

inorganic complexing agent, such as phosphate, to scavenge the released metal by precipitation may help avoid metal toxicity to the microbial population, thus hastening or at least prolonging degradation of EDTA. [Ref. 42]

A higher iron oxide and organic matter content will also increase EDTA retention by soil, although the bond between iron hydrous oxides and EDTA is a relatively weak one. The binding capacity is dependent instead on the oxide content of the soil, and binding and disappearance of EDTA in soils characterized by a high iron oxide content can be significant. This phenomena was recognized as early as 1955 by Wallace *et al.* [Ref. 43] The following year, Lunt *et al* [Ref. 44] reported rapid losses of 26% and 20% EDTA from soil-applied iron-EDTA in calcareous and noncalcareous soils. EDTA disappeared at a 1:1 ratio with Fe loss in the noncalcareous soils, which suggested that the complex was adsorbed intact. Such a substitution and adsorption mechanism may thus be important in controlling the fate of potentially environmentally harmful metal complexes of EDTA, such as lead.

Although EDTA is an anion, it will rarely exist in soil solely as EDTA, and these amounts will be neglible. It will almost always be complexed with a cation. The charge on the cation-EDTA complex is cation- and pH-dependent, with the Zero Point of Charge (ZPC) for cation-EDTA complexes occurring between pH 7.0 and 9.0 depending on the associated cation. Thus, EDTA may be adsorbed onto negatively charged clay micelles as a positively charged moiety at pH values higher than the ZPC. This may reduce movement of EDTA through the soil.

Normally, heavier-textured clay soils will retain EDTA more strongly than will sandy soils. Leaching is thus quite likely in sandy soils. However, the heavier textured soil constitutes only a temporary physical barrier to vertical movement of EDTA, and eventual breakthrough of EDTA can occur.

Obviously, reactions involving metal complexation and metal-chelate interactions in soil are not straightforward, and many variables in the heterogeneous system of a soil will influence the ultimate fate of EDTA and lead in soil. These same reactions can equally be applied to interactions within groundwater systems and their aquifers, and to surface waters as well.

#### 5.2.10.2 Groundwater Sampling - 2000

Groundwater and surface water sampling was conducted only at Site C. Figure 5-5 is an overview drawing showing the pertinent features and the groundwater and surface water sampling locations at Site C. The overall summary of results for the groundwater and surface samplings at Site C is shown in Table 5-39. Individual results for each of the samplings are shown in subsequent tables. All groundwater samples were muddy in appearance upon sampling. The pH of all water samples was about 7.5, which favors reactions of the EDTA with basic cations such as Ca and Mg. An important criteria to be remembered in considering the results of the groundwater samples is that EDTA complexes with lead on a 1:1 ratio. An EDTA to lead ratio greater than 1:1 indicates that lead has been displaced through some mechanism from the EDTA complex and is thus no longer in appreciably water-soluble form.

#### 5.2.10.2.1 April 11, 2000 - First Groundwater Sampling

The analytical results of the April 11, 2000 samples for lead, EDTA, and pH, and the calculated molar ratios of EDTA to lead, are shown in Table 5-40.

The sampling locations for this set of groundwater samples is shown in Figure 5-5 and Figure 5-6. Lead and EDTA concentrations in groundwater samples were consistent with movement through the surface soil in the plot to the groundwater within the plot (Samples GW-5 and GW-6). This was likely due to movement of the soluble lead-EDTA complex caused in part by the physical condition of the site and the shallow and fluctuating groundwater flow through the plot. Realistically, all movement of the EDTA-lead complex did not occur down through the soil, but rather may have occurred in part due to preferential flow through channels caused by debris in the soil or through sand and around clay lenses in the soil. The influence of soil

physical properties is discussed in more detail in Section 5.2.10.3, Deep Core Soil Sampling, below. Also, as the level of groundwater fluctuated, the soil in the upper layers may have been in essence "washed" and EDTA and lead removed to lower depths.

One area (GW6) showed a high concentration of lead (988 mg/L) and of EDTA (4,910 mg/L) in groundwater within the plot. This area was in the poorly drained northwestern quadrant of the plot. This area is also the lowest part of the plot. The high concentrations may have resulted from collection and stagnation of EDTA and solubilized lead from other parts of the plot.

Lead and EDTA concentrations from the other sampling point within the plot (GW5) were much lower, averaging 228 mg/L and 2,265 mg/L for lead and EDTA, respectively. This point was more upgradient of the slope within the plot.

There were four sampling locations outside the plot area, one upgradient (GW1) and three down-gradient (GW2, GW3, and GW4). Neither lead nor EDTA was found in the upgradient sample (GW1) located outside the southeastern corner of the plot according to the TVA analysis. However, a concentration of 71 mg/L was determined by the MDH laboratory. The disparity in the data between MDH and TVA warrants the need for additional measurements, such as samples and monitoring.

Lead and EDTA were present in sample GW2 at concentrations of 274 and 1,210 mg/L respectively. This sample point is located 30 feet to the north of the northeastern corner of the plot. Lead and EDTA were present in the sample from GW4 at concentrations of 573 and 2,310 mg/L, respectively. This sample point is located 30 feet to the northwest of the northwestern corner of the plot. Neither lead nor EDTA were found in down gradient sample GW3. This sample point is located 27 feet due west outside of the plot, 46 feet to the south of GW4.

Lead and EDTA moved outside of the plot boundaries in the groundwater at a slow rate. The rate of groundwater movement at Site C according to the original RI/FS is 0.017 - 55 ft per year. However, there was no indication of lead and only a trace amount (0.5 mg/L) of EDTA

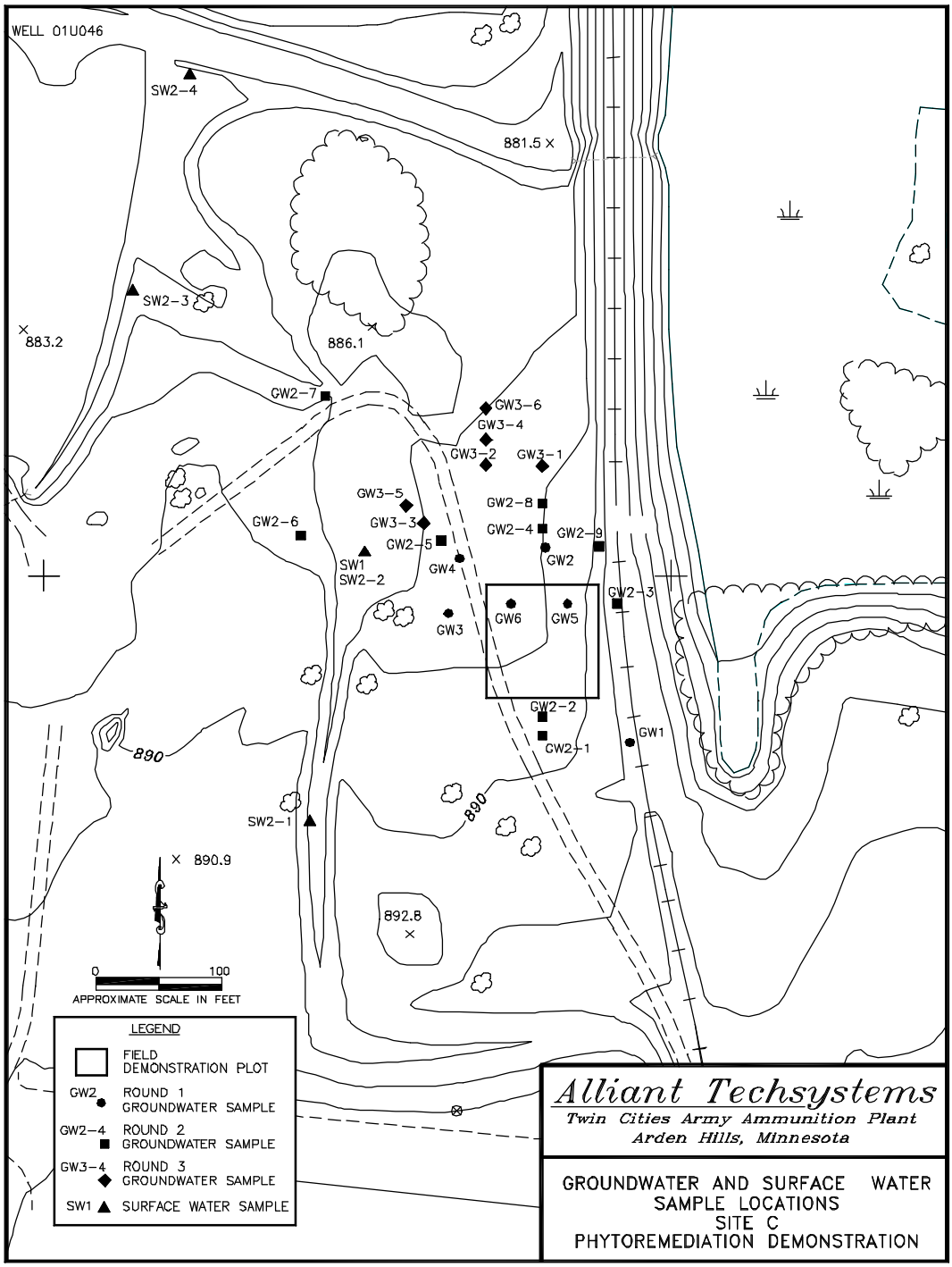



**Figure 5-5**
**Overview of Site C Showing**
**Groundwater and Surface Water Sampling Locations**

## Table 5-39
## Overall Results and Sampling Schedule for Groundwater and Surface Water Samples at Site C

| Sampling Phase | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) | Laboratory[1] | Pb, mg/L | EDTA (as $Na_2EDTA$) mg/L | EDTA (as EDTA) mg/L |
|---|---|---|---|---|---|---|---|---|
| GW -1 | FB1 | Field Blank | 11-Apr-00 | | TVA | <0.02 | <0.03 | <0.03 |
| 1 | RB1 | Rinse Blank | 11-Apr-00 | | TVA | <0.02 | 0.3 | 0.3 |
| 1 | RB2 | Rinse Blank | 11-Apr-00 | | TVA | 0.02 | 0.3 | 0.3 |
| 1 | GW1 | Groundwater Sample | 11-Apr-00 | 7 - 7.5 | TVA (MDH) | <0.02 (71) | 0.2 | 0.2 |
| 1 | GW2 | Groundwater Sample | 11-Apr-00 | 5 - 5.5 | TVA (MDH) | 274 (280) | 1,390 | 1,210 |
| 1 | GW3 | Groundwater Sample | 11-Apr-00 | 5 | TVA (MDH) | <0.02 (1.1) | 0.3 | 0.3 |
| 1 | GW4 | Groundwater Sample | 11-Apr-00 | 4 | TVA (MDH) | 573 (580) | 2,660 | 2,310 |
| 1 | GW5 | Groundwater Sample | 11-Apr-00 | 6 | TVA (MDH) | 228 (270) | 2,590 | 2,250 |
| 1 | GW5 dup | Groundwater Sample | 11-Apr-00 | 6 | TVA (MDH) | 227 (270) | 2,620 | 2,280 |
| 1 | GW6 | Groundwater Sample | 11-Apr-00 | 5.5 | TVA (MDH) | 988 (1100) | 5,650 | 4,910 |
| SW-1 | SW1 | Surface Water Sample | 11-Apr-00 | | TVA (MDH) | <0.02 (4.2) | 0.5 | 0.5 |
| | | | | | | | | |
| SW-2 | PRB2-1-U | Pre-Rinse Blank | 4-May-00 | | | | <0.03 | <0.03 |
| 2 | PRB2-1-F | Pre-Rinse Blank Filtered | 4-May-00 | | CompuChem | 0.0011 | | |
| 2 | FB2-1-U | Field Blank Unfiltered | 4-May-00 | | | | <0.03 | <0.03 |
| 2 | FB2-1-F | Field Blank Filtered | 4-May-00 | | CompuChem | 0.0011 | | |
| 2 | RB2-1-U | Rinse Blank Unfiltered | 4-May-00 | | | | <0.03 | <0.03 |
| 2 | RB2-1-F | Rinse Blank Filtered | 4-May-00 | | CompuChem | 0.0011 | | |
| 2 | SW2-1-U | Surface Water Sample - Unfiltered | 4-May-00 | | | | 0.1 | 0.1 |
| 2 | SW2-1-F | Surface Water Sample - Filtered | 4-May-00 | | CompuChem | 0.0012 | | |
| 2 | SW2-2-U | Surface Water Sample - Unfiltered | 4-May-00 | | | | 0.2 | 0.2 |

**Table 5-39 (Continued)**
**Overall Results and Sampling Schedule for Groundwater and Surface Water Samples at Site C**

| Sampling Phase | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) | Laboratory[1] | Pb, mg/L | EDTA (as $Na_2EDTA$) mg/L | EDTA (as EDTA) mg/L |
|---|---|---|---|---|---|---|---|---|
| 2 | SW2-2-F | Surface Water Sample - Filtered | 4-May-00 | | CompuChem | 0.0019 | | |
| 2 | SW2-3-U | Surface Water Sample - Unfiltered | 4-May-00 | | | | <0.03 | <0.03 |
| 2 | SW2-3-F | Surface Water Sample - Filtered | 4-May-00 | | CompuChem | 0.0011 | | |
| 2 | SW2-4-U | Surface Water Sample - Unfiltered | 4-May-00 | | | | 1.2 | 1.1 |
| 2 | SW2-4-F | Surface Water Sample - Filtered | 4-May-00 | | CompuChem | 0.0118 | | |
| 2 | SW2-4-UD | Surface Water Sample - Unfiltered Duplicate | 4-May-00 | | | | 1.2 | 1.0 |
| SW-2 | SW2-4-FD | Surface Water Sample - Filtered Duplicate | 4-May-00 | | CompuChem | 0.0119 | | |
| | | | | | | | | |
| GW-2 | PRB 2-1U | Pre-Rinse Blank | 17-May-00 | | | | <0.03 | <0.03 |
| 2 | PRB 2-1F | Pre-Rinse Blank Filtered | 17-May-00 | | CompuChem | 0.0017 | | |
| 2 | FB2-1U | Field Blank Unfiltered | 17-May-00 | | | | <0.03 | <0.03 |
| 2 | FB2-1F | Field Blank Filtered | 17-May-00 | | CompuChem | 0.0018 | | |
| 2 | RB2-1U | Rinse Blank Unfiltered | 17-May-00 | | | | <0.03 | <0.03 |
| 2 | RB2-1F | Rinse Blank Filtered | 17-May-00 | | CompuChem | 0.0141 | | |
| 2 | GW2-1U | Groundwater Sample - Unfiltered | 17-May-00 | 9.5 - 10 | | | 6.7 | 5.8 |
| 2 | GW2-1F | Groundwater Sample - Filtered | 17-May-00 | 9.5 - 10 | CompuChem | 0.228 | | |

**Table 5-39 (Continued)**
**Overall Results and Sampling Schedule for Groundwater and Surface Water Samples at Site C**

| Sampling Phase | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) | Laboratory[1] | Pb, mg/L | EDTA (as $Na_2EDTA$) mg/L | EDTA (as EDTA) mg/L |
|---|---|---|---|---|---|---|---|---|
| GW-2 | GW2-2 | DID NOT SAMPLE | 17-May-00 | DID NOT SAMPLE | | | | |
| 2 | GW2-3 | DID NOT SAMPLE | 17-May-00 | DID NOT SAMPLE | | | | |
| 2 | GW2-4U | Groundwater Sample - Unfiltered | 17-May-00 | 9 - 9.5 | | | 788 | 685 |
| 2 | GW2-4F | Groundwater Sample - Filtered | 17-May-00 | 9 - 9.5 | CompuChem | 208 | | |
| 2 | GW2-5U | Groundwater Sample - Unfiltered | 17-May-00 | 5 | | | 701 | 609 |
| 2 | GW2-5F | Groundwater Sample - Filtered | 17-May-00 | 5 | CompuChem | 20 | | |
| 2 | GW2-6U | Groundwater Sample - Unfiltered | 17-May-00 | 8 | | | <0.03 | <0.03 |
| 2 | GW2-6F | Groundwater Sample - Filtered | 17-May-00 | 8 | CompuChem | 0.17 | | |
| 2 | GW2-7 | DRY | 17-May-00 | DRY | | | | |
| 2 | GW2-8U | Groundwater Sample - Unfiltered | 17-May-00 | 7.5 | | | 192 | 167 |
| 2 | GW2-8F | Groundwater Sample - Filtered | 17-May-00 | 7.5 | CompuChem | 54.4 | | |
| 2 | GW2-9 | DRY | 17-May-00 | DRY | | | | |
| | | | | | | | | |
| GW-3 | FB3-1U | Field Blank Unfiltered | 30-May-00 | | | | <0.03 | <0.03 |
| 3 | FB3-1F | Field Blank Filtered | 30-May-00 | | CompuChem | 0.0011 | | |
| 3 | PRB3-1U | Pre-Rinse Blank | 30-May-00 | | | | <0.03 | <0.03 |

**Table 5-39 (Continued)**
**Overall Results and Sampling Schedule for Groundwater and Surface Water Samples at Site C**

| Sampling Phase | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) | Laboratory[1] | Pb, mg/L | EDTA (as $Na_2EDTA$) mg/L | EDTA (as EDTA) mg/L |
|---|---|---|---|---|---|---|---|---|
| 3 | PRB3-1F | Pre-Rinse Blank Filtered | 30-May-00 | | CompuChem | 0.0011 | | |
| 3 | GW3-1U | Groundwater Sample - Unfiltered | 30-May-00 | 8 | | | 0.26 | 0.23 |
| 3 | GW3-1F | Groundwater Sample - Filtered | 30-May-00 | 8 | CompuChem | 0.0015 | | |
| 3 | GW3-2U | Groundwater Sample - Unfiltered | 30-May-00 | 6 | | | 850 | 739 |
| 3 | GW3-2F | Groundwater Sample - Filtered | 30-May-00 | 6 | CompuChem | 1.56 | | |
| 3 | GW3-3U | Groundwater Sample - Unfiltered | 30-May-00 | 8 | | | 570 | 495 |
| 3 | GW3-3F | Groundwater Sample - Filtered | 30-May-00 | 8 | CompuChem | 10.8 | | |
| 3 | GW3-4U | Groundwater Sample - Unfiltered | 30-May-00 | 8 | | | 0.38 | 0.33 |
| 3 | GW3-4F | Groundwater Sample - Filtered | 30-May-00 | 8 | CompuChem | 0.0256 | | |
| 3 | GW3-4U-DUP | Groundwater Sample - Unfiltered | 30-May-00 | 8 | | | 0.37 | 0.32 |
| 3 | GW3-4F-DUP | Groundwater Sample - Filtered | 30-May-00 | 8 | CompuChem | 0.0208 | | |
| 3 | GW3-5U | Groundwater Sample - Unfiltered | 30-May-00 | 3 | | | 410 | 356 |
| 3 | GW3-5F | Groundwater Sample - Filtered | 30-May-00 | 3 | CompuChem | 27.3 | | |

## Table 5-39 (Continued)
## Overall Results and Sampling Schedule for Groundwater and Surface Water Samples at Site C

| Sampling Phase | Sample ID | Description | Sampling Date | Approximate Groundwater Depth (ft) | Laboratory[1] | Pb, mg/L | EDTA (as $Na_2EDTA$) mg/L | EDTA (as EDTA) mg/L |
|---|---|---|---|---|---|---|---|---|
| GW-3 | GW3-6U | Groundwater Sample - Unfiltered | 30-May-00 | 6 | | | 7 | 6 |
| 3 | GW3-6F | Groundwater Sample - Filtered | 30-May-00 | 6 | CompuChem | 1.45 | | |

(1) Laboratory: TVA - Tennessee Valley Authority Specialty Laboratory.
MDH - Minnesota Department of Health.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-40**
**Analysis and Molar Ratios of EDTA:Pb in Groundwater and Surface Water Samples Taken at Site C on April 11, 2000 (First Phase Sampling)**

| Sample | pH | EDTA as $Na_2EDTA$ mg/L | EDTA as EDTA mg/L | EDTA[1] mmoles/L | Pb mg/L | Pb[2] mmoles/L | EDTA:Pb Molar Ratio[3] |
|---|---|---|---|---|---|---|---|
| GW 1 | 7.8 | 0.2 | 0.2 | 0.6 | <0.02 | -- | -- |
| GW 2 | 7.0 | 1,390 | 1,210 | 4,130 | 274 | 1,320 | 3.1 |
| GW 3 | 7.1 | 0.3 | 0.3 | 0.9 | <0.02 | -- | -- |
| GW 4 | 7.5 | 2,660 | 2,310 | 7,910 | 573 | 2,770 | 2.9 |
| GW 5 | 7.2 | 2,590 | 2,250 | 7,700 | 228 | 1,100 | 7.0 |
| GW 5 (Duplicate) | 7.2 | 2,620 | 2,280 | 7,790 | 227 | 1,100 | 7.1 |
| GW 6 | 7.2 | 5,650 | 4,910 | 16,800 | 988 | 4,770 | 3.5 |
| SW 1 | 7.7 | 0.6 | 0.5 | 2 | <0.02 | -- | -- |
| Field Blank | 8.3 | <0.03 | <0.03 | -- | <0.02 | -- | -- |
| Rinse Blank | 8.6 | 0.3 | 0.3 | 0.8 | <0.02 | -- | -- |
| Rinse Blank | 8.6 | 0.3 | 0.3 | 0.8 | 0.02 | 0.1 | -- |

(1) Obtained by dividing mg/L of EDTA by the molecular weight of EDTA (292.24 g/mol) and multiplying by 1000. NOTE: 1 mol EDTA = 1 mol $NA_2EDTA$.
(2) Obtained by dividing mg/L of Pb by the molecular weight of Pb (207.2 g/mol) and multiplying by 1000.
(3) Obtained by dividing µmoles/L of $Na_2EDTA$ by µmoles/L of Pb.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

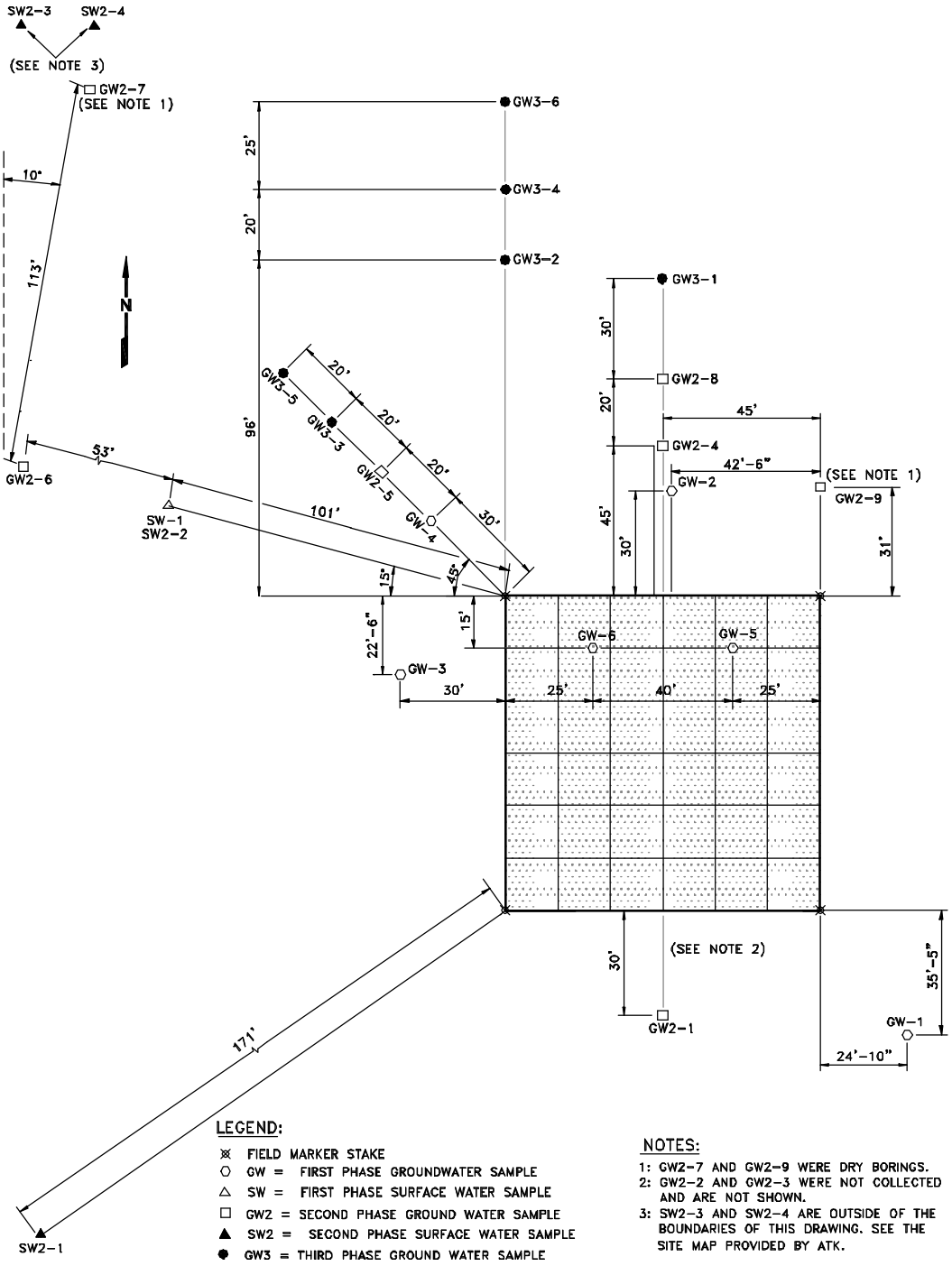



**Figure 5-6**
**Groundwater and Surface Water Sampling Locations**
**Site C - April 2000**

contamination in a surface water sample (SW1) taken from a drainage ditch located 125 feet to the northwest of the plot. The charge mechanism for water in the ditch is unknown, i.e., whether water present in the ditch results from water flow into the ditch across the soil surface or from groundwater flow up into the ditch. However, since the groundwater flow is suspected to be from southeast to northwest, some water present in the ditch could originate from groundwater flow.

EDTA concentrations in the equipment rinse blanks were 0.3 mg/L, or half the EDTA concentration found in the surface water sample. EDTA was not found in the field blank. Lead was not detectable in the rinse blanks or in the field blank.

The change in the 1:1 molar ratio of EDTA to lead indicated that the lead had been displaced by other ions. EDTA was applied twice in 1998 at a molar ratio of 1:1 EDTA to *total lead* in the soil. EDTA was applied once in 1999 at a molar ratio of 1:1 *plant-available* lead (55% of total soil lead). The molar ratios of EDTA to lead at sample points GW2, GW4, GW5, and GW6 were considerably greater than the 1:1 ratio originally applied in 1998 and in 1999. This indicated that lead had been displaced from the EDTA complex. The lead re-precipitated in the soil.

Accordingly, the samples were analyzed for a suite of other cations which could potentially complex with EDTA (Table 5-41). These analyses are given in mg/L and in µmoles/L so that molar quantities of each element may be directly compared with molar quantities of EDTA and lead. Of these cations, calcium (Ca) and magnesium (Mg) were present at the greatest concentration, with iron (Fe) and manganese (Mn) also being present at lower concentrations (Figure 5-7). Although EDTA has greater affinity for lead, the considerably higher concentration of Ca and Mg would, by simple mass action, result in these ions “swamping” the system and displacing the lead from the EDTA complex (refer to Section 5.2.10.1.1).

**5.2.10.2.2 May 17, 2000 - Second Groundwater Sampling**

When splits from the first groundwater samples collected on April 11, 2000, were analyzed by TVA and MDH, the results were consistently a little higher on the samples analyzed by MDH (Table 5-39). A review was made of sample collection practices for the two laboratories. One difference was noted. The Minnesota laboratory utilized 0.45-µ Millipore® filters while the TVA laboratory utilized 0.2-µ Millipore® filters to filter samples prior to digestion and analysis. The 0.45-µ filters utilized by MDH may have allowed silt particles and colloidal material to be collected with the water samples. Insoluble lead tends to be adsorbed on the surface of these particles which have an extremely high surface area. This insoluble lead would then be solubilized during sample digestion and would show up as higher lead concentrations in analysis.

By agreement with MPCA, for the second groundwater sampling, an outside laboratory (CompuChem) was officially responsible for lead analyses. TVA was responsible for EDTA analysis. In addition, the groundwater samples at this sampling were processed in two ways: (1) filtered in the field through a 0.45 micron filter and acidified, then shipped to CompuChem for lead analysis; (2) shipped to TVA unfiltered and unacidified for EDTA analyses. Upon receipt at TVA, the samples were filtered through a 0.45 micron Millipore® syringe filter and analyzed for EDTA. The nine groundwater sample locations for the second sampling are designated by GW2-1 through GW2-9 on Figure 5-6. However, only five water samples were

## Table 5-41
## Analysis for Potential Competing Cations in Groundwater and Surface Water Samples Taken at Site C on April 11, 2000 (First Phase Sampling)

| Sample | pH | EDTA as $Na_2EDTA$ | EDTA as EDTA | Pb | Ca | Fe | Mg | K | Mn | Na | Zn | Sr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **mg/L** | | | | | | | | | | | | |
| GW 1 | 7.8 | 0.2 | 0.2 | <0.02[1] | 78 | <0.002[1] | 15 | 1 | 2 | 4 | 0.03 | 0.3 |
| GW 2 | 7.0 | 1,390 | 1,210 | 274 | 328 | 136 | 62 | 4 | 23 | 11 | 24 | 6 |
| GW 3 | 7.1 | 0.3 | 0.3 | <0.02 | 162 | 1 | 43 | 3 | 3 | 12 | 0.04 | 2 |
| GW 4 | 7.5 | 2,660 | 2,310 | 573 | 321 | 257 | 145 | 7 | 4 | 18 | 10 | 17 |
| GW 5 | 7.2 | 2,590 | 2,250 | 228 | 603 | 321 | 118 | 91 | 39 | 21 | 43 | 3 |
| GW 5 (Duplicate) | 7.2 | 2,620 | 2,280 | 227 | 604 | 308 | 119 | 92 | 39 | 21 | 43 | 3 |
| GW 6 | 7.2 | 5,650 | 4,910 | 988 | 761 | 537 | 141 | 15 | 79 | 40 | 28 | 32 |
| SW 1 | 7.7 | 0.6 | 0.5 | <0.02 | 135 | 0.06 | 67 | 4 | 0.2 | 38 | 0.5 | 2 |
| FB 1 Field Blank | 8.3 | <0.03[1] | <0.03[1] | <0.02 | 23 | <0.002 | 5 | 3 | 0.006 | 6 | 0.04 | 0.05 |
| RB 1 Rinse Blank | 8.6 | 0.3 | 0.3 | <0.02 | 7 | <0.002 | 1 | 0.5 | 0.007 | 2 | 0.03 | 0.02 |
| RB 2 Rinse Blank | 8.6 | 0.3 | 0.3 | 0.02 | 6 | <0.002 | 1 | 0.8 | 0.009 | 2 | 0.05 | 0.02 |
| MDL[1] | --[2] | 0.03 | 0.03 | 0.02 | 0.01 | 0.002 | 0.002 | 0.2 | 0.005 | 0.02 | 0.004 | 0.003 |
| | | | | | | | | | | | | |
| **mmoles/L[3]** | | | | | | | | | | | | |
| GW 1 | -- | 0.7 | 0.6 | <MDL[1] | 1,940 | <MDL[1] | 617 | 36 | 36 | 177 | 0.5 | 4 |
| GW 2 | -- | 4,130 | 4,130 | 1,320 | 8,180 | 2,440 | 2,560 | 89 | 417 | 470 | 370 | 64 |
| GW 3 | -- | 0.9 | 0.8 | <MDL[1] | 4,040 | 23 | 1,770 | 73 | 53 | 526 | 0.7 | 21 |
| GW 4 | -- | 7,910 | 7,910 | 2,770 | 8,010 | 4,600 | 5,970 | 189 | 79 | 783 | 148 | 199 |
| GW 5 | -- | 7,700 | 7,700 | 1,100 | 15,000 | 5,750 | 4,860 | 2,320 | 703 | 905 | 650 | 39 |
| GW 5 (Duplicate) | -- | 7,790 | 7,790 | 1,100 | 15,100 | 5,520 | 4,900 | 2,350 | 712 | 918 | 658 | 39 |
| GW 6 | -- | 16,800 | 16,800 | 4,770 | 19,000 | 9,620 | 5,800 | 394 | 1,430 | 1,749 | 422 | 360 |
| SW 1 | -- | 2 | 2 | <MDL[1] | 3,370 | 1 | 2,770 | 97 | 3 | 1,650 | 8 | 21 |
| FB 1 Field Blank | -- | <MDL[1] | <MDL[1] | <MDL[1] | 569 | <MDL[1] | 192 | 67 | 0.1 | 272 | 0.6 | 0.6 |
| RB 1 Rinse Blank | -- | 0.8 | 0.7 | <MDL[1] | 163 | <MDL[1] | 44 | 14 | 0.1 | 92 | 0.5 | 0.2 |
| RB 2 Rinse Blank | -- | 0.8 | 0.7 | 0.1 | 153 | <MDL[1] | 39 | 21 | 0.2 | 94 | 0.8 | 0.2 |
| MDL | -- | 0.09 | 0.08 | 0.1 | 0.3 | 0.04 | 0.08 | 5 | 0.09 | 0.9 | 0.06 | 0.03 |

(1) Method Detection Limit.

(2) -- Not Applicable.

(3) Obtained µmoles/L by dividing mg/L by the respective molecular weight (g/mol) of each compound or element and multiplying by 1,000.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-41 (Continued)**
**Analysis for Potential Competing Cations in Groundwater and Surface Water Samples Taken at Site C on April 11, 2000 (First Phase Sampling)**

| Sample | Al | As | Ba | Be | Co | Cu | Ni | Sb | Ti | Tl | V |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **mg/L** | | | | | | | | | | | |
| GW 1 | <0.04[1] | 0.4 | 0.1 | <0.002[1] | 0.02 | <0.004[1] | <0.01[1] | <0.06[1] | 0.007 | <0.1[1] | 0.02 |
| GW 2 | <0.07 | 1 | 3 | <0.003 | 0.9 | 0.07 | 2 | 0.3 | 0.02 | 0.4 | 0.2 |
| GW 3 | <0.04 | 0.9 | 0.7 | <0.002 | 0.02 | <0.004 | <0.01 | 0.06 | 0.01 | <0.1 | 0.03 |
| GW 4 | <0.04 | 2 | 22 | <0.002 | 0.5 | 0.4 | 0.5 | 0.2 | 0.02 | 0.9 | 0.1 |
| GW 5 | <0.04 | 3 | 0.9 | 0.002 | 1 | 0.08 | 2 | 0.3 | 0.03 | 0.8 | 0.2 |
| GW 5 (Duplicate) | <0.04 | 3 | 0.8 | <0.002 | 1 | 0.9 | 2 | 0.3 | 0.03 | 0.8 | 0.2 |
| GW 6 | <0.04 | 5 | 4 | 0.003 | 2 | <0.004 | 2 | 0.4 | 0.03 | 1 | 0.6 |
| SW 1 | <0.04 | 0.6 | 0.2 | <0.002 | 0.02 | 0.03 | 0.02 | 0.07 | 0.02 | <0.1 | 0.03 |
| FB 1 Field Blank | <0.04 | 0.1 | 0.02 | <0.002 | 0.02 | 0.01 | <0.01 | <0.06 | 0.02 | <0.1 | 0.02 |
| RB 1 Rinse Blank | <0.04 | <0.04[1] | 0.06 | <0.002 | 0.007 | <0.004 | <0.01 | <0.06 | 0.02 | <0.1 | 0.009 |
| RB 2 Rinse Blank | <0.04 | <0.04 | 0.05 | <0.002 | 0.01 | 0.005 | <0.01 | <0.06 | <0.004[1] | <0.1 | 0.01 |
| MDL[1] | 0.04 | 0.04 | 0.012 | 0.002 | 0.01 | 0.004 | 0.01 | 0.06 | 0.004 | 0.1 | 0.004 |
| **mmoles/L[3]** | | | | | | | | | | | |
| GW 1 | --[2] | 5 | 0.9 | --[2] | 0.4 | --[2] | --[2] | --[2] | 0.2 | --[2] | 0.4 |
| GW 2 | -- | 16 | 22 | -- | 14 | 1 | 30 | 2 | 0.4 | 2 | 3 |
| GW 3 | -- | 12 | 5 | -- | 0.4 | -- | -- | 0.5 | 0.2 | -- | 0.6 |
| GW 4 | -- | 33 | 160 | -- | 8 | 6 | 8 | 1 | 0.4 | 4 | 2 |
| GW 5 | -- | 44 | 6 | 0.2 | 21 | 1 | 30 | 2 | 0.6 | 4 | 4 |
| GW 5 (Duplicate) | -- | 46 | 6 | -- | 22 | 15 | 30 | 2 | 0.6 | 4 | 4 |
| GW 6 | -- | 61 | 28 | 0.3 | 26 | -- | 35 | 3 | 0.6 | 7 | 12 |
| SW 1 | -- | 9 | 1 | -- | 0.3 | 0.5 | 0.3 | 0.6 | 0.4 | -- | 0.6 |
| FB 1 Field Blank | -- | 1 | 0.1 | -- | 0.3 | 0.2 | -- | -- | 0.4 | -- | 0.4 |
| RB 1 Rinse Blank | -- | -- | 0.4 | -- | 0.1 | -- | -- | -- | 0.4 | -- | 0.2 |
| RB 2 Rinse Blank | -- | -- | 0.4 | -- | 0.2 | 0.08 | -- | -- | -- | -- | 0.2 |
| MDL | 1.5 | 0.5 | 0.09 | 0.2 | 0.17 | 0.06 | 0.2 | 0.5 | 0.08 | 0.5 | 0.08 |

(1) Method Detection Limit.

(2) -- Not Applicable.

(3) Obtained µmoles/L by dividing mg/L by the respective molecular weight (g/mol) of each compound or element and multiplying by 1,000.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

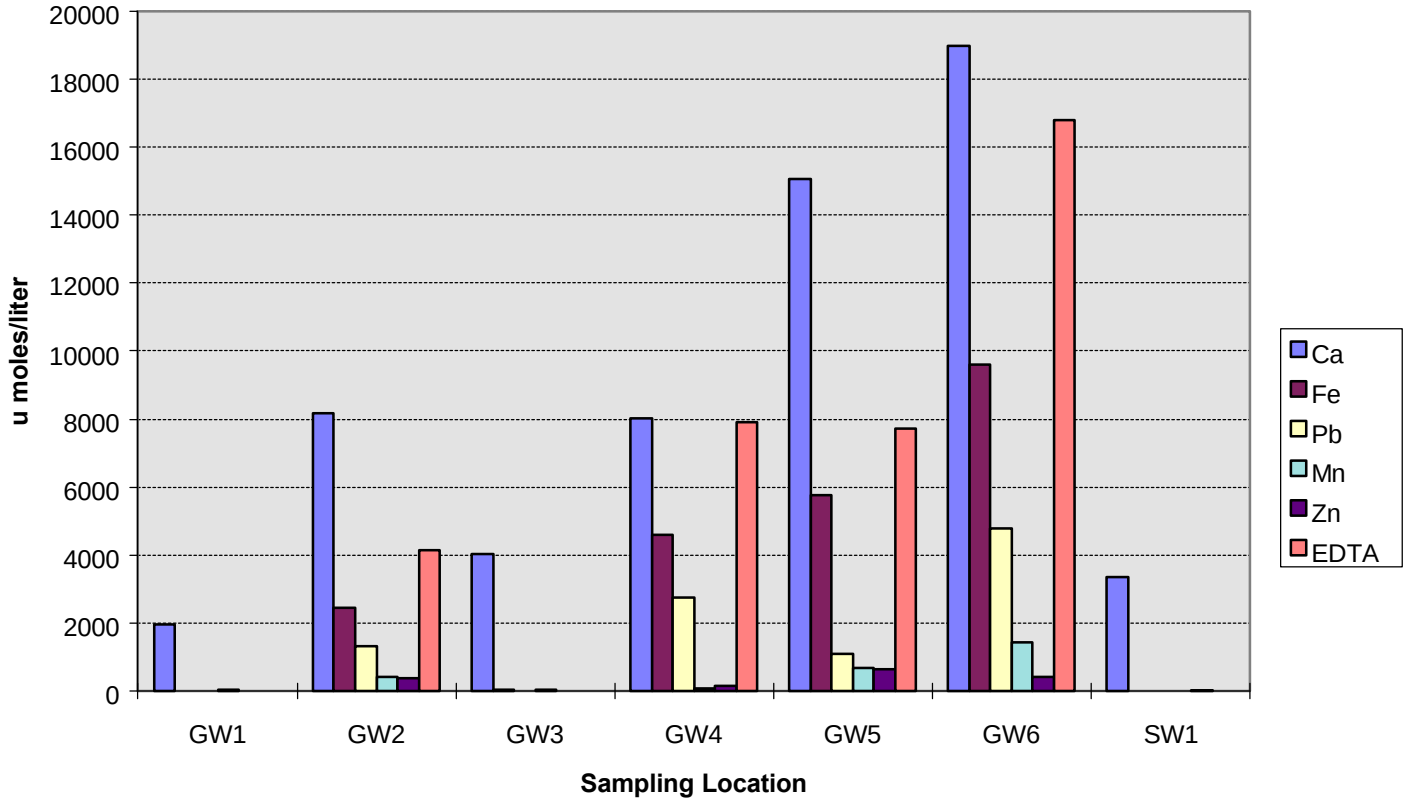



**Figure 5-7**
**Major Competing Cations in Groundwater and Surface Water Samples at Site C**
**(First Sampling)**

**Table 5-42**
**Analysis and Molar Ratios of EDTA:Pb in Groundwater**
**Samples Taken at Site C on May 17, 2000 (Second Phase Sampling)**

| Sample | EDTA as $Na_2EDTA$[1] mg/L | EDTA as EDTA[1] mg/L | EDTA[2] mmoles/L | Pb mg/L | Pb[3] mmoles/L | EDTA:Pb Molar Ratio[4] |
|---|---|---|---|---|---|---|
| GW2-1U[5] | 6.7 | 5.8 | 20 | -- | -- | -- |
| GW2-1F[6] | -- | -- | -- | 0.228 | 1.1 | 18 |
| GW2-2 | no sample[7] | no sample[7] | --[8] | -- | -- | -- |
| GW2-3 | no sample | no sample | -- | -- | -- | -- |
| GW2-4U | 788 | 685 | 2,345 | -- | -- | -- |
| GW2-4F | -- | -- | -- | 208 | 1,004 | 2.3 |
| GW2-5U | 701 | 609 | 2,086 | -- | -- | -- |
| GW2-5F | -- | -- | -- | 20 | 97 | 21.5 |
| GW2-6U | <0.03[9] | <0.03[9] | -- | -- | -- | -- |
| GW2-6F | -- | -- | -- | 0.17 | 1 | -- |
| GW2-7 | dry | dry | -- | -- | -- | -- |
| GW2-8U | 192 | 167 | 571 | -- | -- | -- |
| GW2-8F | -- | -- | -- | 54.4 | 263 | 2.2 |
| GW2-9 | dry | dry | -- | -- | -- | -- |
| Pre-rinse Blank, unfiltered | <0.03 | <0.03 | -- | -- | -- | -- |
| Pre-rinse Blank, filtered | -- | -- | -- | 0.0017 | 0.01 | -- |
| Field Blank, unfiltered | <0.03 | <0.03 | -- | -- | -- | -- |
| Field Blank, filtered | -- | -- | -- | 0.0018 | 0.01 | -- |
| Rinse Blank, unfiltered | <0.03 | <0.03 | -- | -- | -- | -- |
| Rinse Blank, filtered | -- | -- | -- | 0.0141 | 0.1 | -- |

(1) EDTA was determined on samples that were not filtered in the field..
(2) Obtained by dividing mg/L of EDTA by the molecular weight of EDTA (292.24 g/mol) and multiplying by 1000.
NOTE: 1 mol EDTA = 1 mol NA2EDTA.
(3) Obtained by dividing mg/L of Pb by the molecular weight of Pb (207.2 g/mol) and multiplying by 1000.
(4) Obtained by dividing µmoles/L of Na2EDTA by µmoles/L of Pb.
(5) U = Unfiltered, unacidified in the field, filtered and acidified on receipt by TVA.
(6) F = Filtered and acidified in the field.
(7) Time constraints and bad weather prevented taking a sample at this location.
(8) -- Not Applicable.
(9) Method Detection Limit (MDL).

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

taken. Time constraints prevented sampling at GW2-2 and GW2-3 (the two upgradient locations), and the bore holes were dry at GW2-7 and GW2-9. Lead and EDTA concentrations in groundwater for the sampling on May 17 are shown in Table 5-42.

As with the first set of groundwater samples (Section 5.2.10.1.1), the EDTA:lead ratio was consistently greater than 1:1, which indicated that EDTA was associated with elements other than lead and that lead had been displaced from the EDTA complex. Concentrations of EDTA and lead decreased significantly with increasing down-gradient distance north and northwest from the plot.

**5.2.10.2.3 May 30, 2000 - Third Groundwater Sampling**

EDTA had continued to migrate with the groundwater in a northwesterly direction down-gradient of the demonstration plot to the locations where these samples were taken (Figure 5-6, Table 5-43, sample locations GW3-3 and GW3-5), but lead concentrations tended to decrease with distance from the plot. As a consequence, the EDTA to lead ratio remained high in these samples, which indicated that lead was dissociating from EDTA. Concentrations of EDTA and lead decreased as the groundwater moved northward and down-gradient away from the plot (sample locations GW3-2, GW3-4, and GW3-6). The samples were analyzed only for EDTA and lead.

**5.2.10.3 May 4, 2000 - Surface Water Sampling**

Four additional samples were taken from various locations in the ditch (Figure 5.5, Figure 5-6, Table 5-44) to determine if contamination of surface water had occurred. A trace amount of EDTA (0.1 ppm) was found in the upgradient sample (SW2-1) taken 171 feet from the southwest corner of the demonstration plot. A slightly higher concentration of EDTA (0.2 ppm) was found at the original sampling site (SW-1) about 100 feet to the northwest of the plot when this site was re-sampled. However, the concentration had decreased from the 0.5 ppm originally present in the water at that location. This could have been due to dilution by additional influx of water into the ditch, or to movement of EDTA away from the sample point or degradation of the small amount of EDTA. EDTA was not detected in water from the third sampling point (SW2-3) located approximately 475 feet northwest of the plot (Figure 5-5). Notably, lead was not detected in any of the surface water samples, which indicated that EDTA had not mobilized lead into the surface water.

EDTA was present in the water sample from the fourth location (SW2-4, Figure 5-6) at a concentration of 1.1 ppm. This location was 500 feet from the demonstration plot. No lead was associated with the EDTA.

As with the first phase groundwater samples, these surface water samples were analyzed for 19 other cations (Table 5-45). The only cations present in quantities sufficient to compete with lead for complexation by EDTA were Ca and Mg. Potassium and sodium were present at average concentrations of 2 and 41 ppm, respectively, but these cations are not typically complexed by EDTA. The relationship between the competing cations and EDTA for the surface water samples is shown in Figure 5-8.

The concentrations of Ca and Mg in Figure 5-8 are expressed in µmoles/L. The corresponding average concentrations for Ca expressed in mg/L across the four locations (SW2-1, SW2-2, SW2-3, and SW2-4) are 118, 148, 86, and 117 mg/L. For Mg, the corresponding values for the four locations are 21, 58, 23, and 28 mg/L. Since lead was not present in the samples, the small quantity of EDTA present would have been complexed with Ca and Mg.

#### 5.2.10.4 April 11, 2000 - Deep Core Soil Sampling

Site C, and to a lesser extent at Site 129-3, were difficult sites to work. The large amount of debris and the observed different soil types at Site C directly contributed to and greatly exacerbated these problems. Deep core soil sampling was conducted to "dissect" the site and specifically determine and describe some of the factors responsible for the adverse conditions at the site.

The sample locations for deep core samples taken at Site C are shown in Figure 5-9, and for Site 129-3 in Figure 5-10. At Site C, nine samples were taken within the plot and five were taken outside the plot. Two of the samples within the plot at Site C were in the poorly drained northwest quadrant which would tend towards high concentrations of EDTA and lead. Of the five samples taken outside the plot, three were upgradient of the plot and two were down-gradient. At Site 129-3, the plot was divided into quadrants and a sample was taken from each quadrant within the plot. No samples were taken outside the demonstration plot at Site 129-3.

A description of the soil core samples at Site C and Site 129-3 by depth with the concentrations of EDTA and lead in the soil down to 4 feet is given in Table 5-46. The core samples represent 4 feet of soil. The 4-ft sections were cut into two 2-ft sections for shipment to the TVA Analytical Laboratory. Compression occurred during sampling so the length of each core was in many cases less than two feet. However, the amount of soil in each core is representative of two feet of field soil.

Examination of the soil cores revealed the following:

- The dominant soil type identified by the RI/FS for the area at Site C is sandy loam. However, the soil at Site C is extremely heterogeneous, which suggested dumping of soil from other areas when disposal activities occurred.

- Seven soil textures, ranging from sand to clay, were identified during the examination of the cores. The soil varied markedly in texture within each 4-foot core. Frequently, a deposit of each soil type was present in each core sample.

- Clay and sand lenses (i.e., a stratified layer) ranging in thickness from 1 inch to 5 inches, were commonly found in the samples at soil depths of 0.5 to 3.5 ft.

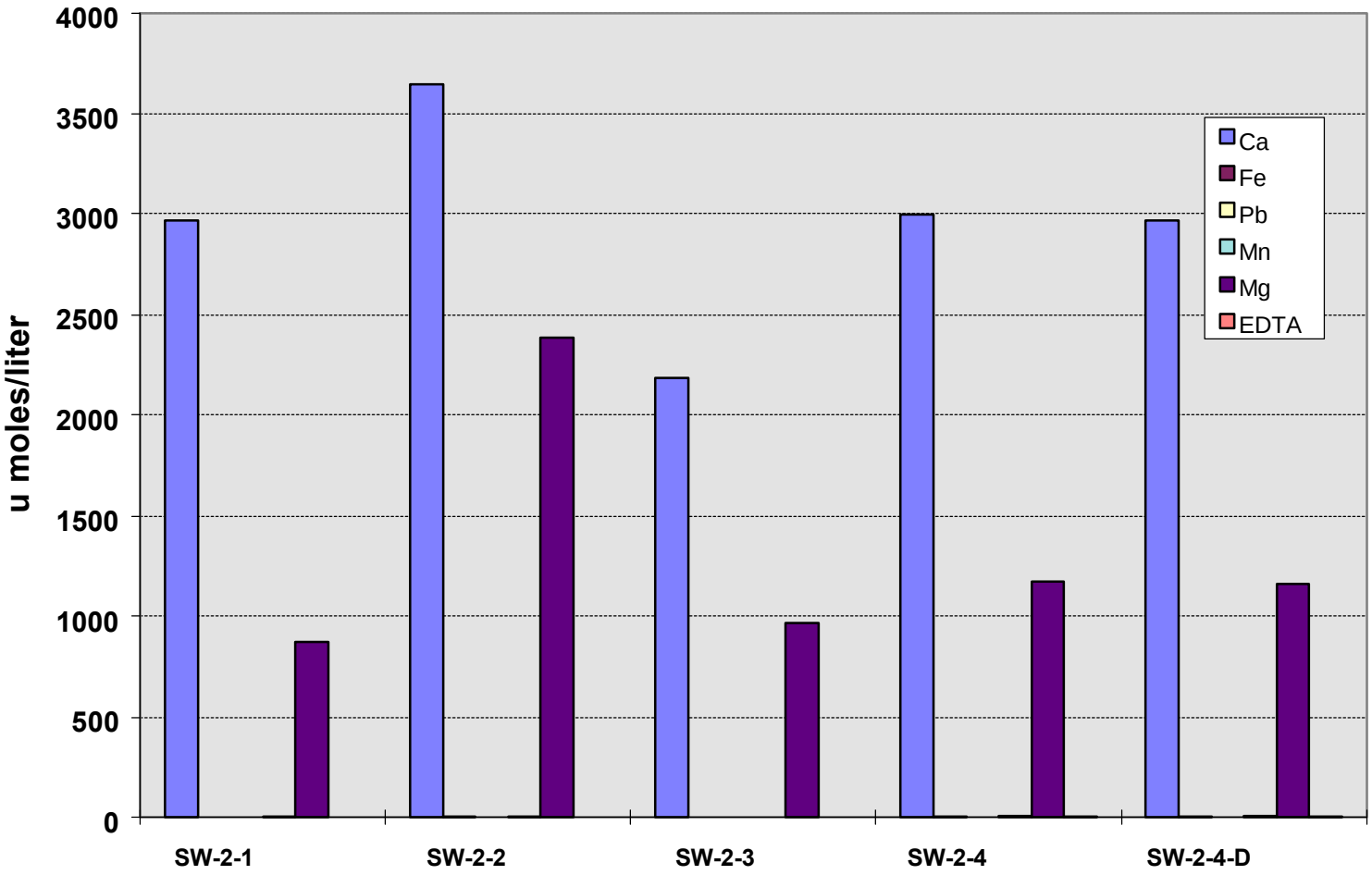



**Figure 5-8**
**Major Competing Cations in Surface Water Samples at Site C**
**(Second Sampling)**

**Table 5-43**
**Analysis and Molar Ratios of EDTA:Pb in Groundwater Samples Taken at Site C on May 30, 2000 (Third Phase Sampling)**

| Sample | EDTA as $Na_2EDTA$[1] mg/L | EDTA as EDTA[1] mg/L | EDTA[2] mmoles/L | Pb mg/L | Pb[3] mmoles/L | EDTA:Pb Molar Ratio[4] |
|---|---|---|---|---|---|---|
| GW3-1U[5] | 0.26 | 0.23 | 0.8 | --[7] | -- | -- |
| GW3-1F[6] | -- | -- | | 0.0015 | 0.01 | 80.0 |
| GW3-2U | 850 | 739 | 2,530 | -- | -- | -- |
| GW3-2F | -- | -- | -- | 1.56 | 8 | 316.0 |
| GW3-3U | 570 | 495 | 1,696 | -- | -- | -- |
| GW3-3F | -- | -- | -- | 10.8 | 52 | 32.6 |
| GW3-4U | 0.38 | 0.33 | 1 | -- | -- | -- |
| GW3-4F | -- | -- | -- | 0.0256 | 0.1 | 10.0 |
| GW3-4U duplicate | 0.37 | 0.32 | 1 | -- | -- | -- |
| GW3-4F duplicate | -- | -- | -- | 0.0208 | 0.1 | 10.0 |
| GW3-5U | 410 | 356 | 1,220 | -- | -- | -- |
| GW3-5F | -- | -- | | 27.3 | 132 | 9.2 |
| GW3-6U | 7 | 6 | 21 | -- | -- | -- |
| GW3-6F | -- | -- | -- | 1.45 | 7 | 3.0 |
| Pre-rinse Blank, unfiltered | <0.03[8] | <0.03[8] | -- | -- | -- | -- |
| Pre-rinse Blank, filtered | -- | -- | -- | 0.0011 | 0.01 | -- |
| Field Blank, unfiltered | <0.03 | <0.03 | -- | -- | -- | -- |
| Field Blank, filtered | -- | -- | -- | 0.0011 | 0.01 | -- |

(1) EDTA was determined on samples that were not filtered in the field..
(2) Obtained by dividing mg/L of EDTA by the molecular weight of EDTA (292.24 g/mol) and multiplying by 1000. NOTE: 1 mol EDTA = 1 mol $NA_2EDTA$.
(3) Obtained by dividing mg/L of Pb by the molecular weight of Pb (207.2 g/mol) and multiplying by 1000.
(4) Obtained by dividing µmoles/L of $Na_2EDTA$ by µmoles/L of Pb.
(5) U = Unfiltered, unacidified in the field, filtered and acidified on receipt by TVA.
(6) F = Filtered and acidified in the field.
(7) Time constraints and bad weather prevented taking a sample at this location.
(8) -- Not Applicable.
(9) Method Detection Limit (MDL).

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

**Table 5-44**
**Analysis of Pb and EDTA in Surface Water Samples**
**Taken from Drainage Ditch at Site C on May 4, 2000**
**(Second Phase Sampling)**

| Sample[1] | pH | EDTA as $Na_2EDTA$[2] mg/L | EDTA as EDTA[2] mg/L | EDTA[3] µmoles/L | Pb mg/L | Pb[4] µmoles/L |
|---|---|---|---|---|---|---|
| SW-2-1U-A | 7.4 | 0.10 | 0.09 | 0.3 | <0.02 [5] | <0.1[5] |
| SW-2-1U-B | | 0.11 | 0.10 | 0.3 | <0.02 | <0.1 |
| SW-2-1F | | NA[6] | NA[6] | -- | <0.02 | <0.1 |
| SW-2-2U-A | 7.7 | 0.20 | 0.17 | 0.6 | <0.02 | <0.1 |
| SW-2-2U-B | | 0.19 | 0.17 | 0.6 | <0.02 | <0.1 |
| SW-2-2F | | NA | NA | -- | <0.02 | <0.1 |
| SW-2-3U-A | 7.6 | <0.03[5] | <0.03[5] | <0.09[5] | 0.02 | 0.1 |
| SW-2-3U-B | | <0.03 | <0.03 | <0.09 | <0.02 | <0.1 |
| SW-2-3F | | NA | NA | -- | <0.02 | <0.1 |
| SW-2-4U-A | 7.3 | 1.21 | 1.05 | 3.6 | <0.02 | <0.1 |
| SW-2-4U-B | | 1.21 | 1.05 | 3.6 | <0.02 | <0.1 |
| SW-2-4F | | NA | NA | -- | <0.02 | <0.1 |
| SW-2-4U-A (dup.)[7] | 7.3 | 1.20 | 1.04 | 3.6 | <0.02 | <0.1 |
| SW-2-4U-B (dup.) | | 1.20 | 1.04 | 3.6 | <0.02 | <0.1 |
| SW-2-4F (dup.) | | NA | NA | -- | <0.02 | <0.1 |
| Pre-Rinse Blank-U-A | 5.5 | <0.03 | <0.03 | <0.09 | <0.02 | <0.1 |
| Pre-Rinse Blank-U-B | | <0.03 | <0.03 | <0.09 | <0.02 | <0.1 |
| Pre-Rinse Blank-F | | NA | NA | -- | <0.02 | <0.1 |
| Rinse Blank-U-A | 6.0 | <0.03 | <0.03 | <0.09 | <0.02 | <0.1 |
| Rinse Blank-U-B | | <0.03 | <0.03 | <0.09 | <0.02 | <0.1 |
| Rinse Blank-F | | NA | NA | -- | <0.02 | <0.1 |
| Field Blank-U-A | 6.2 | <0.03 | <0.03 | <0.09 | <0.02 | <0.1 |
| Field Blank-U-B | | <0.03 | <0.03 | <0.09 | <0.02 | <0.1 |
| Field Blank-F | | NA | NA | -- | <0.02 | <0.1 |

(1) "A" fractions of surface water samples were not filtered or acidified in the field. The samples were filtered through 0.45 micron Millipore® syringe filters upon arrival at the TVA Analytical Lab, then acidified after a subsample taken for EDTA analysis. "B" fractions were filtered at TVA through 0.2 Millipore® syringe filters, subsampled for EDTA analysis, and acidified. "F" fractions were filtered and acidified in the field.

(2) EDTA was determined on samples that were not filtered in the field..

(3) Obtained by dividing mg/L of EDTA by the molecular weight of EDTA (292.2224 g/mol) and multiplying by 1000. NOTE: 1 mol EDTA = 1 mol $NA_2EDTA$.

(4) Obtained by dividing mg/L of Pb by the molecular weight of Pb (207.2 g/L) and multiplying by 1000.

(5) Method Detection Limit.

(6) NA = Not Applicable.

(7) Dup. = duplicate samples collected in field.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

- A major deposit (6-inch thickness) of dense, brittle, consolidated hardpan material was found at the one foot depth in samples from the western-most third of the plot. The color indicated that the pan material is likely iron-rich. The pan sloped toward the low northwestern corner of the field (site of GW-6 sample, Figure 5-6).

- Iron oxide deposition was common throughout the soil.

- Manganese concretions (nodules of manganese sulfide) were found in several samples. Such deposits are indicative of a fluctuating water table level, which results in alternating aerobic and anaerobic zones in the soil and periodic low redox status. Such concretions are caused when Mn is solubilized under low redox and then is re-precipitated as the water recedes and the soil returns to an aerobic, high redox state.

- Several samples (primarily clay) were grey in color at the 3- to 4-ft depth, which indicated poor drainage or periodic water logging.

- Some of the cores were extremely wet, particularly at the 3- to 4 ft-depth, and moisture could be freely expressed from the soil.

- A considerable amount of char as well as unburned wood and what appeared to be rail tie was found. Layers of consolidated and unconsolidated char were found at various depths, ranging from 6 inches to almost 4 feet. Other debris consisted of diverse glass, wood, sheet metal, wire, concrete, copper-clad lead bullets, and brass shell casings.

- Numerous cobbles ranging in size from small pebbles to 12-inch stones were present.

The dominant soil type at Site 129-3 is fine sand. However, the soil at this site also varied in texture from fine sand to clay. No debris was noted in the Site 129-3 soil. The soil in all cores was well drained.

Analysis of deep core samples at Site C showed total lead concentrations in the soil ranging from less than 1 ppm to greater than 44,000 ppm. Water-soluble lead concentrations ranged from less than 1 ppm up to 549 ppm. Concentrations of EDTA in the soil ranged from less than 0.3 ppm to 1,570 ppm. Concentrations of water-soluble lead and EDTA at Site 129-3 were lower due to the lower total lead content of the soil and the correspondingly lower amount of EDTA added to the soil.

The amount of EDTA remaining in the soil at Site C was less than anticipated. Apparently, the heterogeneous soil texture and the many discontinuities within the soil body may have promoted downward movement of EDTA and reduced the contact time of EDTA with the soil and thus expected reactions of EDTA in the soil did not occur. However, degradation of EDTA was not as great as anticipated. Normally the primary mechanisms are aerobic microbial degradation and photo-degradation. Possibly the general microbial population in this soil is low due to the presence of toxic contaminants in the soil.

## Table 5-45
## Analysis for Potential Competing Cations in Surface Water Samples Taken at Site C on May 4, 2000 (Second Phase Sampling)

| Site | pH | EDTA as $Na_2EDTA$ | EDTA as EDTA | Pb | Ca | Fe | Mg | K | Mn | Na | Zn | Sr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mg/L | | | | | | | | | | |
| SW-2-1-U | 7.38 | 0.10 | 0.09 | <0.02[1] | 117 | <0.001[1] | 21 | 1.8 | 0.084 | 10.1 | 0.029 | 0.2 |
| SW-2-1-U | NA[2] | 0.11 | 0.10 | <0.02 | 119 | <0.001 | 21.2 | 1.8 | 0.066 | 10 | 0.031 | 0.2 |
| SW-2-1-F | 1.91 | NA | NA | <0.02 | 118 | <0.001 | 21.2 | 1.7 | 1.2 | 9.25 | 0.009 | 0.21 |
| SW-2-2-U | 7.66 | 0.20 | 0.17 | <0.02 | 146 | 0.061 | 58.3 | 2.7 | 0.111 | 24.5 | 0.111 | 1.75 |
| SW-2-2-U | NA | 0.19 | 0.17 | <0.02 | 146 | 0.06 | 58 | 2.7 | 0.103 | 23.8 | 0.124 | 1.7 |
| SW-2-2-F | 2 | NA | NA | <0.02 | 152 | 0.191 | 56.1 | 2.4 | 0.541 | 22.4 | 0.208 | 1.68 |
| SW-2-3-U | 7.55 | <0.03[1] | <0.03[1] | <0.02 | 88 | <0.001 | 23.8 | 1.1 | 0.005 | 45 | 0.021 | 0.21 |
| SW-2-3-U | NA | <0.03 | <0.03 | <0.02 | 88 | <0.001 | 23.5 | 1 | 0.005 | 43 | 0.024 | 0.21 |
| SW-2-3-F | 1.35 | NA | NA | <0.02 | 82 | 0.068 | 21.7 | 0.9 | 0.111 | 40 | <0.004 [1] | 0.2 |
| SW-2-4-U | 7.33 | 1.21 | 1.05 | <0.02 | 121 | 0.162 | 28.9 | 2.3 | 0.348 | 69.2 | 0.04 | 0.41 |
| SW-2-4-U | NA | 1.21 | 1.05 | <0.02 | 120 | 0.162 | 28.5 | 2.33 | 0.342 | 66.4 | 0.044 | 0.39 |
| SW-2-4-F | 1.35 | NA | NA | <0.02 | 111 | 1.16 | 25.9 | 2.2 | 0.351 | 61.1 | 0.02 | 0.38 |
| SW-2-4-U-D | 7.32 | 1.20 | 1.04 | <0.02 | 121 | 0.162 | 28.7 | 2.4 | 0.351 | 68.7 | 0.038 | 0.41 |
| SW-2-4-U-D | NA | 1.20 | 1.04 | <0.02 | 119 | 0.166 | 28.3 | 2.4 | 0.344 | 66.2 | 0.043 | 0.41 |
| SW-2-4-F-D | 1.33 | -- | -- | <0.02 | 112 | 1.21 | 26.1 | 2.2 | 0.356 | 61.6 | 0.015 | 0.38 |

Note: A fractions were filtered at TVA through 0.45 µ syringe filters and acidified.
B fractions were filtered at TVA through 0.2 µ syringe filters and acidified.
F fractions were filtered and acidified in the field.

(1) Method Detection Limit (MDL).
(2) NA - Not Applicable.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-45 (Continued)
## Analysis for Potential Competing Cations in Surface Water Samples Taken at Site C on May 4, 2000 (Second Phase Sampling)

| Site | pH | EDTA as $Na_2EDTA$ | EDTA as EDTA | Pb | Ca | Fe | Mg | K | Mn | Na | Zn | Sr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mmoles/L[3] | | | | | | | | | | |
| SW-2-1-U | -- | 0.30 | 0.26 | <0.0965[1] | 2920 | <0.018[1] | 864 | 46.0 | 1.53 | 439 | 0.44 | 2.28 |
| SW-2-1-U | -- | 0.33 | 0.28 | <0.0965 | 2970 | <0.018 | 872 | 46.0 | 1.20 | 435 | 0.47 | 2.28 |
| SW-2-1-F | -- | NA[2] | NA[2] | <0.0965 | 2940 | <0.018 | 872 | 43.5 | 21.84 | 402 | 0.14 | 2.40 |
| SW-2-2-U | -- | 0.60 | 0.52 | <0.0965 | 3640 | 1.09 | 2400 | 69.1 | 2.02 | 1070 | 1.70 | 20.0 |
| SW-2-2-U | -- | 0.57 | 0.49 | <0.0965 | 3640 | 1.07 | 2390 | 69.1 | 1.87 | 1030 | 1.90 | 19.4 |
| SW-2-2-F | -- | NA | NA | <0.0965 | 3790 | 3.42 | 2310 | 61.4 | 9.85 | 974 | 3.18 | 19.2 |
| SW-2-3-U | -- | <0.09[1] | <0.09[1] | <0.0965 | 2200 | <0.018 | 979 | 28.1 | 0.09 | 1960 | 0.32 | 2.40 |
| SW-2-3-U | -- | <0.09 | <0.09 | <0.0965 | 2190 | <0.018 | 967 | 25.6 | 0.09 | 1870 | 0.37 | 2.40 |
| SW-2-3-F | -- | NA | NA | <0.0965 | 2030 | 1.22 | 893 | 23.0 | 2.02 | 1740 | <0.06[1] | 2.28 |
| SW-2-4-U | -- | 3.6 | 3.1 | <0.0965 | 3020 | 2.90 | 1190 | 58.8 | 6.33 | 3010 | 0.61 | 4.68 |
| SW-2-4-U | -- | 3.6 | 3.1 | <0.0965 | 2990 | 2.90 | 1170 | 59.6 | 6.22 | 2890 | 0.67 | 4.45 |
| SW-2-4-F | -- | NA | NA | <0.0965 | 2770 | 20.8 | 1070 | 56.3 | 6.39 | 2660 | 0.31 | 4.34 |
| SW-2-4-U-D | -- | 3.6 | 3.1 | <0.0965 | 3020 | 2.90 | 1180 | 61.4 | 6.39 | 2990 | 0.58 | 4.68 |
| SW-2-4-U-D | -- | 3.6 | 3.1 | <0.0965 | 2970 | 2.97 | 1160 | 61.4 | 6.26 | 2880 | 0.66 | 4.68 |
| SW-2-4-F-D | -- | NA | NA | <0.0965 | 2790 | 21.7 | 1070 | 56.3 | 6.48 | 2680 | 0.23 | 4.34 |

Note: A fractions were filtered at TVA through 0.45 µ syringe filters and acidified.
B fractions were filtered at TVA through 0.2 µ syringe filters and acidified.
F fractions were filtered and acidified in the field.

(1) Method Detection Limit (MDL).
(2) NA - Not Applicable.
(3) Obtained µmoles/L by dividing mg/L by the respective molecular weight (g/mol) of each compound or element and multiplying by 1,000.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-45 (Continued)
## Analysis for Potential Competing Cations in Surface Water Samples Taken at Site C on May 4, 2000 (Second Phase Sampling)

| Site | Al | Ba | Be | Co | Cu | Ni | Sb | Ti | Tl | V |
|---|---|---|---|---|---|---|---|---|---|---|
| | mg/L | | | | | | | | | |
| SW-2-1-U | 0.05 | 0.054 | <0.001[1] | <0.005[1] | <0.002[1] | <0.006[1] | <0.03[1] | <0.002[1] | <0.05 [1] | 0.009 |
| SW-2-1-U | 0.06 | 0.057 | <0.001 | <0.005 | 0.003 | <0.006 | <0.03 | 0.006 | <0.05 | 0.009 |
| SW-2-1-F | <0.02[1] | 0.04 | <0.001 | <0.005 | <0.002 | <0.006 | <0.03 | 0.005 | <0.05 | 0.008 |
| SW-2-2-U | 0.03 | 0.195 | <0.001 | <0.005 | 0.016 | 0.006 | <0.03 | <0.002 | <0.05 | 0.009 |
| SW-2-2-U | 0.05 | 0.199 | <0.001 | <0.005 | 0.018 | 0.007 | <0.03 | <0.002 | <0.05 | 0.014 |
| SW-2-2-F | 0.02 | 0.202 | <0.001 | 0.007 | 0.016 | 0.013 | <0.03 | 0.013 | <0.05 | 0.016 |
| SW-2-3-U | 0.05 | 0.088 | <0.001 | <0.005 | <0.002 | <0.006 | <0.03 | <0.002 | <0.05 | 0.005 |
| SW-2-3-U | 0.05 | 0.106 | <0.001 | <0.005 | 0.003 | <0.006 | <0.03 | 0.005 | <0.05 | 0.008 |
| SW-2-3-F | <0.02 | 0.054 | <0.001 | <0.005 | <0.002 | <0.006 | <0.03 | 0.012 | <0.05 | 0.01 |
| SW-2-4-U | 0.04 | 0.191 | <0.001 | <0.005 | 0.002 | <0.006 | <0.03 | <0.002 | <0.05 | 0.008 |
| SW-2-4-U | 0.06 | 0.212 | <0.001 | <0.005 | 0.003 | <0.006 | <0.03 | 0.003 | <0.05 | 0.009 |
| SW-2-4-F | <0.02 | 0.152 | <0.001 | <0.005 | 0.003 | 0.008 | <0.03 | 0.012 | <0.05 | 0.011 |
| SW-2-4-U-D | 0.04 | 0.193 | <0.001 | <0.005 | <0.002 | <0.006 | <0.03 | <0.002 | <0.05 | 0.008 |
| SW-2-4-U-D | 0.06 | 0.203 | <0.001 | <0.005 | <0.002 | <0.006 | <0.03 | 0.005 | <0.05 | 0.008 |
| SW-2-4-F-D | 0.03 | 0.155 | <0.001 | <0.005 | 0.002 | 0.007 | <0.03 | <0.002 | <0.05 | 0.012 |

Note: A fractions were filtered at TVA through 0.45 µ syringe filters and acidified.
B fractions were filtered at TVA through 0.2 µ syringe filters and acidified.
F fractions were filtered and acidified in the field.

(1) Method Detection Limit (MDL).
(2) NA - Not Applicable.

## Table 5-45 (Continued)
## Analysis for Potential Competing Cations in Surface Water Samples Taken at Site C on May 4, 2000 (Second Phase Sampling)

| Site | Al | Ba | Be | Co | Cu | Ni | Sb | Ti | Tl | V |
|---|---|---|---|---|---|---|---|---|---|---|
| | mmoles/L[3] | | | | | | | | | |
| SW-2-1-U | 1.85 | 0.393 | <0.111[1] | <0.119[1] | <0.031[1] | <0.102[1] | <0.246[1] | <0.042[1] | <0.245[1] | 0.177 |
| SW-2-1-U | 2.22 | 0.415 | <0.111 | <0.119 | 0.0472 | <0.102 | <0.246 | 0.125 | <0.245 | 0.177 |
| SW-2-1-F | <0.741[1] | 0.291 | <0.111 | <0.119 | <0.031 | <0.102 | <0.246 | 0.104 | <0.245 | 0.157 |
| SW-2-2-U | 1.11 | 1.420 | <0.111 | <0.119 | 0.252 | 0.102 | <0.246 | <0.042 | <0.245 | 0.177 |
| SW-2-2-U | 1.85 | 1.449 | <0.111 | <0.119 | 0.283 | 0.119 | <0.246 | <0.042 | <0.245 | 0.275 |
| SW-2-2-F | 0.74 | 1.471 | <0.111 | 0.119 | 0.252 | 0.221 | <0.246 | 0.271 | <0.245 | 0.314 |
| SW-2-3-U | 1.85 | 0.641 | <0.111 | <0.119 | <0.031 | <0.102 | <0.246 | <0.042 | <0.245 | 0.098 |
| SW-2-3-U | 1.85 | 0.772 | <0.111 | <0.119 | 0.0472 | <0.102 | <0.246 | 0.104 | <0.245 | 0.157 |
| SW-2-3-F | <0.741 | 0.393 | <0.111 | <0.119 | <0.031 | <0.102 | <0.246 | 0.251 | <0.245 | 0.196 |
| SW-2-4-U | 1.48 | 1.391 | <0.111 | <0.119 | 0.03148 | <0.102 | <0.246 | <0.042 | <0.245 | 0.157 |
| SW-2-4-U | 2.22 | 1.544 | <0.111 | <0.119 | 0.04721 | <0.102 | <0.246 | 0.063 | <0.245 | 0.177 |
| SW-2-4-F | <0.741 | 1.107 | <0.111 | <0.119 | 0.04721 | 0.136 | <0.246 | 0.251 | <0.245 | 0.216 |
| SW-2-4-U-D | 1.48 | 1.405 | <0.111 | <0.119 | <0.031 | <0.102 | <0.246 | <0.042 | <0.245 | 0.157 |
| SW-2-4-U-D | 2.22 | 1.478 | <0.111 | <0.119 | <0.031 | <0.102 | <0.246 | 0.104 | <0.245 | 0.157 |
| SW-2-4-F-D | 1.11 | 1.129 | <0.111 | <0.119 | 0.0315 | 0.119 | <0.246 | <0.042 | <0.245 | 0.236 |

Note: A fractions were filtered at TVA through 0.45 µ syringe filters and acidified.
B fractions were filtered at TVA through 0.2 µ syringe filters and acidified.
F fractions were filtered and acidified in the field.

(1) Method Detection Limit (MDL).
(2) NA - Not Applicable.
(3) Obtained µmoles/L by dividing mg/L by the respective molecular weight (g/mol) of each compound or element and multiplying by 1,000.

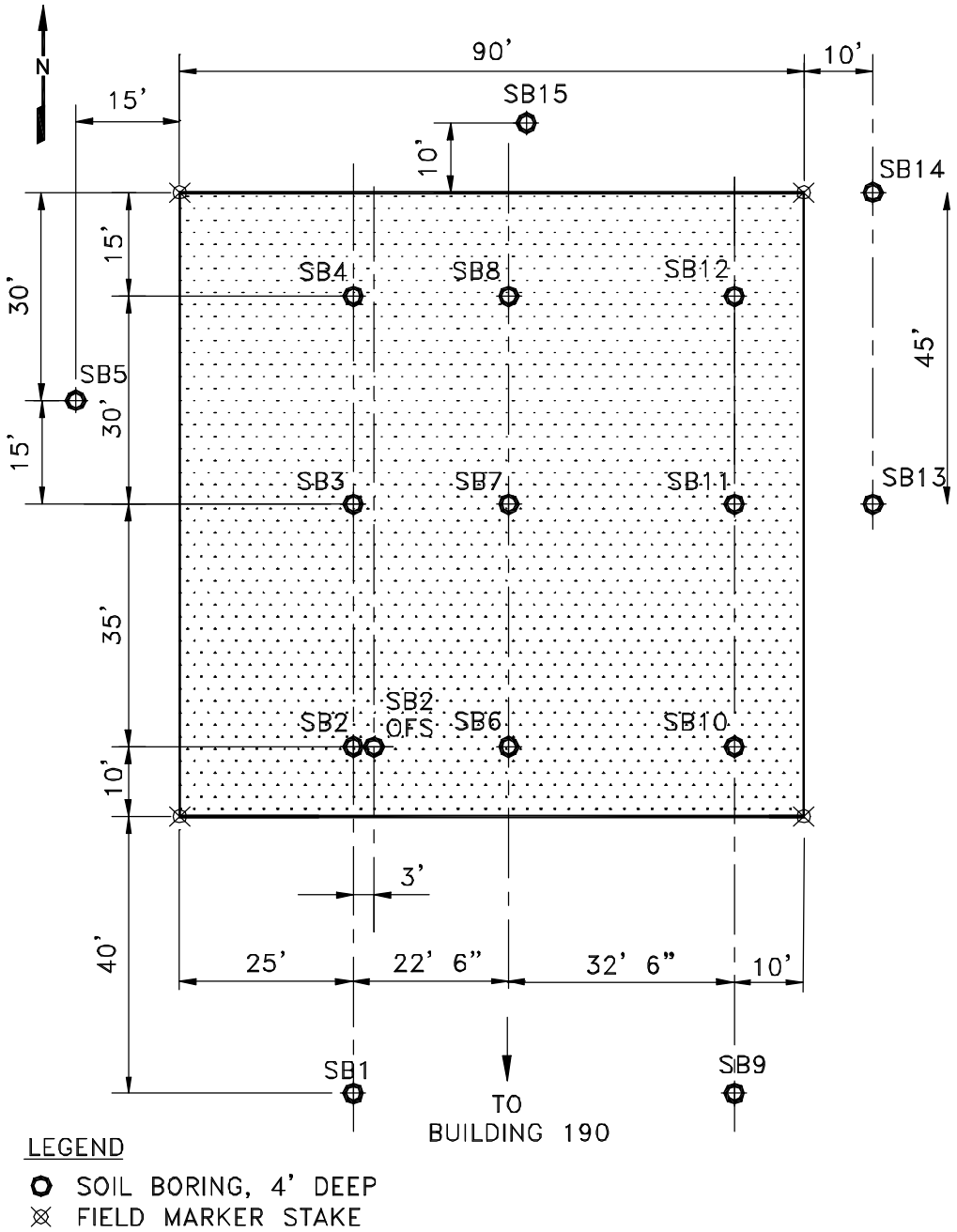



**Figure 5-9**
**Location for Deep Core Soil Samples Taken at Site C**
**April 11, 2000**

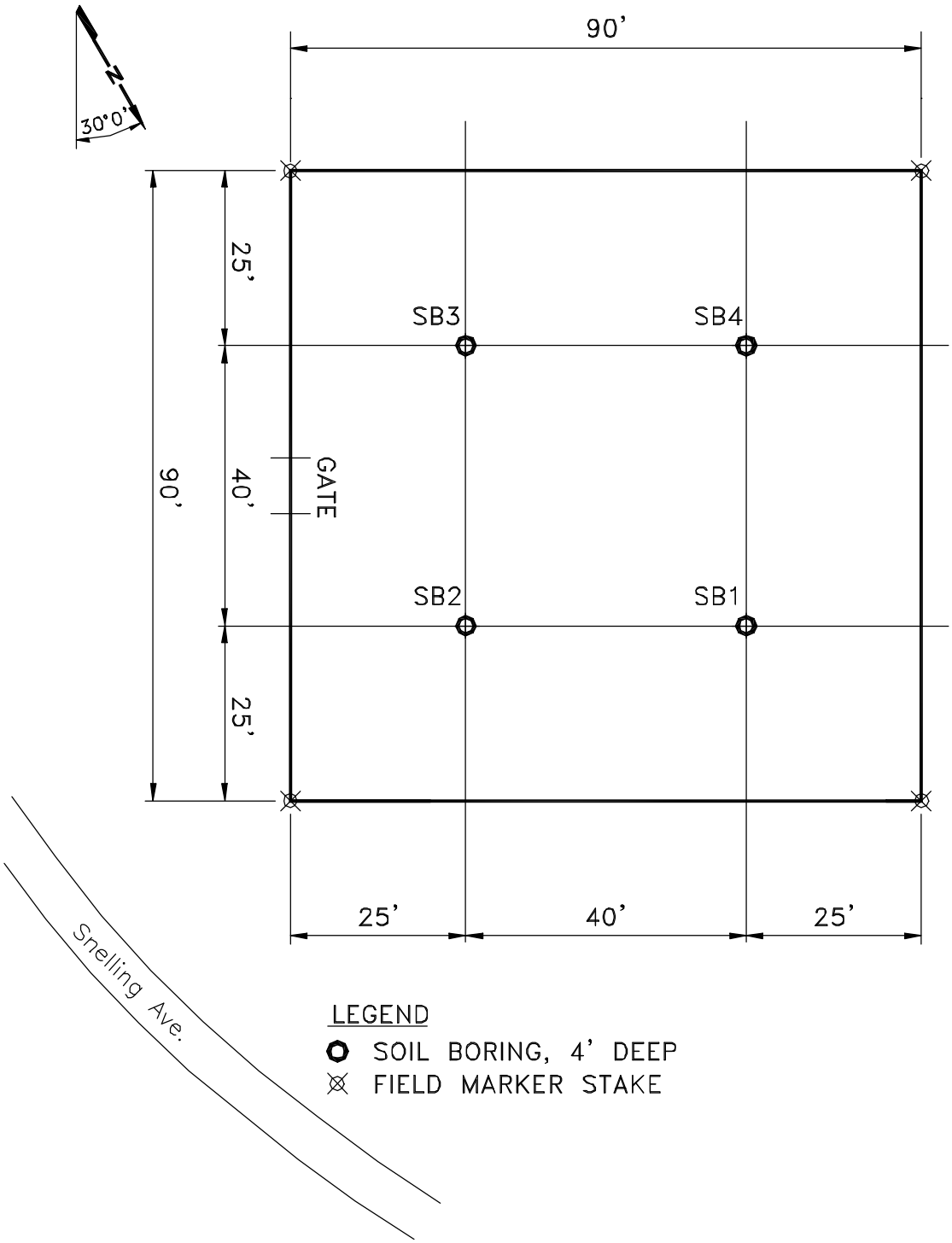



**Figure 5-10**
**Locations for Deep Core Soil Samples Taken at Site 129-3**
**April 11, 2000**

## Table 5-46
## Visual Characterization and Description of Soil Cores taken to Four Foot Depth at Site C and Site 129-3

| DESCRIPTION[1] | | | | ANALYSIS | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | Nominal Depth (ft) | Column Length[2] (in.) | | Depth[3] (ft) | Total Pb, mg/kg | $H_20$-sol. Pb, mg/kg | EDTA as $Na_2$EDTA, mg/kg | EDTA as EDTA, mg/kg |
| ----------Site C---------- | | | | | | | | |
| SB-1 | 0-2 | 20.5 | 10 " - dark brown sandy clay, char material throughout, iron oxide accumulations;<br>5.5" - a layer of consolidated, extremely dense, red pan material;<br>5" - medium brown, fine sandy loam | 1<br>2 | 32<br><1 | <1<br><1 | <0.3<br><0.3 | <0.3<br><0.3 |
| SB-1 | 2-4 | 15.75 | 11" - light brown fine loamy sand;<br>4" - heavy, dark brown clay, albic mottling | 3<br>4 | <1<br><1 | <1<br><1 | <0.3<br><0.3 | <0.3<br><0.3 |
| SB-2 | 0-2 | 14.0 | 13.5" mixed, mottled, sandy clay throughout;<br>pronounced char material mixed throughout;<br>clay lenses present;<br>$Fe_2O_3$ inclusions and splotching throughout<br>top 2.5 " darker layer | 1<br>2 | 888<br>7,440 | 16<br>116 | <0.3<br>5 | <0.3<br>4 |
| SB-2 | 2-4 | 13.5 | 3" dark brown sandy clay;<br>4" char mixed with gray-brown clay;<br>5.5" unburned wood | 3<br>4 | 1,860<br>325 | 49<br>49 | 15<br>340 | 13<br>296 |
| SB-2 (offset)[4] | 0-2 | 15.0 | 2" dark brown organic layer;<br>2" medium brown sand;<br>2.5" clay with char;<br>3" medium brown fine loamy sand;<br>3" dark brown coarse sandy loam, char material | 1<br>2 | 1,440<br>3,100 | 45<br>66 | 5<br>4 | 4<br>3 |
| SB-2 (offset) | 2-4 | 12.75 | 1" medium brown coarse sand<br>10" char and unburned wood; a clay lens at 8" | 3<br>4 | 1,610<br>212 | 31<br>21 | 82<br>116 | 71<br>101 |

(1) Soil is described incrementally from the top to the bottom of each column.

(2) Length as taken from field which represents a two-foot depth increment in the soil. Compaction during sampling reduced the length of the sample to less than two feet.

(3) Depth is in 1-foot increments. Compaction during sampling reduced the incremental length of the soil sample to less than one foot.

(4) Sample location offset 3 feet to the east of the original designated location due to obstruction.

**NOTE:** Analytical results are based on comparison with $Na_2$EDTA standards and are calculated as mg/kg or mg/L $Na_2$EDTA. Earlier reports on this project reported EDTA results calculated as $Na_2$EDTA without note. This Results Report shows the data calculated as $Na_2$EDTA and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2$EDTA) = 0.8692.

## Table 5-46 (Continued)
## Visual Characterization and Description of Soil Cores taken to Four Foot Depth at Site C and Site 129-3

| DESCRIPTION[1] | | | | ANALYSIS | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | Nominal Depth (ft) | Column Length[2] (in.) | | Depth[3] (ft) | Total Pb, mg/kg | $H_20$-sol. Pb, mg/kg | EDTA as Na2EDTA, mg/kg | EDTA as EDTA, mg/kg |
| ----------Site C---------- | | | | | | | | |
| SB-3 | 0-2 | 14.0 | 3.5" dark brown fine loamy sand;<br>3" medium brown fine loamy sand;<br>2" sandy clay<br>3" char<br>1" clay | 1<br>2 | 432<br>23,200 | 6<br>245 | <0.3<br>7 | <0.3<br>6 |
| SB-3 | 2-4 | 12.25 | sample was very wet;<br>2" mixture of dark brown coarse loamy sand mixed with dark clay;<br>9.5 "coarse loamy sand mixed with medium brown smooth gravel | 3<br>4 | 152<br>127 | 43<br>50 | 94<br>192 | 82<br>167 |
| SB-4 | 0-2 | 19.0 | 6" dark brown sandy clay;<br>12.5" light brown, fine loamy sand;<br>numerous $Fe_2O_3$ inclusions | 1<br>2 | 149<br>44,100 | 2<br>12 | <0.3<br>25 | <0.3<br>22 |
| SB-4 | 2-4 | 18.5 | 18" medium brown loamy sand;<br>very wet in the last 6";<br>numerous $Fe_2O_3$ inclusions and Mn concretions | 3<br>4 | 33,700<br>15,200 | 36<br>16 | 80<br>220 | 70<br>191 |
| SB-5 | 0-2 | 19.0 | 2" dark organic layer;<br>3" medium brown sandy loam;<br>5.5" char/unburned wood layer;<br>8"medium brown fine loamy sand | 1<br>2 | 3,720<br>30 | 46<br>8 | <0.3<br>52 | <0.3<br>45 |
| SB-5 | 2-4 | 19.5 | 16" medium brown uniform coarse loamy sand;<br>3" heavy yellow-orange clay;<br>1" gravel | 3<br>4 | <1<br><1 | <1<br><1 | <0.3<br><0.3 | <0.3<br><0.3 |

(1) Soil is described incrementally from the top to the bottom of each column.

(2) Length as taken from field which represents a two-foot depth increment in the soil. Compaction during sampling reduced the length of the sample to less than two feet.

(3) Depth is in 1-foot increments. Compaction during sampling reduced the incremental length of the soil sample to less than one foot.

(4) Sample location offset 3 feet to the east of the original designated location due to obstruction.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-46 (Continued)
## Visual Characterization and Description of Soil Cores taken to Four Foot Depth at Site C and Site 129-3

| DESCRIPTION[1] | | | | ANALYSIS | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | Nominal Depth (ft) | Column Length[2] (in.) | | Depth[3] (ft) | Total Pb, mg/kg | $H_20$-sol. Pb, mg/kg | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg |
| ----------Site C---------- | | | | | | | | |
| SB-6 | 0-2 | 16.5 | 6.5" dark brown fine sandy clay;<br>6" light brown fine sandy loam w/ $Fe_2O_3$ inclusions;<br>3.5" dark brown sandy clay w/ $Fe_2O_3$ inclusions and char material | 1<br>2 | 13,500<br>3,440 | 42<br>56 | 7<br>66 | 6<br>57 |
| SB-6 | 2-4 | 24.0 | 5" dark sandy clay w/ char material;<br>19" medium brown loamy sand w/ $Fe_2O_3$ inclusions and Mn concretions | 3<br>4 | 203<br>68 | 34<br>27 | 52<br>79 | 45<br>69 |
| SB-7 | 0-2 | 18.5 | 6" dark brown fine loamy sand;<br>9.5" medium brown fine loamy sand, Mn concretions;<br>3" medium yellow-brown clay | 1<br>2 | 4,820<br>270 | 53<br>13 | 7<br>4 | 6<br>3 |
| SB-7 | 2-4 | 11.5 | 11.5" medium brown coarse loamy sand, Mn concretions, very wet | 3<br>4 | 1,090<br>5,850 | 32<br>7 | 15<br>7 | 13<br>6 |
| SB-8 | 0-2 | 19.0 | 6" dark brown sandy loam, with clay lens at 5";<br>13" light brown fine loamy sand with clay lens at 12";<br>Several $Fe_2O_3$ inclusions and Mn concretions throughout | 1<br>2 | 100<br>13,600 | 92<br>117 | 1,800<br>363 | 1,570<br>316 |
| SB-8 | 2-4 | 15.5 | 15.5" medium brownish-gray coarse loamy sand w/ $Fe_2O_3$ inclusions and Mn concretions throughout, numerous pebbles | 3<br>4 | 24,200<br>830 | 84<br>48 | 377<br>815 | 328<br>708 |

(1) Soil is described incrementally from the top to the bottom of each column.

(2) Length as taken from field which represents a two-foot depth increment in the soil. Compaction during sampling reduced the length of the sample to less than two feet.

(3) Depth is in 1-foot increments. Compaction during sampling reduced the incremental length of the soil sample to less than one foot.

(4) Sample location offset 3 feet to the east of the original designated location due to obstruction.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-46 (Continued)
## Visual Characterization and Description of Soil Cores taken to Four Foot Depth at Site C and Site 129-3

| DESCRIPTION [1] | | | | ANALYSIS | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | Nominal Depth (ft) | Column Length[2] (in.) | | Depth[3] (ft) | Total Pb, mg/kg | $H_20$-sol. Pb, mg/kg | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg |
| ----------Site C---------- | | | | | | | | |
| SB-9 | 0-2 | 19.5 | 19.5" full depth medium brown loamy sand, Mn concretions | 1<br>2 | 7,000<br>126 | 81<br>2 | <0.3<br><0.3 | <0.3<br><0.3 |
| SB-9 | 2-4 | 20.0 | 4" medium brown sandy clay;<br>16" medium brown fine loamy sand | 3<br>4 | <1<br><1 | <1<br><1 | <0.3<br><0.3 | <0.3<br><0.3 |
| SB-10 | 0-2 | 19.0 | 7.5" dark brown loamy sand w/ char material;<br>2" light brown sand;<br>2" char material;<br>8" medium brown loamy sand, $Fe_2O_3$ inclusions | 1<br>2 | 427<br>10,400 | 42<br>73 | 81<br>37 | 70<br>32 |
| SB-10 | 2-4 | 19.5 | 2"char, sandy clay;<br>10" light brown fine sand, $Fe_2O_3$ inclusions;<br>6.5" mottled brown sandy loam mixed with char, several Mn concretions | 3<br>4 | 161<br>171 | 56<br>70 | 180<br>205 | 156<br>178 |
| SB-11 | 0-2 | 22.0 | 8.5" dark brown loamy sand mixed with char, w/ $Fe_2O_3$ inclusions;<br>7"medium brown fine loamy sand w/ $Fe_2O_3$ inclusions;<br>7" medium brown sandy clay | 1<br>2 | 1,980<br>313 | 253<br>136 | 500<br>736 | 435<br>640 |
| SB-11 | 2-4 | 14.0 | 2" dark brown fine loamy sand;<br>4" mottled clay w/ Mn concretions;<br>8" dark brown coarse loamy sand and gravel | 3<br>4 | 355<br>87 | 178<br>14 | 570<br>65 | 495<br>56 |
| SB-12 | 0-2 | 13.5 | 5.5" medium brown loamy sand w/ $Fe_2O_3$ inclusions;<br>3" brown clay mixed with char material;<br>6" medium brown loamy sand $Fe_2O_3$ inclusions | 1<br>2 | 525<br>17,800 | 96<br>549 | 293<br>350 | 255<br>304 |

(1) Soil is described incrementally from the top to the bottom of each column.

(2) Length as taken from field which represents a two-foot depth increment in the soil. Compaction during sampling reduced the length of the sample to less than two feet.

(3) Depth is in 1-foot increments. Compaction during sampling reduced the incremental length of the soil sample to less than one foot.

(4) Sample location offset 3 feet to the east of the original designated location due to obstruction.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-46 (Continued)
## Visual Characterization and Description of Soil Cores taken to Four Foot Depth at Site C and Site 129-3

| DESCRIPTION [1] | | | | ANALYSIS | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | Nominal Depth (ft) | Column Length[2] (in.) | | Depth[3] (ft) | Total Pb, mg/kg | $H_20$-sol. Pb, mg/kg | EDTA as $Na_2$EDTA, mg/kg | EDTA as EDTA, mg/kg |
| ----------Site C---------- | | | | | | | | |
| SB-12 | 2-4 | 13.5 | 5” medium brown fine loamy sand;<br>2” medium brown clay;<br>4” medium brown fine loamy sand;<br>1” dark black clay;<br>1” fine sand, cobbles | 3<br>4 | 729<br>890 | 281<br>296 | 1,370<br>1,390 | 1,191<br>1,208 |
| SB-13 | 0-2 | 15.5 | 8” dark brown loamy sand, high O.M. content;<br>1” limestone gravel;<br>2” dark brown loamy sand, high O.M. content;<br>4.5” light brown fine sand | 1<br>2 | 2,100<br>6 | 25<br><1 | <0.3<br><0.3 | <0.3<br><0.3 |
| SB-13 | 2-4 | 17.0 | 1.5” light brown fine sand;<br>1” dark organic fine sand;<br>6” light brown fine sand;<br>9” medium brown fine sand w/ numerous cobbles | 3<br>4 | <1<br><1 | <1<br><1 | <0.3<br><0.3 | <0.3<br><0.3 |
| SB-14 | 0-2 | 11.0 | 4” dark brown organic loamy sand;<br>8” light brown fine sand mixed with char material | 1<br>2 | 4,820<br><1 | 156<br><1 | 199<br><0.3 | 173<br><0.3 |
| SB-14 | 2-4 | 17.5 | 2” light brown fine sand;<br>2” char material;<br>13” light brown fine sand | 3<br>4 | <1<br><1 | <1<br><1 | <0.3<br>10 | <0.3<br>9 |
| SB-15 | 0-2 | 15.0 | 4” dark organic loamy sand and char;<br>11” medium brown sandy loam, clay slicks and char material throughout | 1<br>2 | 3,870<br>1,160 | 42<br>13 | <0.3<br>5 | <0.3<br>4 |
| SB-15 | 2-4 | 17.75 | 2” dark woody fragments;<br>16” medium brown sandy clay $Fe_2O_3$ inclusions, Mn concretions | 3<br>4 | 969<br>8,880 | 3<br>19 | 16<br>73 | 14<br>63 |

(1) Soil is described incrementally from the top to the bottom of each column.

(2) Length as taken from field which represents a two-foot depth increment in the soil. Compaction during sampling reduced the length of the sample to less than two feet.

(3) Depth is in 1-foot increments. Compaction during sampling reduced the incremental length of the soil sample to less than one foot.

(4) Sample location offset 3 feet to the east of the original designated location due to obstruction.

**NOTE:** Analytical results are based on comparison with $Na_2$EDTA standards and are calculated as mg/kg or mg/L $Na_2$EDTA. Earlier reports on this project reported EDTA results calculated as $Na_2$EDTA without note. This Results Report shows the data calculated as $Na_2$EDTA and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2$EDTA) = 0.8692.

## Table 5-46 (Continued)
## Visual Characterization and Description of Soil Cores taken to Four Foot Depth at Site C and Site 129-3

| DESCRIPTION[1] | | | | ANALYSIS | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | Depth (ft) | Column length[2] (in.) | | Depth[3] (ft) | Total Pb, mg/kg | $H_20$-sol. Pb, mg/kg | EDTA as $Na_2EDTA$, mg/kg | EDTA as EDTA, mg/kg |
| ----------Site 129-3---------- | | | | | | | | |
| 129-3/SB-1 | 0-2 | 21.0 | 21" light brown fine sand | 1<br>2 | <1<br><1 | <1<br><1 | 4<br><0.3 | 3<br><0.3 |
| 129-3/SB-1 | 2-4 | 20.5 | 16" medium brown fine sandy loam with sandy clay lenses;<br>4" medium brown fine sandy loam | 3<br>4 | <1<br><1 | <1<br><1 | <0.3<br>2 | <0.3<br>2 |
| 129-3/SB-2 | 0-2 | 16.25 | 16.5" medium brown fine sandy loam | 1<br>2 | 30<br>18 | <1<br><1 | 7<br><0.3 | 6<br><0.3 |
| 129-3/SB-2 | 2-4 | 18.0 | 14" medium brown fine sandy loam;<br>4" medium brown fine sandy clay | 3<br>4 | 14<br>6 | <1<br><1 | 1<br><0.3 | 1<br><0.3 |
| 129-3/SB-3 | 0-2 | 19.0 | 7" light brown fine sand, organic material;<br>5" dark brown clay lense w/ woody particles;<br>2" light brown fine sand;<br>5" medium brown sandy clay | 1<br>2 | 49<br>16 | 2<br><1 | 3<br><0.3 | 3<br><0.3 |
| 129-3/SB-3 | 2-4 | 19.0 | 13" medium brown fine sandy loam;<br>5.5" medium brown fine sandy clay | 3<br>4 | 162<br>33 | 17<br>2 | 44<br>11 | 38<br>10 |
| 129-3/SB-4 | 0-2 | 16.25 | 2" organic fine sand;<br>12.5" medium brown fine sand;<br>3" dark brown sandy clay | 1<br>2 | <1<br>5 | <1<br><1 | 8<br>1 | 7<br>1 |
| 129-3/SB-4 | 2-4 | 21.0 | 10" medium brown fine loamy sand;<br>6 " albic clay layer;<br>4" medium brown loam | 3<br>4 | <1<br><1 | 1<br>1 | 10<br><0.3 | 9<br><0.3 |

(1) Soil is described incrementally from the top to the bottom of each column.

(2) Length as taken from field which represents a two-foot depth increment in the soil. Compaction during sampling reduced the length of the sample to less than two feet.

(3) Depth is in 1-foot increments. Compaction during sampling reduced the incremental length of the soil sample to less than one foot.

(4) Sample location offset 3 feet to the east of the original designated location due to obstruction.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

Also, EDTA is not amenable to degradation by all microorganisms, and the particular population required for maximum removal may be lacking or low in this soil. The top two feet of this soil generally appeared to be in an aerobic state. The carbonate content in the top two feet and the higher pH was an indication that degradation had occurred in this zone. The greater than 1:1 molar ratio of EDTA to lead in all groundwater samples indicates that dissolution of the EDTA complex did likely occur, with subsequent release and re-precipitation of lead in the soil. However, the lower soil layers showed signs of waterlogging which most likely resulted in a reduced population of the appropriate aerobic microorganisms. Movement to groundwater depths obviously precluded photodegradation.

A full appreciation for the generally coarse-textured nature of the soil at Site C and the amount and variety of debris present was not gained until the deep core soil samples were taken and dissected at the end of the demonstration. At that time the true diversity of the soils, and of the waste materials and the potential effect on the outcome of the demonstration became apparent. It is likely that some leaching of EDTA (and lead) occurred from the upper layers due to these factors. Periodic water saturation of the upper soil layers due to a fluctuating water table of unknown height may have resulted in "washing" of the soil, and EDTA that was bound in the soil may have been re-solubilized and carried into the lower depths. Preferential flow and channeling caused by debris may have promoted movement in to the groundwater stream.

The data in Table 5-47 for the analysis of other cations in the soil at Site C clearly shows the potential for other cations to compete with lead for complexation by EDTA. The predominance of the basic cations Ca and Mg, as well as high concentrations of Fe, radically change the molar balance between EDTA and lead. There was an average of about 20 moles of lead in the soil over the 4-ft depth range; for Ca, Fe, and Mg, the averages were 276, 222, and 202. From these results, it is not surprising to see the increased EDTA:lead ratio in water samples due to displacement of lead in the EDTA complex by these cations.

#### 5.2.10.5 Overview of 2000 Groundwater, Surface Water, and Deep Core Soil Sampling Activities and Results at Site C

##### 5.2.10.5.1 Sample Collection

On April 11, 2000, the Army (AEC, TCAAP) and the MPCA collected splits of six groundwater hydro-punch samples and one drainage ditch surface water sample. On May 4, 2000, four surface water samples were collected at Site C:

- Upgradient to the previous sampled location.
- At the previous location.
- Down-gradient to the previous location.
- Exiting Site C further down-gradient to the previous location.

Additional groundwater samples were taken on May 17 and May 30, 2000, to identify the extent of the impacted area. A total of 12 groundwater samples and a combined total of 5 field and rinse blanks were collected using the hydro-punch technique.

Soil borings, to a depth of four feet, were collected on April 11, 2000 (Figures 5-9, 5-10), by TCAAP and sent to TVA for EDTA and lead analyses. Sampling locations were internal to the plot with several taken outside the plot perimeter.

**5.2.10.5.2 Analysis and Results**

Based on the analytical results from the four surface water samples in the drainage ditch (SW2-1, SW2-2, SW2-3, and SW2-4), and the discontinuous surface water in the drainage ditch, lead does not appear to be migrating from the phytoremediation plot due to solubilization by EDTA. Site C-1 is located just north of the drainage ditch flowing east to west. The proximity of this site to the drainage ditch, the slope toward the ditch, combined with the past burning and disposal operations at this site are strong indicators that Site C-1 is the probable cause of the lead detection at the last sampling point. It should be cautioned, however, that the detection of lead for a single sampling event is not indicative of contamination. Historical soil borings from Site C-1 do indicate the presence of lead in quantities sufficient enough to produce the levels of lead in the drainage ditch running east to west. The data also proves out that surface water contamination has not occurred and there is no immediate risk to the environment.

The analytical results indicated that the lead concentration in the groundwater was dropping rapidly moving away from the plot, basically dropping from 1100 ppm to 1 ppm in approximately 100 feet. Most likely lead levels would continue to decrease rapidly. Considering that the impacted groundwater is in Unit 1, an alluvium, extreme variations are probable within short distances in the aquifer. Based on the two periods of sampling, depths to groundwater are highly variable. During the April sampling event, groundwater was found at approximately 5 feet below the surface; during the May sampling at approximately 10 feet below the surface. The higher the groundwater the more likely the transport of EDTA due to "washing" of the soil by the fluctuating water table. This question could be answered by the placement of monitoring wells and monitoring over several seasons to understand water level changes as well as contaminant flow rates. Also, the ratios of EDTA:lead rise as distance away from the plot increases. This supports a basic conceptual model that the longer the EDTA exists in the groundwater the more likely it is for other cations to outcompete the lead in solution, leading to a general reduction of lead in solution over time and as distance from the plot increases.

EDTA and lead were found throughout the plot, with the concentration of total lead being greater than the concentration of lead which had complexed with EDTA. EDTA values were less than those of total lead within the plot and tended to be below the detection limit outside of the plot. The soil analytical results indicated that while EDTA and lead were found in the shallow soils (less than 4 feet), these levels were lower than were observed in the April round of groundwater sampling. Soil concentrations for EDTA ranged from less than 0.3 ppm to 1,570 ppm. Concentrations of EDTA in the April groundwater samples were from less than 0.03 ppm up to 4,910 ppm. Only three of the soil samples were higher than the highest values seen in the May groundwater sampling of 739 ppm. Water soluble lead concentrations in the soil ranged from less than 1 ppm to 549 ppm; lead concentrations in the April groundwater samples ranged from less than 0.02 ppm to 988 ppm. It would appear from this data that the overall concentrations of EDTA are decreasing in the soil column and that the EDTA is degrading at the site as was originally expected.

## Table 5-47
## Analysis of Other Cations in Deep Soil Cores Taken from Site C

| Soil Boring Location | Depth (ft) | pH | Pb (Total) | Pb (Water Soluble) | EDTA as $Na_2EDTA$ | EDTA as EDTA | Al | Sb | As | Ba | Be | Ca | Co | Cu | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mg/kg | | | | | | | | | | | | | |
| 1 | 1 | 8.68 | 32 | <1.04[1] | <0.3[1] | <0.3[1] | 7,400 | <2[1] | <1[1] | 85 | 0.58 | 14,000 | 6.0 | 19 | 11,300 |
| 1 | 2 | 8.68 | <1[1] | <1.04 | <0.3 | <0.3 | 6,350 | <2 | <1 | 71 | 0.54 | 6,260 | 6.6 | 16 | 12,300 |
| 1 | 3 | 8.61 | <1 | <1.07 | <0.3 | <0.3 | 5,140 | <2 | <1 | 38 | 0.50 | 5,590 | 4.4 | 11 | 9,700 |
| 1 | 4 | 8.65 | <1 | <1.11 | <0.3 | <0.3 | 7,170 | <2 | <1 | 47 | 0.54 | 9,390 | 4.5 | 14 | 9,660 |
| 2 | 1 | 8.17 | 888 | 16 | <0.3 | <0.3 | 5,310 | <2 | <1 | 183 | 0.51 | 14,800 | 4.9 | 192 | 11,000 |
| 2 | 2 | 9.55 | 7,440 | 116 | 5 | 4 | 5,780 | <2 | <1 | 2,470 | 0.48 | 11,500 | 5.9 | 665 | 20,200 |
| 2 | 3 | 9.04 | 1,860 | 49 | 15 | 13 | 6,500 | <2 | <1 | 334 | 0.52 | 16,300 | 4.6 | 238 | 10,900 |
| 2 | 4 | 8.03 | 325 | 49 | 340 | 296 | 2,940 | <3 | <2 | 77 | 0.63 | 20,400 | 3.2 | 109 | 12,600 |
| 2 Dup.[2] | 1 | 9.33 | 1,440 | 45 | 5 | 4 | 4,960 | <1[1] | <1 | 131 | 0.25 | 21,700 | 5.4 | 348 | 13,700 |
| 2 Dup.[2] | 2 | 9.46 | 3,100 | 66 | 4 | 3 | 5,520 | <1 | <0.9[1] | 747 | 0.26 | 12,000 | 5.5 | 289 | 10,100 |
| 2 Dup.[2] | 3 | 8.48 | 1,610 | 31 | 82 | 71 | 4,800 | <2 | <1 | 471 | 0.24 | 13,500 | 3.7 | 608 | 8,630 |
| 2 Dup.[2] | 4 | 7.97 | 212 | 21 | 116 | 101 | 1,760 | <1 | <1 | 31 | 0.11 | 9,770 | 2.5 | 44 | 5,680 |
| 3 | 1 | 9.14 | 432 | 6 | <0.3 | <0.3 | 4,700 | <2 | <1 | 134 | 0.19 | 10,000 | 4.4 | 209 | 14,500 |
| 3 | 2 | 9.61 | 23,200 | 245 | 7 | 6 | 5,390 | 206 | <1 | 843 | 0.18 | 16,500 | 4.6 | 1,500 | 10,600 |
| 3 | 3 | 9.51 | 152 | 43 | 94 | 82 | 5,650 | <2 | <1 | 42 | 0.25 | 13,100 | 4.3 | 56 | 11,700 |
| 3 | 4 | 9.42 | 127 | 50 | 192 | 167 | 5,030 | <2 | <1 | 44 | 0.24 | 6,570 | 4.8 | 84 | 8,850 |
| 4 | 1 | 7.76 | 149 | 2 | <0.3 | <0.3 | 8,960 | <1 | <1 | 37 | 0.24 | 6,230 | 11.6 | 72 | 17,400 |
| 4 | 2 | 9.74 | 44,100 | 12 | 25 | 22 | 3,980 | 232 | <1 | 386 | 0.13 | 18,000 | 4.2 | 6,750 | 11,400 |
| 4 | 3 | 9.75 | 33,700 | 36 | 80 | 70 | 4,900 | 349 | <1 | 209 | 0.23 | 12,600 | 5.2 | 3,920 | 12,800 |
| 4 | 4 | 9.09 | 15,200 | 16 | 220 | 191 | 5,010 | 2 | <1 | 411 | 0.22 | 18,100 | 5.0 | 1,530 | 12,000 |
| 5 | 1 | 8.58 | 3,720 | 46 | <0.3 | <0.3 | 5,680 | <2 | <1 | 190 | 0.25 | 15,000 | 4.8 | 460 | 10,600 |
| 5 | 2 | 8.49 | 30 | 8 | 52 | 45 | 4,220 | <1 | <1 | 38 | 0.22 | 3,370 | 4.5 | 17 | 9,070 |
| 5 | 3 | 8.91 | <1 | <1.10[1] | <0.3 | <0.3 | 3,950 | <2 | <1 | 24 | 0.19 | 4,190 | 4.3 | 14 | 8,670 |
| 5 | 4 | 8.94 | <1 | <1.07[1] | <0.3 | <0.3 | 6,110 | <2 | <1 | 33 | 0.32 | 6,230 | 5.7 | 12 | 12,400 |
| 6 | 1 | 9.27 | 13,500 | 42 | 7 | 6 | 5,300 | <2 | <1 | 172 | 0.47 | 21,400 | 5.2 | 9,080 | 19,300 |
| 6 | 2 | 8.92 | 3,440 | 56 | 66 | 57 | 7,020 | <2 | <1 | 669 | 0.55 | 9,260 | 6.0 | 745 | 10,300 |

(1) MDL - Method Detection Limit.
(2) Dup. - Duplicate Sample.
(3) Moisture (%) refers to the moisture content of the soil as received from the field. All analyses are reported on an oven dry weight basis.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-47 (Continued)
## Analysis of Other Cations in Deep Soil Cores Taken from Site C

| Soil Boring Location | Depth (ft) | pH | Pb (Total) | Pb (Water Soluble) | EDTA as $Na_2EDTA$ | EDTA as EDTA | Al | Sb | As | Ba | Be | Ca | Co | Cu | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mg/kg | | | | | | | | | | | | | |
| 6 | 3 | 8.86 | 203 | 34 | 52 | 45 | 5,370 | <1 | <1[1] | 39 | 0.25 | 15,500 | 4.3 | 9 | 11,300 |
| 6 | 4 | 8.74 | 68 | 27 | 79 | 69 | 7,450 | <2 | <1 | 47 | 0.29 | 7,340 | 5.6 | 11 | 12,900 |
| 7 | 1 | 9.24 | 4,820 | 53 | 7 | 6 | 5,910 | <1 | <0.9 | 302 | 0.22 | 20,300 | 4.7 | 672 | 11,100 |
| 7 | 2 | 8.60 | 270 | 13 | 4 | 3 | 18,600 | <2 | <1 | 83 | 0.71 | 3,570 | 6.7 | 46 | 30,200 |
| 7 | 3 | 9.02 | 1,090 | 32 | 15 | 13 | 6,550 | <2 | <1 | 127 | 0.27 | 7,060 | 5.6 | 164 | 15,300 |
| 7 | 4 | 8.99 | 5,850 | 7 | 7 | 6 | 4,500 | <1 | <1 | 296 | 0.19 | 12,200 | 4.4 | 426 | 16,500 |
| 8 | 1 | 9.68 | 100 | 92 | 1,800 | 1,565 | 6,080 | <2 | <1 | 65 | 0.27 | 8,680 | 3.6 | 62 | 9,650 |
| 8 | 2 | 9.04 | 13,600 | 117 | 363 | 316 | 6,000 | <1 | <0.9 | 337 | 0.21 | 19,400 | 5.6 | 1,470 | 12,300 |
| 8 | 3 | 9.06 | 24,200 | 84 | 377 | 328 | 6,000 | 92 | <1 | 229 | 0.20 | 34,800 | 5.3 | 1,100 | 12,800 |
| 8 | 4 | 8.95 | 830 | 48 | 815 | 708 | 4,190 | <2 | <1 | 66 | 0.20 | 4,920 | 4.0 | 545 | 8,200 |
| 9 | 1 | 8.76 | 7,000 | 81 | <0.3[1] | <0.3[1] | 8,250 | <1 | <0.9 | 316 | 0.20 | 21,200 | 5.6 | 1,070 | 11,000 |
| 9 | 2 | 8.78 | 126 | 2 | <0.3 | <0.3 | 6,210 | <1 | <1 | 127 | 0.33 | 6,220 | 7.5 | 22 | 13,300 |
| 9 | 3 | 8.25 | <1[1] | <1.00[1] | <0.3 | <0.3 | 3,980 | <1 | <1 | 24 | 0.18 | 2,140 | 4.0 | 9 | 8,620 |
| 9 | 4 | 8.35 | <1 | <1.02 | <0.3 | <0.3 | 5,070 | <2 | <1 | 27 | 0.23 | 2,530 | 4.7 | 11 | 10,100 |
| 10 | 1 | 9.53 | 427 | 42 | 81 | 70 | 4,820 | <1 | <0.9 | 84 | 0.49 | 4,000 | 5.0 | 117 | 10,300 |
| 10 | 2 | 9.71 | 10,400 | 73 | 37 | 32 | 5,650 | <1 | <1 | 562 | 0.43 | 15,200 | 5.2 | 742 | 12,000 |
| 10 | 3 | 9.55 | 161 | 56 | 180 | 156 | 3,960 | <2 | <1 | 57 | 0.43 | 1,580 | 3.5 | 52 | 9,050 |
| 10 | 4 | 9.43 | 171 | 70 | 205 | 178 | 4,880 | <1 | <1 | 43 | 0.52 | 5,020 | 3.5 | 46 | 9,230 |
| 11 | 1 | 9.69 | 1,980 | 253 | 500 | 435 | 7,660 | <2 | <1 | 264 | 0.37 | 25,200 | 4.4 | 268 | 15,700 |
| 11 | 2 | 9.10 | 313 | 136 | 736 | 640 | 7,180 | <2 | <1 | 76 | 0.31 | 7,290 | 5.6 | 77 | 12,200 |
| 11 | 3 | 8.45 | 355 | 178 | 570 | 495 | 6,580 | <2 | <1 | 54 | 0.30 | 8,700 | 7.5 | 115 | 13,300 |
| 11 | 4 | 8.51 | 87 | 14 | 65 | 56 | 5,040 | <2 | <1 | 37 | 0.22 | 6,430 | 4.9 | 32 | 11,000 |
| 12 | 1 | 7.93 | 525 | 96 | 293 | 255 | 8,030 | <2 | <1 | 108 | 0.28 | 7,240 | 6.3 | 4,880 | 15,200 |
| 12 | 2 | 9.27 | 17,800 | 549 | 350 | 304 | 4,970 | <1 | <1 | 426 | 0.15 | 15,700 | 5.1 | 8,860 | 27,300 |

(1) MDL - Method Detection Limit.
(2) Dup. - Duplicate Sample.
(3) Moisture (%) refers to the moisture content of the soil as received from the field. All analyses are reported on an oven dry weight basis.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-47 (Continued)
## Analysis of Other Cations in Deep Soil Cores Taken from Site C

| Soil Boring Location | Depth (ft) | pH | Pb (Total) | Pb (Water Soluble) | EDTA as $Na_2EDTA$ | EDTA as EDTA | Al | Sb | As | Ba | Be | Ca | Co | Cu | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mg/kg | | | | | | | | | | | | | |
| 12 | 3 | 9.21 | 729 | 281 | 1,370 | 1,191 | 6,000 | <1 | <0.9 | 56 | 0.29 | 9,620 | 4.0 | 191 | 11,200 |
| 12 | 4 | 8.80 | 890 | 296 | 1,390 | 1,208 | 7,630 | <2 | <1 | 75 | 0.33 | 12,700 | 7.7 | 274 | 15,300 |
| 13 | 1 | 8.44 | 2,100 | 25 | <0.3 | <0.3 | 7,000 | <2 | <1 | 149 | 0.59 | 9,640 | 6.8 | 517 | 15,900 |
| 13 | 2 | 8.38 | 6 | <1.00 | <0.3 | <0.3 | 3,170 | <1 | <1 | 19 | 0.15 | 2,100 | 3.6 | 10 | 7,160 |
| 13 | 3 | 8.20 | <1 | <0.99 | <0.3 | <0.3 | 2,780 | <1 | <1 | 13 | 0.13 | 1,620 | 3.1 | 7 | 6,480 |
| 13 | 4 | 8.39 | <1 | <1.01 | <0.3 | <0.3 | 5,780 | <1 | <1 | 37 | 0.28 | 3,980 | 7.5 | 11 | 12,500 |
| 14 | 1 | 9.77 | 4,820 | 156 | 199 | 173 | 5,370 | <1 | <1 | 319 | 0.22 | 20,400 | 4.5 | 460 | 10,000 |
| 14 | 2 | 8.63 | <1[1] | <1.01[1] | <0.3[1] | <0.3[1] | 4,270 | <1[1] | <1[1] | 21 | 0.18 | 4,150 | 4.1 | 10 | 8,610 |
| 14 | 3 | 8.36 | <1 | <1.01 | <0.3 | <0.3 | 4,530 | <2 | <1 | 26 | 0.21 | 2,020 | 4.5 | 9 | 9,210 |
| 14 | 4 | 8.55 | <1 | <1.01 | 10 | 9 | 4,990 | <1 | <1 | 29 | 0.29 | 4,710 | 5.0 | 11 | 12,400 |
| 15 | 1 | 8.52 | 3,870 | 42 | <0.3 | <0.3 | 6,250 | <2 | <1 | 227 | 0.25 | 12,100 | 5.6 | 539 | 11,800 |
| 15 | 2 | 8.65 | 1,160 | 13 | 5 | 4 | 5,600 | <1 | <1 | 184 | 0.23 | 13,800 | 5.3 | 918 | 14,900 |
| 15 | 3 | 8.86 | 969 | 3 | 16 | 14 | 6,000 | <2 | <1 | 201 | 0.27 | 21,200 | 6.0 | 1,020 | 14,700 |
| 15 | 4 | 8.73 | 8,880 | 19 | 73 | 63 | 4,050 | <2 | <1 | 506 | 0.09 | 11,300 | 47.1 | 2,010 | 19,300 |

(1) MDL - Method Detection Limit.
(2) Dup. - Duplicate Sample.
(3) Moisture (%) refers to the moisture content of the soil as received from the field. All analyses are reported on an oven dry weight basis.

**NOTE:** Analytical results are based on comparison with $Na_2EDTA$ standards and are calculated as mg/kg or mg/L $Na_2EDTA$. Earlier reports on this project reported EDTA results calculated as $Na_2EDTA$ without note. This Results Report shows the data calculated as $Na_2EDTA$ and as EDTA. The conversion factor is (292.24g/mol EDTA)/(336.21g/mol $Na_2EDTA$) = 0.8692.

## Table 5-47 (Continued)
## Analysis of Other Cations in Deep Soil Cores Taken from Site C

| Soil Boring Location | Depth (ft) | Mg | Mn | Ni | K | Na | Sr | Tl | Ti | V | Zn | Moisture (%) [3] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mg/kg | | | | | | | | | | |
| 1 | 1 | 7,200 | 342 | 14.9 | 1,260 | 145 | 37 | <3[3] | 463 | 33 | 32 | 6.34 |
| 1 | 2 | 3,980 | 482 | 16.3 | 771 | 215 | 31 | <3 | 490 | 31 | 26 | 6.10 |
| 1 | 3 | 3,500 | 193 | 11.7 | 758 | 146 | 25 | <3 | 426 | 22 | 23 | 8.79 |
| 1 | 4 | 5,180 | 200 | 12.3 | 840 | 156 | 34 | <3 | 374 | 27 | 26 | 11.69 |
| 2 | 1 | 5,110 | 179 | 12.7 | 1,940 | 159 | 89 | <3 | 378 | 26 | 75 | 12.96 |
| 2 | 2 | 5,800 | 241 | 14.1 | 1,240 | 288 | 1,180 | <3 | 432 | 25 | 146 | 6.24 |
| 2 | 3 | 5,210 | 212 | 11.8 | 1,860 | 288 | 278 | <3 | 449 | 24 | 65 | 16.70 |
| 2 | 4 | 3,280 | 620 | 20.1 | 1,790 | 207 | 65 | <5 | 232 | 12 | 69 | 57.07 |
| 2 Dup.[2] | 1 | 8,400 | 296 | 11.8 | 1,210 | 221 | 69 | <2 | 435 | 26 | 71 | 4.56 |
| 2 Dup.[2] | 2 | 6,530 | 216 | 12.2 | 981 | 256 | 461 | <2 | 442 | 19 | 70 | 4.46 |
| 2 Dup.[2] | 3 | 3,810 | 186 | 8.7 | 1,530 | 163 | 334 | <3 | 264 | 18 | 59 | 26.52 |
| 2 Dup.[2] | 4 | 1,810 | 267 | 8.1 | 395 | 117 | 31 | <2 | 177 | 8 | 30 | 7.40 |
| 3 | 1 | 6,440 | 144 | 11.1 | 1,570 | 166 | 41 | <3 | 358 | 18 | 88 | 10.55 |
| 3 | 2 | 6,900 | 509 | 11.4 | 1,120 | 293 | 554 | <2 | 365 | 19 | 207 | 7.55 |
| 3 | 3 | 5,750 | 181 | 11.9 | 1,300 | 252 | 32 | <3 | 439 | 26 | 35 | 10.42 |
| 3 | 4 | 3,740 | 209 | 9.3 | 1,340 | 184 | 23 | <3 | 696 | 21 | 31 | 10.75 |
| 4 | 1 | 6,750 | 277 | 25.4 | 876 | 449 | 30 | <2 | 718 | 33 | 66 | 3.95 |
| 4 | 2 | 6,920 | 251 | 10.3 | 974 | 225 | 485 | <3 | 407 | 17 | 614 | 8.94 |
| 4 | 3 | 7,070 | 248 | 15.0 | 1,150 | 198 | 217 | <3 | 489 | 24 | 385 | 13.09 |
| 4 | 4 | 7,530 | 263 | 11.1 | 723 | 296 | 421 | <2 | 413 | 24 | 189 | 8.21 |
| 5 | 1 | 4,660 | 225 | 11.0 | 722 | 264 | 138 | <3 | 366 | 25 | 90 | 13.05 |
| 5 | 2 | 2,300 | 204 | 9.4 | 502 | 167 | 28 | <2 | 457 | 27 | 18 | 6.52 |
| 5 | 3 | 2,490 | 172 | 9.6 | 478 | 174 | 21 | <3 | 403 | 24 | 17 | 11.86 |
| 5 | 4 | 3,440 | 156 | 12.7 | 925 | 291 | 43 | <3 | 629 | 35 | 21 | 11.82 |
| 6 | 1 | 6,600 | 215 | 15.3 | 1,450 | 166 | 110 | <3 | 391 | 25 | 809 | 8.28 |
| 6 | 2 | 5,130 | 217 | 14.6 | 1,350 | 197 | 397 | <3 | 554 | 30 | 91 | 11.59 |
| 6 | 3 | 9,120 | 365 | 9.8 | 794 | 126 | 62 | <2 | 404 | 24 | 28 | 6.90 |
| 6 | 4 | 4,370 | 164 | 11.8 | 1,150 | 201 | 102 | <3 | 576 | 36 | 25 | 7.66 |
| 7 | 1 | 4,930 | 185 | 10.6 | 1,130 | 269 | 205 | <2 | 549 | 25 | 116 | 4.65 |
| 7 | 2 | 3,530 | 102 | 15.1 | 2,860 | 71 | 112 | 10.10 | 442 | 72 | 45 | 16.94 |
| 7 | 3 | 4,400 | 206 | 12.2 | 1,290 | 170 | 84 | <3 | 598 | 31 | 68 | 10.74 |
| 7 | 4 | 4,990 | 333 | 9.5 | 664 | 166 | 211 | <2[1] | 410 | 21 | 100 | 7.87 |

(1) MDL - Method Detection Limit.
(2) Dup. - Duplicate Sample.
(3) Moisture (%) refers to the moisture content of the soil as received from the field. All analyses are reported on an oven dry weight basis.

## Table 5-47 (Continued)
## Analysis of Other Cations in Deep Soil Cores Taken from Site C

| Soil Boring Location | Depth (ft) | Mg | Mn | Ni | K | Na | Sr | Tl | Ti | V | Zn | Moisture (%)[3] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mg/kg | | | | | | | | | | |
| 8 | 1 | 4,380 | 128 | 8.4 | 3,080 | 137 | 25 | <3 | 371 | 27 | 31 | 6.77 |
| 8 | 2 | 8,570 | 313 | 13.4 | 1,210 | 323 | 304 | <2 | 497 | 25 | 223 | 6.80 |
| 8 | 3 | 8,860 | 274 | 12.1 | 1,330 | 169 | 339 | <3 | 448 | 22 | 171 | 12.24 |
| 8 | 4 | 2,590 | 182 | 8.4 | 1,090 | 102 | 52 | <3 | 404 | 22 | 75 | 10.77 |
| 9 | 1 | 7,610 | 205 | 16.3 | 690 | 528 | 730 | <2 | 401 | 24 | 170 | 4.66 |
| 9 | 2 | 4,410 | 268 | 11.6 | 699 | 109 | 54 | <2 | 550 | 24 | 32 | 6.07 |
| 9 | 3 | 1,780 | 215 | 9.2 | 586 | 127 | 49 | <2 | 372 | 19 | 13 | 3.53 |
| 9 | 4 | 2,040 | 158 | 9.9 | 695 | 132 | 45 | <3 | 458 | 28 | 15 | 6.77 |
| 10 | 1 | 3,050 | 205 | 13.6 | 1,350 | 171 | 23 | <2 | 385 | 23 | 94 | 4.08 |
| 10 | 2 | 6,580 | 197 | 12.6 | 1,420 | 313 | 391 | <2 | 500 | 22 | 167 | 5.04 |
| 10 | 3 | 1,770 | 182 | 10.7 | 1,250 | 105 | 15 | <3 | 353 | 21 | 29 | 5.42 |
| 10 | 4 | 3,140 | 178 | 8.7 | 1,990 | 97 | 45 | <2 | 353 | 25 | 36 | 8.04 |
| 11 | 1 | 10,400 | 292 | 9.7 | 3,920 | 176 | 133 | <3 | 336 | 38 | 112 | 8.76 |
| 11 | 2 | 4,150 | 404 | 11.8 | 2,490 | 242 | 22 | <3 | 568 | 37 | 67 | 7.94 |
| 11 | 3 | 5,640 | 299 | 17.5 | 1,540 | 244 | 31 | <3 | 693 | 32 | 79 | 10.16 |
| 11 | 4 | 4,100 | 355 | 11.4 | 732 | 206 | 29 | <3 | 490 | 24 | 27 | 7.12 |
| 12 | 1 | 4,710 | 209 | 13.8 | 1,840 | 274 | 30 | <3 | 675 | 34 | 666 | 8.21 |
| 12 | 2 | 5,050 | 251 | 28.0 | 1,300 | 340 | 257 | 12.60 | 366 | 19 | 908 | 4.28 |
| 12 | 3 | 4,340 | 292 | 9.6 | 2,040 | 128 | 25 | <2 | 393 | 26 | 124 | 4.55 |
| 12 | 4 | 5,900 | 439 | 22.7 | 2,270 | 280 | 112 | <3 | 576 | 33 | 123 | 24.98 |
| 13 | 1 | 5,340 | 447 | 17.2 | 887 | 161 | 61 | <3 | 369 | 26 | 486 | 7.09 |
| 13 | 2 | 1,550 | 207 | 7.6 | 402 | 117 | 16 | <2 | 303 | 16 | 13 | 2.87 |
| 13 | 3 | 1,300 | 197 | 7.3 | 356 | 94 | 13 | <2 | 278 | 14 | 11 | 2.98 |
| 13 | 4 | 3,500 | 409 | 14.4 | 575 | 177 | 16 | <2 | 687 | 31 | 23 | 3.81 |
| 14 | 1 | 6,090 | 178 | 10.7 | 1,580 | 240 | 192 | <2 | 466 | 22 | 121 | 6.69 |
| 14 | 2 | 2,180 | 187 | 9.3 | 455 | 187 | 12 | <2 | 342 | 19 | 16 | 2.83 |
| 14 | 3 | 1,590 | 267 | 8.6 | 559 | 122 | 11 | <3 | 435 | 25 | 14 | 4.37 |
| 14 | 4 | 2,470 | 252 | 9.3 | 734 | 162 | 16 | <2 | 513 | 25 | 19 | 5.17 |
| 15 | 1 | 5,230 | 262 | 12.2 | 786 | 154 | 179 | <3 | 467 | 27 | 104 | 7.44 |
| 15 | 2 | 6,520 | 385 | 11.8 | 841 | 255 | 145 | <2 | 451 | 27 | 129 | 6.05 |
| 15 | 3 | 9,070 | 363 | 13.8 | 683 | 304 | 73 | <3 | 627 | 27 | 162 | 8.60 |
| 15 | 4 | 4,130 | 2,870 | 102.0 | 287 | 202 | 190 | 619 | 342 | 28 | 211 | 10.22 |

(1) MDL - Method Detection Limit.
(2) Dup. - Duplicate Sample.
(3) Moisture (%) refers to the moisture content of the soil as received from the field. All analyses are reported on an oven dry weight basis.

The soils at Site C were found to be much more heterogeneous than was originally anticipated. Seven soil types ranging from sand to clay were identified in the cores from the latest sampling events. This is contrary to the single soil type identified in the RI/FS. Clay and sand lenses were common throughout the soil, and a considerable amount of burned as well as unburned wood was found. Debris consisting of glass, metal, wire, concrete, bullets, and brass shell casings was found throughout the plot. Iron oxide deposition was common in the cores as were manganese sulfide concretions (usually a representation of alternating aerobic and anaerobic zones in the soil profile, likely caused by a fluctuating water table). In soils the major mechanisms determining the fate of EDTA and therefore its ability to continue to solubilize lead are:

- Adsorption to iron oxide and soil organic matter
- Binding to clay particles
- Reactions with soil cations
- Microbial degradation
- Rates of movement through soil

Most likely the extreme heterogeneous nature of these shallow soils accelerated movement of EDTA through the soil column and reduced the contact time of EDTA in the soils, which affected the rate at which the reductive fate processes were taking place. It is also possible that the microbial population in the shallow soils was (is) low, due to other toxic contaminants and debris in the soils and perhaps the slow draining of the soils, which would lead to waterlogging during significant periods of the year. In addition, of interest is the relatively high pH of the shallow soils, which averages from 8.5 to 9.5. This may be partly attributed to degradation of EDTA and release of ammonia from the amine groups and the formation of carbonate compounds from the $CO_2$ that is also released. As lead is more soluble at lower pH, the amount of soluble lead available for movement will continue to decline. A natural drop in soil pH to a level that would re-solubilize lead is highly unlikely.

In conclusion, results of the soil, groundwater, and surface water sampling suggested that, although the EDTA has lasted longer in the soil and in groundwater than originally expected, the concentrations of soluble lead within and outside the demonstration plot are falling through time and will continue to fall. These conclusions can be verified through monitoring over time of the soils, groundwaters, and surface waters.

#### 5.2.10.6 Summary and Conclusions

This project was funded by ESTCP from January 1998 through May 2000 as reported here. A summary showing the lead concentrations in plants, crop yields, and the amount of lead removed in the plant biomass for the two year demonstration in 1998 and 1999 is shown in Table 5-48. A detailed discussion of these results is presented immediately following this table. Selection of the demonstration sites by TCAAP and ATK based on information in the RI/FS was done in October 1997. The sites chosen were a 0.2-acre area on Site C (total area - 16.4 acres) and a 0.2-acre area on Site 129-3 (total area - 1.5 acres) at TCAAP. Due to time constraints for beginning the project, soil samples for preliminary site characterization were collected under snow cover in November 1997, and a complete visual and physical assessment of the sites was not possible. For Site C, the preliminary assessment did not reveal how heterogeneous the soil

was and the nature and quantity of debris that had been dumped at the site. Site 129-3 was composed of a variety of glacial till debris which also was problematic to the demonstration.

The preliminary soil samples were analyzed to map lead concentrations within each area. Site C contained moderate to high levels of lead, whereas Site 129-3 had levels approaching or below the cleanup standard. The demonstration at Site 129-3 was intended to illustrate the effectiveness of phytoextraction methods near the conclusion of a remediation program, or for situations in which the level of contamination is low and the use of a “polishing treatment" is desirable. A high degree of spatial variability in lead concentrations, particularly at Site C, (standard deviations were equal to means) indicated the presence of particulate lead in addition to ionic lead forms.

Upon completion of preliminary analyses, the draft Technology Demonstration Plan was developed and submitted to ESTCP, AEC, TCAAP, USEPA, and MPCA. The draft Technology Demonstration Plan was thoroughly reviewed and comments were provided by each organization. The Technology Demonstration Plan was revised based on the comments, and written responses to comments were provided to the originating organization. The demonstration was conducted in accordance with the revised Technology Demonstration Plan.

The demonstration was initiated in 1998 with the planting of a grain corn crop. At Site C, large quantities of diverse scrap and debris (concrete, glass, wire, scrap metal, rail ties, burned and unburned wood, large cobbles, etc.) were unearthed during field preparation and had to be removed before the crop could be planted. In addition, an old hardpan and gravel road bed, from 6 to 12 inches beneath the soil surface, ran through the western half of the plot. Visually variously dark and light areas throughout the plot indicated burn areas and differing soil types. Apparently soil of different types was deposited at the site when scrap from other areas on the installation was brought in for disposal on the site. About one-third of the 1962 Pit (a burn and burial area for decontamination of large equipment that was backfilled with diverse soil) intruded on the southeastern quadrant of the plot. The topography of Site C was a depression consisting of a three-way concave slope east to west and south to north. Large boulders and cobbles deterred proper tillage at Site 129-3. The plot at Site 129-3 consisted of a three-way convex slope, with a north to south downhill slope.

Problems with growth and nutrition developed early on at Site C in the form of phosphorus and iron deficiencies in the plants. The deficiencies were treated by foliar applications of Fe and P which corrected visual symptoms, but the plants remained stunted and did not realize full yield potential, particularly in the western half of the plot underlain by the hardpan. The plants grew more normally in the eastern half of Site C, but the considerable debris and likely presence of other toxic soil contaminants limited full growth potential of the crop. Plant growth was much better at the more agronomically-suitable Site 129-3.

**Table 5-48**
**Summary of Phytoextraction Results for 1998 Corn and White Mustard and 1999 Corn at Site C and Site 129-3**

| Crop | Average Pb Concentration in Crop, % [1] | Yield, lb/acre | Pb Removed in Crop, lb |
|---|---|---|---|
| Site C, 1998 | | | |
| Grain corn | 0.65 | 4,250 | 27.6 |
| White mustard | 0.083 | 4,280 | 3.6 |
| | | | |
| Site 129-3, 1998 | | | |
| Grain corn | 0.13 | 7,155 | 9.3 |
| White mustard | 0.034 | 3,890 | 1.3 |
| | | | |
| Site C, 1999 [2] | | | |
| Silage corn | 0.854 | 2,076 | 17.7 |
| | | | |
| Site 129-3, 1999 [3] | | | |
| Silage corn | 0.010 | NA[4] | NA |
| | | | |

(1) Range in lead concentration in crop:
1998 grain corn - Site C: 0.330% - 1.130%;
Site 129-3: 0.0009% - 0.438%
1998 white mustard - Site C: 0.036% - 0.196%
Site 129-3: 0.044% - 0.173%
1999 silage corn - Site C: 0.034% - 0.138%
Site 129-3:
(2) Only 12 grids were sampled and harvested in 1999.
(3) Only 2 grids were sampled and harvested in 1999.
(4) NA = Not Applicable due to limited data.

Soil amendments (acetic acid to reduce soil pH to 5.5 and EDTA equimolar to the average total soil lead content) were applied in July 1998 to solubilize soil lead in order to facilitate uptake of lead into the plants. The amendments were applied based on results obtained in previous greenhouse studies and the average total lead content of the soil. However, the amount of EDTA was reduced by one-third from the maximum effective rate demonstrated in the greenhouse studies to partially offset any environmental effects of large chelate additions. The amendments were added in an amount of solution intended to saturate only the top two feet of soil (i.e., the rooting zone). The varying infiltration rates of the soil due to diverse soil textures and the three-way slope at Site C caused some run-off of amendments (primarily acetic acid, with a small amount of EDTA) from the plot area, and nearby cottonwood trees were affected. Although these trees are considered a "nuisance" tree, they were left in place at the beginning of the project at the request of AEC to minimize the environmental impact of the demonstration. Although not recognized initially, the roots from these trees extended into and throughout the plot. The runoff was only partially responsible for the damage to the trees which would have been affected regardless.

Lead uptake by the 1998 corn crop was promising, averaging 0.65% at Site C and 0.13% at Site 129-3. The range in concentration at Site C was from 0.33% to 1.13%, and at Site 129-3, lead concentrations in the crop ranged from less than 0.001% up to 0.44%. The biomass produced was less than anticipated, and consequently the amount of lead removed from the soil was not as great as anticipated. However, the extreme variability in soil lead concentrations, quite likely due to the presence of particulate lead, precluded a direct assessment of the amount of lead removed from the soil. Modern statistical procedures (i.e., parametric statistics, geostatistics, kriging analysis) were employed to distinguish differences in before and after lead concentrations in soil, but the variability in soil lead was simply too great to detect differences.

Uptake of EDTA by the 1998 corn constituted a viable mechanism for reducing the amount of EDTA remaining in the soil. Concentrations up to 72,000 mg EDTA/kg plant tissue were measured in plants from Site C and up to 11,000 mg/kg in plants at Site 129-3. This may have indicated uptake of the intact EDTA-lead complex by the plant, and thus a significant mechanism for removal of EDTA from the soil. Also possible was passive influx of EDTA into the plant due to root damage by EDTA, ion imbalance due to excessive influx of ions complexed by EDTA, or by solubilized lead.

Lysimeters were installed in the plots to monitor potential movement of lead or EDTA below the rooting zone. Intensive tillage and irrigation was performed during the month between harvest of the corn crop and planting of a white mustard crop to stimulate degradation of EDTA. Lead and EDTA were detected in the soil solution at Site C about two weeks after amendment addition and harvest of the corn. The concentration of EDTA and lead at Site C reached a maximum the first week in October 1998. However, these concentrations represented the contribution from only one lysimeter of the twelve that were installed, and the values from this lysimeter radically skewed the averaged results. When soil solution was not collected in this lysimeter, the average concentration of lead and EDTA in the solution decreased dramatically.

The lysimeter was installed correctly according to the manufacturer's instructions, and was effective in collecting the soil solution, although the amounts collected from week to week were somewhat erratic (Table 5-23). However, the lysimeter was installed in the area of the 1962 Pit, an area of the plot where extensive alteration to the native soil occurred due to dumping, burning, and soil excavation and replacement. Quite likely, the decomposing debris in the pit left channels and voids in the soil through which water from the surface could channel and collect. The porous cup may have been inserted into a void, and lead and EDTA-contaminated water from the treated upper soil layer may have pooled around the cup, thus accounting for the elevated concentrations of lead and EDTA in the solution. Alternately, a leakage could have occurred in the bentonite clay seal around the neck of the lysimeter at the soil surface, and leakage would have allowed channeling from the surface. Such a break would not have been obvious to an observer, since tilling operations normally covered the clay cap.

A white mustard crop was planted in August 1998 as the second crop in the demonstration year. The poor conditions at Site C, possibly some carryover EDTA, and toxic contaminants in the soil, likely thallium, combined to reduce viable stands at Site C by half. The final stand at Site 129-3 was about 90%. However, plants at both sites had a shallow rooting system caused by the excess rainfall. The white mustard crop at Site C had very woody, solid stems; the plants growing at Site 129-3 had hollow stems. Typically, mustard plants exhibit woody, solid stems.

A drip delivery system was used to supply EDTA to the 1998 white mustard crop over a 7-8 hour period. However, the slow rate of EDTA delivery through the system resulted in damage to the mustard before a desired level of lead uptake was achieved. The shallow root system was inefficient in scavenging lead much below 6 inches in the soil. The average EDTA concentration in white mustard at Site C was almost 8% and at Site 129-3 was almost 5%. EDTA is toxic to plants, and the high levels in these plants may have been a combination of prolonged exposure to EDTA and damage to root membranes which allowed passive influx of EDTA into the plant, and actual plant uptake of EDTA.

Overall, at both sites, there was no change in the total lead content in the top two feet of soil after the 1998 corn crop. Water-soluble lead had greatly increased since that was the reason for adding soil amendments in the first place, but higher concentrations of water-soluble lead were found in the top foot than in the lower layer. There was no change in soil pH after the corn crop. About three times as much EDTA was present in the top foot of soil as was found in the two foot depth. EDTA complexes with lead on a one-to-one molar basis. If the EDTA:lead ratio is greater than 1:1, this means that lead has been displaced from the EDTA by another cation. The equimolar EDTA:lead ratio originally imposed in the soil when the amendments were applied had increased from 1:1, which indicated that EDTA had complexed with elements other than lead. Lead had been displaced, quite likely by the abundance of calcium and magnesium ions, which at the soil pH of 8.0-8.3 would "swamp" the system, and lead would re-precipitate into insoluble form in the soil.

Immediately prior to adding amendments to 1998 white mustard, concentrations of water-soluble lead and EDTA were significantly higher in the two-foot soil depth. This may have been a result of downward movement due to multiple irrigation events. Again the EDTA:lead ratio had

shifted from 1:1, which indicated that lead had been displaced from the EDTA complex and had likely been re-precipitated in the soil.

**1999 Season**

A higher yielding, deeper rooting silage corn instead of grain corn was used in 1999 in an attempt to maximize lead uptake by the crop. Planting of corn was delayed by excessive rainfall until late May 1999. Heavy rainfall and cool temperatures shortly after planting caused poor stand establishment, and extensive bird damage necessitated several replantings, resulting in a plant stand of various growth stages. Due to insufficient growth of the corn that resulted in bare areas in the plots, only selected areas were designated to receive soil amendments of acetic acid and EDTA. Only these areas were used for pre-amendment plant and soil sampling. Only 12 grids at Site C and two grids at Site 129-3 received soil amendments in 1999.

Soil total lead concentrations in the 12 grids sampled before amendment application to 1999 corn were lower overall than observed in the 1998 growing season after amendment application to white mustard. Both EDTA and water-soluble lead in the soil were present at very low concentrations in samples taken immediately before soil amendment application in 1999. This may have been due to degradation of EDTA, adsorption of EDTA onto organic matter and soil minerals (e.g., iron oxides and hydroxides), with re-precipitation of lead in the soil, movement of EDTA and lead to soil depths below the sampling zone of 2 feet, or a combination of these factors.

Plant lead concentrations in 1999 plants before adding soil amendments were as low or lower than observed for corn and mustard prior to amendment additions in 1998. EDTA concentrations in the 1999 plants prior to amendment additions were below the method detection limit. This indicated that there was no carry-over lead or EDTA from the previous year taken up into the plant.

For the amendment application at Site C, a drip delivery system was used that contrasted with the 1998 system by having triple the number of delivery tubes which provided a much faster rate of amendment application. Amendments were applied by hand at Site 129-3 using a hose, since only two grids were selected for amendment application. On August 11, 1999, acetic acid and EDTA solutions were applied to the designated grids at Site C and at Site 129-3. Two to three days after amendment application, the treated areas were sampled for soil and plant lead, EDTA, and other COCs. Additionally, four locations at Site C immediately adjacent to the treated area were sampled for soil lead, EDTA, and other COCs to determine if lateral movement of amendments occurred. Attempts to collect soil solution samples before and after amendment application were unsuccessful.

The lysimeters did not collect soil solution in 1999. Random lysimeters pulled from the field did not show evidence of clogging due to algal growth or other obvious cause. A complicating factor in addition to the poor soil conditions and the variety of debris in the soil which affected performance may have been that the lysimeters were left in place in the soil during the winter of 1998, in accordance with the manufacturer's instructions (SoilMoisture Equipment Corp., P.O. Box 30025, Santa Barbara, CA 93105). However, freezing and thawing of the soil during the winter and the following spring likely led to shrinking of the soil away from the porous cup. This

would have prevented proper contact with the soil and a poor suction vacuum in the lysimeter during sampling attempts, although this was not obvious until attempts were made to collect soil solution in 1999. When contacted in regards to this problem, the manufacturer supported the position that loss of contact of the porous cup with the surrounding soil due to freezing and thawing could have been a cause for the lack of water infiltration into the lysimeters.

The concentration of EDTA applied in 1999 was reduced by one-third from the concentration applied in 1998. Although a sufficient volume of EDTA solution was applied to wet the top 24 inches of soil, EDTA was localized primarily in the top 12 inches of soil. Higher concentrations of water-soluble lead were found at the 0- to 12-inch depth, corresponding to the higher concentrations of EDTA in the upper soil layer. Total lead concentrations were highly variable, and no discernible patterns of lead distribution in the soil were observed. Soil sampling adjacent to the treated areas at Site C indicated that lateral movement of EDTA did not occur.

A sequential fractionation analysis procedure performed on pre-amendment soil samples showed that potentially plant-available lead concentrations overall were about 55% of the total lead concentrations in the soil. If the concentration of potentially plant-available lead were to be used as the criterion for calculating the amount of EDTA to be added to the soil rather than total lead concentrations, the amount of EDTA required could be reduced accordingly.

The lead concentration in corn plants at Site C averaged 854 mg/kg. These values were tenfold less than obtained in corn treated in 1998. Conditions in 1999 were not optimal for lead uptake, as the corn crop at this site exhibited several different growth stages, ranging from immature, non-tasseled plants to mature plants with ears. Root development was limited to the top 6-8 inch soil layer. EDTA concentrations in the 1999 corn averaged approximately 40% lower than found in the corn crop in 1998, but still averaged 26,200 mg/kg in 1999. Lead uptake by corn in the two grids sampled at Site 129-3 averaged 104 mg/kg.

The overall results of the phytoremediation technology during the 1998-1999 demonstration were less than hoped for with respect to crop growth, plant lead uptake, and removal of lead from the soil. In order for this technology to be effective, greater uptake of lead by plants from the soil will have to be realized. This may be difficult to achieve in the site conditions such as those at TCAAP, particularly at Site C. The poor chemical and physical condition of the soil, and the extreme heterogeneity of both the concentration and the form of lead in the soil were factors that were not known prior to undertaking the demonstration at this site.

**2000 Season**

There were plans to demonstration phytoextraction at Site 129-3. After observation of lead and EDTA in groundwater, no phytoextraction activities were conducted in 2000. Instead, three groundwater sampling events and two surface water sampling events were carried out by TCAAP and MPCA personnel during April and May 2000. Groundwater samples were taken upgradient from the demonstration plot, from within the plot, and down-gradient of the plot. Surface water samples were taken upgradient and down-gradient of the plot from a drainage ditch near the plot. These samples were taken to determine how much of the 16-acre area of Site C proper had been impacted by demonstration activities. In addition, deep core soil samples were taken by TVA to “dissect” and more fully characterize the demonstration area.

It is important to note that the demonstration plot at Site C constituted only a 0.2 acre portion of a highly contaminated 16.5 acre area, and that the soil in the entire 16.5-acre area was scheduled to be excavated and treated in 2000 to chemically stabilize lead in the soil before disposal in a landfill.

Based on analysis of four surface water samples, lead did not appear to be migrating to surface waters from the phytoremediation plot due to solubilization by EDTA. Site C-1, an area within Site C proper, is located just north of the drainage ditch flowing east to west. The proximity of this site to the drainage ditch, the slope toward the ditch, combined with the past burning and disposal operations at this site indicate that Site C-1 may have been the probable cause of the lead detection (1 ppm) at the sampling point most distant from the plot. Historical data in the RI/FS indicated the presence of lead at Site C-1 in quantities that would produce the levels of lead in the drainage ditch running east to west. The data also proved that surface water contamination had not occurred and there was no immediate risk to the environment.

For groundwater samples, results indicated that the lead concentration in the groundwater had decreased rapidly with distance away from the plot. Lead concentrations decreased from 1,100 ppm to 1 ppm in approximately 100 feet. This rapid decline indicated that lead levels would continue to decrease. Considering that the impacted groundwater is in Unit 1, an alluvium, extreme variations would likely be observed within short distances in the aquifer. The depths to groundwater in the area were highly variable. A higher level of the water table could have resulted in “washing” of the soil and transport of EDTA. The fluctuation could have been due to demonstration irrigation activities as well as rainfall.

The ratios of EDTA:lead in the groundwater increased as the distance from the plot increased. This supported a basic conceptual model that the longer the EDTA exists in the groundwater the more likely it is for other cations to out-compete lead for complexation by EDTA, which will reduce lead in solution over time and as distance from the plot increases. Degradation of EDTA also played a role in lead re-deposition.

EDTA and lead were found throughout the plot, with the concentration of total lead being greater than the concentration of lead which had complexed with EDTA. EDTA values were less than those of total lead within the plot and tended to be below the detection limit outside of the plot. The soil analytical results indicated that while EDTA and lead were found in the shallow soils (less than 4 feet), the concentrations of these were lower than were observed in the April round of groundwater sampling. Soil concentrations for EDTA ranged from less than 0.3 to 1,570 ppm.

Concentrations of EDTA in the April groundwater samples were from less than 0.03 up to 4,910 ppm EDTA. Only three of the soil samples were higher than the highest values seen in the May groundwater sampling of 739 ppm. Water-soluble lead concentrations in the soil ranged from less than 1 to 549 ppm; lead concentrations in the April groundwater samples ranged from less than 0.02 ppm to 988 ppm. This data suggested that the overall concentrations of EDTA were decreasing in the soil and that the EDTA is degrading at the site as was originally expected.

The soils at Site C were found to be much more heterogeneous than was originally anticipated. Seven soil types, ranging from sand to clay, were identified in deep soil cores which is contrary to the single soil type identified in the RI/FS. Clay and sand lenses were common throughout the soil, and a considerable amount of burned and unburned wood was found. Debris consisting of glass, metal, wire, concrete, bullets, and brass shell casings was found throughout the plot. Iron oxide deposition was common in the cores as were manganese sulfide concretions (usually a representation of alternating aerobic and anaerobic zones in the soil profile, likely caused by a fluctuating water table).

EDTA did not degrade as rapidly as expected, based on current information in the literature. However, degradation did occur, as evidenced by the relatively high pH of the shallow soils (8.5 to 9.5) which may be attributed to degradation of EDTA and release of ammonia from the amine groups, and to the formation of carbonate compounds from the $CO_2$ that is also released. In soils the major mechanisms which determine the fate of EDTA and therefore its ability to solubilize lead are:

- Adsorption to iron oxide and soil organic matter.
- Binding to clay particles.
- Reactions with soil cations.
- Microbial degradation.
- Rates of leaching.

In addition, lead solubility in soil during a phytoextraction scheme is controlled by reactions of:

- Dissolution of inorganic lead compounds.
- Complexation of lead by EDTA.
- Displacement of lead from EDTA by competing cations and re-precipitation of lead in soil.
- Degradation of EDTA and reaction of lead in soil to form insoluble compounds.

The competing cation effect was significant in this soil. A departure from a 1:1 EDTA to lead ratio in both soil and groundwater was a result of lead displacement in EDTA by another cation(s). The data showed these cations to be calcium and magnesium. As lead was displaced, reprecipitation in the soil occurred and lead was not subject to leaching or was it otherwise bioavailable. As lead is more soluble at lower pH, the amount of soluble lead will continue to decline. Given the mineralogy of this soil a natural drop in soil pH to a level that would re-solubilize lead is highly unlikely.

Most likely the extreme heterogeneous nature of these shallow soils accelerated movement of EDTA through the soil column and reduced the contact time of EDTA in the soils, which affected the rate at which the reductive fate processes were taking place. It is also possible that the microbial population in the shallow soils was (is) low, due to other toxic contaminants and debris in the soils and perhaps the slow draining of the soils, which would lead to waterlogging during significant periods of the year.

The results of the soil, groundwater, and surface water sampling suggested that, although the EDTA persisted in the soil and in groundwater longer than originally expected, the concentrations of soluble lead within and outside the demonstration plot are decreasing with time and will continue to decrease.

### 5.3 Technology Comparison

Several procedures for remediating metals-contaminated soil sites are currently available. These include traditional and proven *ex situ* methods, as well as emerging, state-of-the-art *in situ* technologies. Conventional *ex situ* methodologies include:

- Landfilling of contaminated soil.

- Soil washing (separation) - excavation of soil followed by soil washing, return of clean soil to the site, and landfilling of soil which is still contaminated.

- Incineration - excavation and incineration, with the remaining mineral fraction returned to the original site or landfilling if decontamination is not complete.

- Solidification - excavation and *ex situ* solidification with pozzolanic agents and landfilling of the stabilized material.

These methods are effective; however, they usually involve long-term monitoring and permanent and sometimes drastic alterations to the original site.

In contrast, the following *in situ* methods, except containment and flushing, provide a clean site and normally avoid future liability and restrictions to site use:

- *In situ* soil flushing - in-place washing of soil using acid or chelate solutions followed by pumping of contaminated soil solution to the surface for treatment.

- Solidification/Stabilization - similar to *ex situ*, but involves proprietary reagent delivery and mixing systems and may be less costly for large soil volumes and depths greater than 10 feet.

- Containment - placing an impermeable cap on the contaminated site to eliminate water infiltration into the contaminated soil.

- Electrokinetics - use of low intensity direct current fields between electrodes in soil to mobilize and capture contaminants at the electrodes for removal.

- Phytoremediation - a broad term for the use of plants to remediate contaminated soil and water. (The phytoextraction technique is a category of phytoremediation methods, whereby metal-accumulating plant species are used to extract lead from the soil and are then harvested.)

If applicable to the site, phytoextraction may be among the lowest cost options, but it also requires the longest amount of time. If remediation can be accomplished on areas of moderate-level contamination within one to five years, phytoextraction may be an attractive alternative to existing methods.

From the results of this project, the scope of application for the technology appears to be very limited, the remediation time would be unrealistically long, and sites that would be suitable candidates for phytoextraction appear to be scarce. In addition, some of the operating parameters are still in need of refinement. These include growing practices, plant species selection, chelate selection, amendment application methods, and amendment application rates.

# Section 6.0
# Cost Assessment

## 6.1 Cost Performance

Phytoextraction can be broken into three tasks: crop production, extraction amendment addition, and harvesting. The costs shown below are based on treating an area equal to one acre using a corn crop. The quantities of amendment are based on laboratory studies and knowledge gained from the field demonstration at TCAAP. The costs associated with producing and harvesting the corn crop are shown in Table 6-1. The costs for purchasing, mixing, transporting, and applying the extraction amendments are shown in Table 6-2. The costs for the irrigation system used to water the crop and apply extraction amendments are shown in Table 6-3.

Total cost for using phytoextraction to remediate one acre is $42,145 per crop (Table 6-4). This includes a managing contractor fee of 20% of the direct costs. Assuming that the process treats the top 12 inches of soil, the cost for remediation is equivalent to $26.13 per cubic yard per crop based on an initial soil lead concentration of 1500 mg/kg and a remediation target of 1000 mg/kg. The remediation would require 27 crops over a period of 14 years for a total cost of $706 per cubic yard. To remediate from 1200 mg/kg to 1000 mg/kg would require 11 crops over a six year period, at an approximate cost of $287 per cubic yard.

Reagent costs (EDTA, acetic acid, other soil amendments) will account for a substantial portion of total costs. Costs for site preparation, i.e., clearing and removal of trees, removal of buildings and debris, etc., would be site-specific and would be in addition to the above cost.

### 6.1.1 Soil Remediation Time Calculator

The number of crops and time required for phytoremediation to treat a field to a desired cleanup level can easily be estimated. A few basic inputs are required as shown in Table 6-5.

Starting lead concentration (A) - The initial concentration of lead in the soil (400-2000 mg/kg) to be remediated is determined during initial site assessments. The higher the initial lead concentration, the longer the time required to reach a set cleanup goal and the more expensive the process becomes. When the initial lead concentration is too high, then other remediation techniques will be less costly.

Target lead concentration (B) - A cleanup level will be established for a site by agreement with the regulatory agencies. The current industrial cleanup level is 1,000 mg Pb per kg of soil. The current residential cleanup level is 400 mg/kg.

Plant available lead (% of total) (C) - Lead exists in the soil in various forms. Some of the lead compounds can be made available to plants by soil amendments used during phytoextraction, but some of the lead will be inaccessible to the plants even after soil amendment additions. Analysis of the soil lead by sequential extraction with various extractants can identify the fraction of the total lead that is available to the plant during phytoextraction. At TCAAP, the plant available lead was 55% of the total lead. Plant available lead concentrations usually range from 25-75% of total.

**Table 6-1**
**Corn Production and Harvesting Costs[1] Per Crop**

| Item | Unit Cost | Quantity | Total Cost |
|---|---|---|---|
| Seed | $5/lb | 12 lb | $60 |
| Fertilizer[2] | N=$0.24/lb<br>P=$0.25/lb<br>K=$0.14/lb | 180 lb N from 341 lb Urea<br>60 lb P from 130 lb DAP<br>120 lb K from 200 lb KCl | $70 |
| Fertilizer Application | $15/acre | 1 acre | $15 |
| Tillage | $20/acre | 1 acre | $20 |
| Planting | $20/acre | 1 acre | $20 |
| Harvesting | $20/acre | 1 acre | $20 |
| Herbicide and Misc | $25/acre | 1 acre | $25 |
| Sampling[3] - Soil<br>- Biomass | $50/sample<br>$50/sample | 12 samples<br>12 samples | $600<br>$600 |
| Smelting | $100/ton | 8 tons | $800 |
| Subtotal | | | $2,230 |

(1) Costs are based on typical production agriculture with large scale equipment.
(2) Prices based on bulk quantities. Sources are urea, diammonium phosphate, and potassium chloride.
(3) Unit cost includes labor for collecting samples.

**Table 6-2**
**Extraction Amendment Costs[1] Per Crop**

| Item | Unit Cost | Quantity at Site C, lb | Quantity Per Acre, lb | Total Cost Per Acre |
|---|---|---|---|---|
| KOH[2] | $336/ton | 1,100 | 5,900 | $990 |
| EDTA[3] | $4,125/ton | 1,400 | 7,500 | $15,500 |
| Acetic Acid[4] | $1,520/ton | 2,000 | 10,750 | $8,200 |
| KOH and EDTA Mixing | $100/ton EDTA | | | $375 |
| Acetic Acid Dilution | $100/ton acid | | | $550 |
| KOH-EDTA Shipping | $40/ton[5] | | 52,500 | $1,050 |
| Acetic Acid Shipping | $30/ton[6] | | 75,000 | $1,130 |
| Labor for Application[7] | | | | $960 |
| Subtotal | | | | $28,755 |

(1) Based on an initial soil lead concentration of 1,500 mg/kg and a clean-up goal of 1,000 mg/kg.
(2) 45% solution.
(3) Cost per dry ton.
(4) Acid requirement will vary according to site soil.
(5) EDTA makes up about 1/7 of the total weight of the water-KOH-EDTA mixture.
(6) Glacial acetic acid makes up about 1/7 of the diluted mixture.
(7) Based on 16 man-hours at $60 per man-hour.

**Table 6-3**
**Cost Per Crop for Amendment Drip Application/Irrigation System[1]**

| Item | Unit Cost | Quantity | Total Cost |
|---|---|---|---|
| Drip Tape | $0.03/ft | 53,000 ft | $1,590 |
| 2-Inch Main | $0.30/ft | 300 ft | $90 |
| Filters | $160 | 4 | $640 |
| Flow Regulator | $106 | 2 | $216 |
| Barbs | $0.48 | 250 | $120 |
| Other Plumbing Parts | | | $200 |
| Installation Cost[2] | | | $1,280 |
| Subtotal | | | $4,136 |

(1) Area to be treated is assumed to be square in shape.
(2) Installation costs based on 32 man-hours at $40 per man-hour.

**Table 6-4**
**Total Cost Per Crop for Phytoextraction of One Acre of Lead-Contaminated Soil to Reduce Soil Lead Content from 1,500 mg/kg to 1,000 mg/kg**

| Item | Cost |
|---|---|
| Corn Production and Harvesting Costs | $2,230[1] |
| Extraction Amendment Costs | $28,755[2] |
| Cost for Amendment Drip Application/Irrigation System | $4,136[3] |
| Subtotal of Direct Costs | $35,121 |
| Managing Contractor Fee (20% of direct costs) | $7,024 |
| **Total** | **42,145** |

(1) Subtotal for Table 6-1.
(2) Subtotal for Table 6-2.
(3) Subtotal for Table 6-3.

**Table 6-5**
**Input Required for Calculating the Number of Crops and Number of Years Required to Phytoremediate a One Acre Field**

| Variable | Units | Input | Range for Inputs |
|---|---|---|---|
| Starting Lead Concentration | mg/kg | A | 400 - 2,000 |
| Target Lead Concentration | mg/kg | B | 400 (residential), 1,000 (industrial) |
| Plant Available Lead (% of Total Lead) | % | C | 25 - 75 |
| Soil Depth to Remediate | in. | D | 1 - 12 |
| Soil Bulk Density (Dry Basis) | lb/cu ft | E | 60 - 150 |
| Biomass Production | tons/acre | F | 1 - 15 |
| Concentration of Lead in Biomass | % | G | 0 - 1 (1% = 10,000 mg/kg) |
| Number of Crops Per Year | crops/yr | H | 1 - 3 |

Soil depth to remediate (D) - Lead contamination exists to different depths in the soil. The depth of contamination is a factor in determining the total soil volume to be treated. Phytoextraction is more effective and economical when the contamination is shallow, 12 inches or less.

Soil bulk density (dry basis) (E) - Soil density varies substantially depending on the content of clay, sand, and other components. The moisture content also affects the soil density, but this factor can be eliminated by using a dry basis for the soil density. A reasonable value for soil bulk density is 1,600 kg/m$^3$, which is approximately 100 lb/ft$^3$.[Ref. 45,46]

Biomass production (F) - Each crop will produce an average weight of biomass (dry basis) per area which normally ranges from 1 to 15 tons per acre. The crop yield is dependent on many factors such as soil fertility, weather conditions during the growing season, length of growing season, number of crops planted per year, presence of toxic compounds in the soil, etc. Crops grown for phytoextraction have amendments applied and are harvested just prior to full maturity. Therefore, the anticipated yields are slightly lower than the published yields. The planting of multiple crops in a single year may shorten the growing time and yield for each crop. The yield may be reduced during subsequent years of phytoremediation due to repeated applications of soil amendments.

Concentration of lead in biomass (G) - There are many factors that affect uptake of the solubilized lead by the crops. The concentration of plant-available lead in the soil directly affects how much lead will be taken up by the crops. Other factors such as root growth, moisture in the soil, rate of amendment application, etc., can influence the lead uptake. Lead concentrations in the plants may range from 0 to 1%.

Crops per year (H) - The number of crops that can be grown in a year is impacted by the climate at the site and the fertility of the soil. A northern U.S. climate may restrict a project to one crop, a southern U.S. climate might allow two crops, and a tropical climate might even allow 3 three crops per year.

The inputs discussed above can be used to calculate the number of crops required to remediate a contaminated field. The calculated values that can be derived are shown in Table 6-6.

Lead to be removed (J) - The requirement for removing lead can be determined by subtracting the *Target lead concentration* from the *Starting lead concentration*. This amount of lead has to be removed from the site to reach the cleanup goal.

$$\text{(J) lb Pb/acre} = \frac{\text{(A-B) mg Pb}}{\text{kg soil}} \cdot \frac{2.205 \times 10^{-6}\ \text{lb/mg}}{2.205\ \text{lb/kg}} \cdot \frac{\text{E lb soil}}{\text{ft}^3} \cdot \frac{43{,}560\ \text{ft}^2}{\text{acre}} \cdot \frac{\text{D in.}}{12\ \text{in./ft}}$$

Maximum possible lead removal (K) - Not all of the lead in the soil can be phytoextracted. The lead that can be is based on the percentage of the total lead that is in the plant-available forms. The Maximum possible lead removal can be calculated by multiplying the *Starting lead concentration* (A) by the *Plant available lead (% of total)* (C). If the Lead to be removed (J) is

greater than the Maximum possible lead removable (K), then it would be impossible to reach the cleanup level using in situ phytoextraction alone.

$$\text{(K) lb Pb/acre} = \frac{\text{A mg Pb}}{\text{kg soil}} \cdot \frac{\text{C \%}}{100\%} \cdot \frac{2.205 \times 10^{-6}\ \text{lb/mg}}{2.205\ \text{lb/kg}} \cdot \frac{\text{E lb soil}}{\text{ft}^3} \cdot \frac{43{,}560\ \text{ft}^2}{\text{acre}} \cdot \frac{\text{D in.}}{12\ \text{in./ft}}$$

**Table 6-6**
**Calculated Values for the Number of Crops and Number of Years Required to Phytoremediate a One Acre Field**

| Calculated Values | Units | Output |
|---|---|---|
| Lead to be Removed | lb/acre | J |
| Maximum Possible Lead Removal | lb/acre | K |
| Lead Removal Per Crop | lb/acre | L |
| Number of Crops | crops | M |
| Number of Years | yr | N |

Lead removal per crop (L) - The average amount of lead removed per crop will determine the number of crops required to reach the cleanup level. The crop biomass and the lead removal per crop may potentially decrease over time, but the lead removal per crop is assumed to be constant for the purpose of calculation. The Lead removal per crop is calculated by multiplying the *Biomass production* (F) by the *Concentration of lead in biomass* (G).

$$\text{(L) lb Pb/acre} = \frac{\text{F tons biomass}}{\text{acre}} \cdot \frac{2{,}000\ \text{lb}}{\text{ton}} \cdot \frac{\text{G \%}}{100\ \%}$$

Number of crops (M) - The number of crops required is calculated by dividing the *Lead to be removed* (J) by the *Lead removal per crop* (L). This calculations assumes that the weather will be cooperative every growing season. A contingency factor could be applied here depending on the meteorological history of the site.

$$\text{(M) Crops} = \frac{\text{J lb Pb/acre}}{\text{L lb Pb/acre}}$$

Number of years (N) - The number of years required to clean up a site with phytoextraction can be calculated by dividing the *Number of crops* (M) by the *Crops per year* (H).

$$\text{(N) Yr} = \frac{\text{M crops}}{\text{H crops/year}}$$

An example calculation is shown below. The values used in this example are based on expected performance of phytoextraction in a southern U.S. area at a site that has fertile soil and weather conducive to growing two crops in a year with no decrease in biomass production during remediation. The inputs are based on lessons learned from the TCAAP demonstration and from information developed from greenhouse studies. The assumed variables for input shown in Table 6-7 provide the calculated outputs shown in Table 6-8.

As shown in Table 6-8, the time required for remediation of the example site would be 14 years. It assumes that 27 crops would be successfully grown with consistent biomass production. The time and costs would be prohibitive under the assumptions shown in Table 6-7 to remediate a field from 1,500 mg/kg to 1,000 mg/kg. Other remediation technologies are available that would be more cost effective. However, if the starting lead concentration was 1,200 mg/kg, then the site could be reduced by 200 mg/kg with 11 crops in 6 years.

**Table 6-7**
**Example Inputs for Calculating the Number of Crops and Number of Years Required to Phytoremediate a Field**

| Variable | Units | Input | Range for Inputs |
|---|---|---|---|
| Starting Lead Concentration | mg/kg | A=1,500 | 400 - 2,000 |
| Target Lead Concentration | mg/kg | B=1,000 | 400 (residential), 1,000 (industrial) |
| Plant Available Lead (% of Total Lead) | % | C=55 | 25 - 75 |
| Soil Depth to Remediate | in. | D=12 | 1 - 12 |
| Soil Bulk Density (Dry Basis) | lb/cu ft | E=100 | 60 - 150 |
| Biomass Production | tons/acre | F=8 | 1 - 15 |
| Concentration of Lead in Biomass | % | G=0.50 | 0 - 1 (1% = 10,000 mg/kg) |
| Number of Crops Per Year | crops/yr | H=2 | 1 - 3 |

**Table 6-8**
**Example Calculated Values for the Number of Crops and Number of Years Required to Phytoremediate a Field**

| Calculated Values | Units | Output |
|---|---|---|
| Lead to be Removed | lb/acre | J=2,178 |
| Maximum Possible Lead Removal | lb/acre | K=3,594 |
| Lead Removal Per Crop | lb/acre | L=80 |
| Number of Crops | crops | M=27 |
| Number of Years | yr | N=14 |

The calculated values for the example inputs shown in Table 6-7 are:

Lead to be Removed (J) = (A-B) x $10^6$ x E x 43,560 x D/12
= (1,500-1,000) x $10^6$ x 100 x 43,560 x 12/12
= 2,178 lb/acre

Maximum Possible Lead Removed (K) = A x C/100 x $10^6$ x E x 43,560 x D/12
= 1,500 x 55/100 x $10^6$ x 100 x 43,560 x 12/12
= 3,594 lb/acre

Lead Removal Per Crop (L) = F x 2,000 x G/100
= 8 x 2,000 x 0.50/100 = 80 lb/acre

Number of Crops (M) = J/L = 2,178/80 = 27 crops

Number of Years (N) = M/H = 27/2 = 14 years

Based on the results of this demonstration, TVA estimated the cost for phytoextraction of one acre to a depth of one foot to be $42,145 per crop, assuming:

- The starting lead concentration is 1500 mg/kg.
- The clean-up goal is 1000 mg/kg.
- Plant-available lead is 55% of the total lead.
- The biomass production is 8 tons per acre.
- The concentration of lead in the biomass is 0.5%.
- Two crops per year are grown at the site.

The cost is equivalent to $26.13 per cubic yard per crop. This remediation would require 27 crops over a period of 14 years, for a total cost of $706 per cubic yard. All other assumptions remaining constant, if the initial soil lead concentration were 1200 mg/kg, the remediation would require 11 crops over a six-year period, at an approximate cost of $287 per cubic yard.

Based on these costs, *in situ* phytoextraction as a sole technology would be economical only when the initial lead concentration is close to the clean-up goal. Costs for site preparation, i.e., clearing and removal of trees, removal of buildings and debris, etc., would be site-specific and would be in addition to the above cost. The total cost includes a managing contractor fee of 20% of the direct costs. Reagent costs (EDTA, acetic acid, other soil amendments) will account for a substantial portion of total costs.

# Section 7.0
# Regulatory Issues

To gain acceptance for the demonstration from the regulatory agencies, the draft Technology Demonstration Plan was provided to both USEPA Region 5 and the MPCA for their review and comment in February 1998. The USAEC Program Manager scheduled a meeting in early March 1998 with representatives from USEPA Region 5 and the MPCA to discuss the demonstration project in more detail and to answer and address any initial questions or concerns. Shortly after the meeting, both agencies provided written comments on the draft Technology Demonstration Plan. The project team then revised the Technology Demonstration Plan and prepared written responses to all of the comments submitted by the regulatory agencies. The team also provided additional follow-up when necessary. The demonstration was conducted in accordance with the revised Technology Demonstration Plan.

To gain acceptance for the demonstration project from the public and to keep the public informed, the USAEC Program Manager gave a presentation about the demonstration project to the TCAAP Restoration Advisory Board (RAB) at the March 1998 RAB meeting. The RAB was also provided with the draft Technology Demonstration Plan and given an opportunity to comment. Several RAB members did review the document and submitted written comments to the project team. After the Technology Demonstration Plan was revised, written responses to the RAB's comments were prepared by the project team; no additional comments or concerns were presented by the RAB to the USAEC Program Manager. In addition, an Environmental Assessment (EA) was prepared for the project and a public notice asking for review and comment of the EA was placed in a high circulation area newspaper. No public comments were received.

This technology was not well accepted by regulators and the public because of the observation of lead and EDTA in the groundwater. It is likely that regulators would require controls such as liners and leachate collection prior to approval of future phytoextraction at sites such as this.

# Section 8.0
# Technology Implementation

## 8.1 DoD Need

The Department of Defense established the DERP in 1984 to promote and coordinate efforts for evaluation and remediation of contamination at DoD facilities. Congress established the DERA in 1986 as a part of the SARA. The Army uses the Defense Site Environmental Restoration Tracking System (DSERTS) to manage and track environmental restoration processes at installations. The DSERTS database is the principal source of information for the Environmental Restoration Annual Report to Congress.

DSERTS was used to identify sites that have had lead contamination in soils. The database was screened to eliminate sites where the maximum reported concentrations of lead were less than the USEPA established cleanup levels. Sites that have already been remediated were also screened out. There were a total of 458 sites that have at some time in the past shown lead contamination levels above the residential cleanup levels (400 mg/kg). Of these sites, 319 sites had lead contamination above the industrial cleanup levels (1,000 mg/kg).

Navy and Air Force sites are not included in DSERTS, but the majority of lead contamination should be within Army installations because of the large number of firing ranges and the number of ammunition plants on Army sites. The number for the Army sites will be high since there are some sites that will not be remediated because risk analyses have shown that some of these sites do not pose a risk to human health or to the environment. However, the DSERTS data are an indication of the magnitude of the problem. In the 1999 DSERTS data, there were 889 sites with metals contamination that exceeded the risk-based levels.

Of the 889 sites, there were 450 sites that were scheduled to be cleaned up because of metals contamination. According to a query of the DSERTS database, these 450 sites had approximately 2,285,000 cubic yards of soil that required remediation at an estimated cost of $1,038 million. In addition, there were 2,861 acres that were to be capped or isolated within a fence.

## 8.2 Transition

Phytoextraction technology does not appear to be practical or economical for implementation *in situ* under the conditions at sites such as TCAAP, and a discussion of some of the problems encountered in the application of the field demonstration is in order before a decision can be made on a proper transition process. The major obstacles to phytoremediation at TCAAP were:

- Variability of soil types
- High precipitation area
- Toxic contaminants
- History of open burn/open detonation - large pieces of debris that induced channeling; compounds toxic to crops.

- Shallow hardpan at Site C which prevented deep rooting and caused water-logging.
- Shallow groundwater

Some of these obstacles are inherent to phytoremediation and some were site-specific to TCAAP. Many of these factors were interrelated and produced problems with plant growth and nutrition from the outset of the demonstration The symptoms were treated but plants did not realize full yield potential and lead uptake capacity. These obstacles have been addressed in the Implementation Plan, Section 8.3.

After the first year demonstration, TVA recognized that it would be difficult to evaluate lead removal from the soil due to the extreme variability in soil lead concentrations across the plot areas. Soil lead variability was complicated by the fact that large quantities of solid debris (burned and unburned wood, rail ties, concrete, scrap metal, etc.) and particulate lead contaminants were found at the site during the initial soil cultivation and planting that was not anticipated from review of the RI/FS and discussions with on-site personnel. Therefore, lead removal in the crop biomass was the only suitable means to evaluate removal of lead from the soil. TVA did not expect to be able to detect a change in soil lead concentration after one year, or possibly even after two years because of the high variability. For phytoextraction to work at such sites, screening of debris and particulates and homogenizing of the soil would be a required step. However, the nature of the debris and particulates would require complete excavation of the contaminated areas, in which case one of the *ex situ* remediation methods would probably be more economical and efficient to use.

In this demonstration, lysimeters were installed to monitor potential EDTA or lead movement through the soil. However, due to the nature of the soil these did not perform consistently. For future studies, a better approach would be a water balance simulation which includes meteorological data and hydraulic conductivity of the soils. Weekly precipitation data collected at the test plots could be used as well as local meteorological data (temperature, wind speed, humidity, etc.) obtained from resources in the vicinity (e.g., NOAA, airports, etc.). Hydraulic conductivity of site soils should be another facet of this technology to enable more accurate estimation of the amounts and the rate of application of soil amendments applied. Because of the heterogeneous texture of the soil at TCAAP, sampling to adequately determine the overall hydraulic conductivity of the sites to perform a mass water balance was impractical and prohibitively expensive. An accurate assessment of the hydraulic conductivity of this site would have required samples to have been taken in close proximity (sample to sample) to account for the varying texture and varying soil infiltration rates.

Unfavorable weather and other environmental factors prevented valid assessment of crop removal of lead during the latter two crops of the demonstration. In the short growing season in the TCAAP area, the cropping scheme and plant species were changed after the 1998 demonstration in order to increase the remediation effectiveness in 1999. Plant density was increased by planting on 15-inch rows in 1999, while corn in 1998 was planted on 30-inch rows. The corn used in 1998 was a field corn variety; in 1999 a silage variety was used to increase biomass yield. However, the variability of soil types and lead concentrations within the sites (more particularly, Site C), the relatively short growing season, and the high concentrations of

lead in the soil would likely require many more years than originally anticipated for successful remediation by crops. A complete discussion of the factors involved in calculating the times required for remediation is shown in Section 6.0 The time requirements should be carefully considered before initiating a phytoextraction scheme in under less than ideal conditions.

### 8.3 Draft Implementation Guidance Document

This document is intended to provide overall guidance for conducting a phytoextraction project in situations where constraints to implementation are minimal and contamination levels are not much above the desired cleanup level. This document does not endorse implementation under conditions of extreme heterogeneity, such as military disposal sites in general, and Site C at TCAAP in particular.

The procedures outlined in this document are based on the results of a two-year demonstration. Some practices, such as crop selection, cultural practices, types of soil amendments, and methods of application, changed after the first year of the demonstration. Therefore, this document is not complete and can only serve as a general guide. Some of the recommendations may still need to be modified for maximum treatment effectiveness. However, the experience of the researchers working under extremely difficult and heterogeneous conditions has resulted in some definite guidelines that, without doubt, should be carefully considered before implementing a phytoextraction project at any given site. Experience has shown that this phytoextraction technology likely will not work *in situ* to maximum effectiveness for removal of lead at sites where open burn/open detonation practices have been followed, such as at Site C at TCAAP. Such sites will usually be poor candidates for growing plants because the soil is likely heavily contaminated with a variety of solid debris, other toxic contaminants and, oftentimes, particulate lead. The solid debris essentially destroys soil structure and proper hydraulic properties. Unless the soil is first excavated, the debris screened out, and the soil made uniform, channeling and preferential flow will render the soil entirely unsuitable for application of chelates which solubilize and thus possibly promote leaching of lead. In addition, unless particulate lead is first removed, it will be impossible to measure any realistic reductions in soil lead through plant uptake.

Even under conditions where lead is present in the ionic form (e.g., battery disposal operations, lead smelters, lead styphnate production facilities), the circumstances may still be less than ideal for the culture of growing plants, and some adjustments to procedure will likely be necessary even after the process has begun. Each contaminated site will be unique with its own set of challenges which may limit or reduce the effectiveness of the technology. The main focus of this technology is to maximize lead concentration in the plants and to maximize biomass production in order to achieve the greatest lead uptake by the crops under the existing conditions. Thus, the flexibility to change and adapt as required is an integral part of the remediation plan. Plant sampling after each harvest will monitor the progress of the remediation and provide a feedback loop to allow for procedural adjustments, as needed.

The general guidelines for implementation of a phytoextraction project are shown below. Definitive recommendations and procedures will, by necessity, be site-specific. These steps must be implemented under the oversight of a professional agronomist or other qualified

personnel with a background in soil chemistry, soil fertility, soil taxonomy, and plant science. It is most strongly advised that someone with an agronomic or farm background be responsible for day-to-day field operations and maintenance of the growing crops. This individual would guidance on a regular basis, but should also be able to independently distinguish any abnormalities that might arise during the project and, after discussion with the professional, act to counter such problems.

Under a very specific and narrow range of conditions, phytoextraction may offer the potential as a relatively inexpensive remediation method compared to other technologies. Factors which will directly control the success of the technology may be:

- Soil type
- Soil fertility levels
- Type of lead present in soil
- Potential plant availability of lead in the soil
- Soil lead concentration
- The presence of other contaminants

In addition, there are very few known plant species that may be suitable for this technology. Thus, field demonstrations with a variety of plant species have yet to be implemented. The focus of this project was not to determine or screen plant species for maximum lead uptake. At the time of this writing, the following are being used in field demonstrations for remediation of lead:

- Indian mustard
- White mustard
- Corn
- Sunflower

Crops that may be used to remediate other heavy metals include:

- Amaranthus (radioactive cesium and strontium)
- Sunflower (radionuclides)
- Oat and barley (zinc)
- Alpine pennycress (cadmium)
- Indian mustard (copper and selenium)
- Alyssum species (nickel)

There are certainly other plant species that have the potential to accumulate lead and other metals in their aboveground tissues; these may eventually be categorized by identifying certain basic biochemical pathways for metal metabolism. For now, however, the technology is still in stages of development and refinement, and a comprehensive listing of such plants is not available.

The following list is a detailed, but not necessarily all inclusive, guide to use when undertaking a phytoextraction effort:

1. Planning for utilizing phytoextraction at a specific site will start by obtaining detailed site information from the remedial investigation/feasibility study (RI/FS). The information needed would be the general nature of the site, specific COCs, type and concentration of COCs, climate, geology, hydrogeology, etc.

2. Determine the extent of past site characterization and the extent of future characterization that may be required. Do not rely on the RI/FS to be comprehensive or totally accurate since it may not focus on the site characteristics pertinent to phytoremediation.

3. Obtain a soil characterization for other contaminants present that would inhibit plant growth and prevent the use of phytoextraction methods altogether, e.g., beryllium and thallium.

4. Obtain a soil characterization for chemical and physical properties that affect agronomic suitability for growing plants, e.g., pH, indigenous nutrient levels, cation exchange capacity, organic matter, soil texture, water holding capacity, shallow hardpan, and infiltration rates, etc.

5. Determine the depth to groundwater, direction of flow, rate of flow, and hydraulic properties of the soil.

6. Determine if phytoextraction is suitable based on:

    - Type and concentration of COCs, i.e., contaminant in ionic form and present at a concentration that can be remediated within a reasonable timeframe

    - Depth and extent of COCs, i.e., accessibility of COCs to plant rooting system

    - Other contaminants present, e.g., beryllium or thallium, that might inhibit plant growth and prevent the use of phytoextraction methods altogether

    - Logistics of site, i.e., accessibility to irrigation water, equipment, and personnel

    - Climate suitable for proposed remediation crops, multiple crops/year

    - Geology and hydrogeology, i.e., difficulty in sampling, field preparation, and depth to groundwater

    - Site terrain, i.e., slope, wooded verses open field, presence of rocks/obstructions, etc.

7. Based on the above information, determine if the process can be implemented *in situ*, or if the soil should be excavated, screened, and homogenized, and a liner installed to control movement of solubilized lead.

8. Consult with appropriate regulatory agencies (state, federal, and local if required) as to permitting and legal requirements and obtain clearance to proceed.

9. Conduct intensive soil sampling and comprehensive analyses. Soil sampling should be performed with power sampling equipment to conserve labor and maximize cost-effectiveness. The analyses are conducted to:

   - Determine soil pH. This factor is the single most important soil parameter measured. Soil pH governs both efficiency of nutrient utilization and potential toxicities from elements such as aluminum and manganese. The optimum pH range for most agricultural crops is 6.0-7.0, although crops can tolerate a somewhat lower or higher range. If soil pH is on either side of this range, proper nutrient utilization is greatly reduced and chances of toxicities may be increased. Soil pH also serves as the starting point from which buffer curves are determined in order to calculate the proper application rate of acetic acid.

   - Determine soil texture, i.e., sand, silt, and clay content, which affects cultural practices such as tillage and irrigation; potential leaching, as well as runoff of nutrients and soil amendments; plant rooting depth; and the aeration status of soils. Sandy soils will require supplemental irrigation and nutrients for best crop production. However, the potential for movement from the rooting zone of both of nutrients and EDTA, is greatly increased and shallow root systems may develop from over watering. Sampling difficulty may be greatly increased in rocky, sandy soils. A high clay soil may exhibit poor/reduced infiltration, anaerobic areas after heavy rains, restricted rooting depth, and significant sorption capacity for EDTA which may reduce chelate effectiveness. This, in turn, will increase the amount of chelate required and add to project costs.

   - Determine the nutrient status of the soil for the macronutrients nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur if the soil is sandy and the mineralogy indicates a lack of sulfur-containing minerals. Also, included in these analyses may be the micronutrients copper, iron, manganese, and zinc. These elements are just as essential for proper growth, although required by agronomic crops in very small amounts and at a fraction of the amounts needed for macronutrients.

   - Determine the cation exchange capacity (CEC) and the organic matter content of the soil. The CEC is a measure of the soil attraction, or the strength of attraction, for various cations, whether these be nutrients such as K or a metal such as lead. This parameter may be useful in determining fertilizer recommendations and may influence decisions regarding the amount of EDTA to apply to a given soil. A soil with high CEC will have a strong affinity for metal contaminants. The exchange capacity is also directly related to the buffering capacity (resistance to change in pH) of a soil. Organic matter influences

other important chemical and physical properties of the soil, such as fertility, CEC, and moisture-holding capacity. It also affects reactions of inorganic contaminants such as metals and oxyanions, e.g., arsenic and selenium, both before and after amendment additions to soil.

- Map the concentration and distribution of COCs within the proposed remediation area. These analyses are also necessary to (1) establish baseline concentrations of COCs; (2) map concentrations and locations of potentially phytotoxic elements such as Be or Tl; and (3) calculate the amounts of soil amendments needed to remediate the primary COCs (Pb). However, a point for consideration is that there may be significant variability, or heterogeneity, in COCs concentrations across the area, which will result in "hot" and "cold" spots. These areas of higher- or lower-than-average concentration may be anomalies, or may persist throughout the course of the project, and interpretations of data should be made with this factor in mind. Multiple tillings may somewhat even out the concentrations across the field.

10. Perform acetic acid buffer curves on a bulk soil sample, which is a composite of all samples collected across the remediation area. This is done to determine the amount of acetic acid required to reduce the soil pH to 5.5 in order to maximize lead solubilization before adding EDTA. The determination produces a curve which shows in stepwise fashion the amount of pH reduction resulting from each milliequivalent (meq) of acetic acid added per gram (g) of soil. The total amount of acetic acid required to reduce the soil pH to 5.5 is read from this curve.

11. Calculate the amount of acetic acid needed. This is done by converting the proper value of acetic acid obtained from the buffer curve to a pound per acre basis. This amount of acetic acid will be diluted approximately 1:6 with water for application to the field.

12. Determine potentially plant-available forms of lead using a sequential extraction procedure. This method uses progressively stronger extractants to determine various forms of lead in soil, which range from easily extractable (likely to be plant-available) to very resistant (non-available) forms. The procedure fractionates soil lead into water-soluble, exchangeable, carbonate-bound, oxide-bound, organic-bound, and crystalline matrix bound forms of lead. Typically, the first three forms are the most amenable to extraction by a chelate and are thus considered the most plant available. The concentration of lead in these forms will be less than the total soil lead concentration.

13. Calculate the amount of EDTA to add to the soil. This is based on the results of the sequential extraction procedure. The amount of EDTA should be adequate to solubilize sufficient lead across the remediation area for plant uptake while minimizing chelate movement out of the root zone. The ideal amount is a 1:1 molar ratio of EDTA to *plant-available* lead in the soil. However, since Pb concentrations tend to be quite variable in the soil, a 1:1 ratio cannot be consistently achieved across an entire remediation area. Therefore, a practical application rate may be achieved by examining the mean, the median, and the frequency distribution of plant-available lead across the field, then basing the EDTA

application on a rate that provides a 1:1 ratio for 75% of the field. This is a conservative approach which will mean in some areas the chelate is under-applied, while in other areas it will be over-applied, but this minimizes the risk for movement of the lead-EDTA complex out of the rooting zone.

14. Determine suitable warm and cool season crops (within a group previously selected for maximum contaminant uptake) for the area. Professional guidance is essential to this step and selection should be done in consultation with the project technical manager and knowledgeable local or university extension service personnel. Recommendations are made based on the climate, length of growing season, and potential for maximum yield of selected crops. The order of planting will depend on the season when operations commence.

15. Determine fertilizer requirements for the crop. Recommendations of N-P-K will be based on the normal agronomic rate adjusted for the amount of nutrient already present in soil and the crop removal rates for each nutrient. The fertilizer rate then will be adjusted upward in order to maximize vegetative biomass yield. This is done to obtain the greatest removal of contaminants in the plant biomass. Fertilizers typically employed if a corn crop is planted are ammonium nitrate to supply N, triple superphosphate for P, and potassium sulfate ($K_2SO_4$) or potassium chloride (KCl) for K. For a mustard crop, urea is the preferred N source, but the P and K sources are the same. Sufficient P should be applied to maintain adequate levels in soil for the entire growing season. This is particularly important since a deficiency in this element in early growth stages of the crop is difficult to overcome and the strong precipitation and adsorption of P in fertilizers with soil into non-plant-available forms typically mandates application at rates considerably in excess of predicted plant requirements. Also, lead will react with phosphate fertilizers to precipitate P into non-plant-available forms and over-application of the P fertilizers will likely be required to compensate. However, these reactions preclude the surface application method normally employed for split applications of a fertilizer. A split application will supply part of the needed fertilizer at planting and the rest a third or midway through the growing season. This technique is usually recommended for easily leached elements like N and K to optimize fertilizer use by the crop and to prevent leaching of unused fertilizer.

16. Install protective fencing around the area, if required, and establish work and decontamination zones.

17. Eradicate existing vegetation and remove trees as needed. Tree removal is especially critical not only to eliminate shading, but because roots may extend for considerable distances from the main trunk. If such roots extend into the remediation zone, they not only will use soil moisture at the expense of the crop, but they may also be affected by soil amendments and solubilized lead to the point where damage or death of the tree occurs.

18. To facilitate farming operations, visible obstructions, such as large rocks and metal scrap, should be removed from the area.

19. If necessary, excavate the soil, dry screen to remove debris, and wet sieve to remove particulate lead. Based on the soil texture and hydraulics, install a liner and leachate collection system and replace the soil.

20. Till the area with the appropriate equipment. For proper seed bed preparation, it is recommended that tillage be to a depth of at least a foot, if possible. Tillage should be done in at least two passes at right angles to each other. This may be done with a tractor-mounted, power takeoff-driven Rototiller.

21. Apply and incorporate fertilizer using the appropriate application equipment. This step may also be performed simultaneously with planting.

22. Install irrigation systems for the remediation area. These may be either overhead sprinkler, center pivot, or drip systems, depending on the crop and the logistics and physical layout of the remediation area. A drip delivery system, either surface or subterranean, may also serve as the soil amendment delivery system. However, the system should supply amendments at a delivery rate that will rapidly saturate the soil without causing runoff. Rapid saturation is required to maximize the amount of soil lead solubilized for plant uptake while minimizing potential damage to the plant by the soil amendments.

23. Apply necessary pre-emergent herbicides as recommended by extension service. The herbicides prevent weed establishment by killing the weed as it germinates in the soil. The herbicides are crop and site-specific.

24. Plant the crop with commercial tractor-mounted farming equipment. If a row crop such as corn is the first crop planted, a conventional seed drill may be used. If a broadcast-seeded crop is used as the first crop, a tractor-mounted hurricane seeder/spreader will be used. Plant seed at recommended agronomic rates to promote optimum stand establishment, growth, and biomass yields.

25. Tend the crops by cultivation to destroy weeds, or alternately, apply post-emergent herbicides recommended by extension service. These herbicides are specific for location and general class (broadleaf or grass) of weed. Apply recommended fungicides as needed during periods of excess rainfall when crops are susceptible to fungus infestation. Apply recommended insecticides specific for the insect pest, as needed.

26. Routinely inspect crops (especially early in the growing season) to evaluate any unusual coloration or other symptoms which might indicate a fertilizer or mineral deficiency and use a foliar application of chemicals to correct the deficiency before the crop growth is significantly stunted. Some common and most obvious symptoms to look for include purple stems and leaves, which may indicate P deficiency; the yellow leaves, which may indicate N deficiency; and the light-colored striping on leaves, which may indicate Fe or Zn deficiency. Other symptoms include: stunting, curled leaves, dead spots on leaves, or lacking other obvious visual signs, a general difference in appearance from the total plant population.

27. Commence pre-amendment sampling immediately before addition of soil amendments to solubilize lead. This will involve obtaining a limited number (12 per acre) of soil samples at 0- to 12-inch depth across the entire remediation area. This sampling will be done only once at the beginning of the project to establish background concentrations of COCs in soil before adding soil amendments. Thereafter, this sampling will not be necessary.

28. Add soil amendments. The application should saturate the soil quickly, without exceeding the infiltration rate of the soil, in order to reduce puddling and standing of solutions on the soil surface or surface flow of solutions across the plot area. Complete elimination of surface movement will be difficult if the site is on a slope, since uniform infiltration will not occur across the entire remediation area. This is caused by differences in soil texture. Areas of higher clay content will exhibit slower infiltration and may be conducive to surface flow. As a precaution, berms should be constructed around areas where reduced infiltration may occur, particularly on slopes, to prevent runoff of amendments outside of the plot boundaries. However, the rapid rate is required to minimize damage to the plants by the amendments. Ideally the contamination will be no more than one-foot deep, and thus the acetic acid and EDTA should be added to acidify the soil and solubilize lead to a depth of one foot.

29. Allow sufficient time for maximum lead uptake by the crop and subsequent plant senescence. These time periods will allow sampling and harvest before the plants become desiccated and brittle to the point where the tissue shatters with handling. For example, if corn and mustard are the remediation crops, this will be about four days for corn plants and two days for mustard plants. The time may vary with different plant species and the plants should be monitored accordingly.

30. After the appropriate senescence period, conduct post-amendment addition plant sampling in the same fashion as the pre-amendment sampling. This sampling will be done to confirm the effectiveness of the amendment application in stimulating adequate lead uptake by the plants. The amount of lead in the plant is the direct measure of the technology effectiveness. The amount of plant tissue may also be used to calculate crop yields if an area of known size is sampled and the area equated to the entire field. The plant sampling will be done after each crop. This will be used to evaluate results and make necessary adjustments to “fine tune” the technology for each specific area. Conduct soil sampling at the end of three years to estimate the amount of lead reduction that has occurred in the soil, keeping in mind that it may be difficult to differentiate changes due to the inherent variability of lead concentrations in the soil. This will also provide ongoing monitoring of treatment effectiveness. The time required for remediation is based on the initial lead concentration in the soil and the predicted and calculated amount of lead removed from the soil each year. At the end of the proposed remediation period, for instance five years, comprehensive soil sampling will again be performed to evaluate the overall effectiveness of the program and to determine if continuation of the remediation effort is warranted.

31. Harvest the crop with commercial harvesting equipment such as combines for larger areas of one acre or more. The harvested crop is spread in a suitable area, usually within the

remediation area itself, and allowed to dry for 7-10 days, depending on ambient temperature. This will reduce the total weight taken to a smelter or landfill.

32. Transport the dried plant material to a smelter or landfill. Obtain a dry weight for the entire crop (yield) either by weighing on scales at the destination or by obtaining subsamples (4-6 standard size paper grocery bags of material), weighing the samples, drying at 150°F for 48 hours, and then re-weighing to determine the amount of moisture lost.

33. Perform a post-crop evaluation after each crop to determine the effectiveness of the treatment regime at that particular site. This evaluation will include a determination on the quantity of biomass generated by each crop and comparing it with known quantities of biomass from like crops grown in that region. If there is a noticeable deviation in biomass generated, then a detailed evaluation must be undertaken to understand the cause of the problem. Areas to be concerned about are incipient nutrient deficiencies which may not manifest visible symptoms, yet which reduce yields; similar effects of incipient toxicities; obvious toxicities caused by other contaminants, such as Be or Tl; insect infestations, fungus infections; soil-borne pathogens, such as nematodes; under-fertilization or leaching of added nutrients before being fully utilized by the crop; or the crop not tolerant of conditions at the site. It may be possible to substitute higher yielding varieties or silage-type crops to increase biomass yield and to use crops which are more specific for the area.

34. The post-crop evaluation must also include an interpretation of the quantity of lead removed per crop. If the quantity of lead removed is below the planned quantity, then the determination should be made as to whether the cause is related to the crop or the soil system or to a previous amendment application. If a crop was planted in an area where no previous chelate application has been made, possible corrections to the plant system include: (1) investigate use of alternate plant varieties or alternate crops which have equal capacity for lead uptake, but have a longer growing season and are higher yielding, and (2) investigate use of shorter growing season crops which may produce less biomass, but have greater capacity for lead uptake and then plant multiple crops. If the problem is soil related, then possibly adjusting the amendment rate to solubilize more lead may increase uptake by the crop. Lead plant uptake may be increased by using a faster delivery rate of the chelate to maintain a saturated medium in the soil for passive diffusion of lead to the plant root and to maintain the lead in the solution phase of the soil. If amendments were previously applied, possible remedies include deep-tilling soil to the depth of the liner or underlying intact soil strata to bring any lead that may have moved downward due to a previous chelate application back closer to the surface. This will allow more extensive root contact with soil lead.

35. Perform geostatistical analyses on soil sample data to re-map the area for lead concentrations and to determine the reduction in soil lead. This data may be used in conjunction with plant lead data to form a more complete picture of removal rates.

# Section 9.0
# Lessons Learned

Procedures and methodology that could be modified to improve the technology application are as follows:

1. Do not rely on past historical documentation for site characterization.

2. Thoroughly investigate the site history, soil hydraulics, and groundwater data before beginning. Site history would reveal if alteration of normal soil characteristics had occurred due to activities such as excavation, dumping and burial of debris, burning of wastes, and introduction of varying soil types as fill material. An accurate assessment of soil hydraulic conductivity would allow a valid mass water balance that would take into account varying soil texture, infiltration rates, and amounts of precipitation. Existing groundwater data will provide information about the concentration of contaminants in the groundwater prior to phytoextraction.

3. Realize that an area having a shorter growing season may preclude the use of multiple crops in a season.

4. Establish a strong and empathetic working relationship with the appropriate regulatory authorities from the outset. Freely provide information and accede to requests for additional information.

5. Do not try to implement *in situ* phytoextraction as a sole remediation technology on areas of heterogeneous waste, debris, and unknown contaminants. Instead, limit implementation of *in situ* to sites where lead is known to be in ionic form and sites which are homogeneous.

6. If a site is non-homogeneous and particulate lead will be a problem, use screening and separation techniques to make the soil at the site as uniform as possible and to remove particulate lead.

7. Install a leachate containment and collection system if soil properties are conducive to leaching.

8. Determine plant available forms of lead and use as the basis for the amount of EDTA that will be applied.

9. Consider sacrificing maximum lead uptake and extending the remediation period by using minimal quantities of EDTA. The nature of the chelate, the effect of carry-over EDTA on subsequent crops, and the toxicity thresholds for plants have not been established, and the mechanism for plant damage has not been determined. Root damage may occur directly from exposure to the chelate, and the electrolyte balance within the plant may be upset by increased ion uptake due to the chelate. These problems will have to be addressed and

resolved before the true potential of the technology is realized. This can only be done by further bench-scale laboratory and greenhouse research. Quite possibly, some of the second-generation chelates recently approved for use in land systems may overcome these problems. Although these chelates have weaker affinity for metals (and other nutrient cations), their half-life in soil is much less. Possibly, these chelates can be safely added in multiple increments that do not harm plants and thus may prove useful in establishing a "chronic" exposure to a given element rather than the "acute" dose with EDTA. The reduced affinity for other ions may also prevent overload of the ion uptake mechanism. However, only additional research can address these questions.

10. Investigate the use of second generation chelates. According to representatives of BASF Corporation (BASF Corporation, 3000 Continental Drive - North, Mount Olive, New Jersey 07828-1234) second generation derivatives of EDTA have several properties which may make such chelates desirable for use in phytoextraction schemes. Depending upon specific circumstances, these chelates 1) may degrade more quickly and easily than EDTA; 2) have less affinity for lead, which greatly decreases the potential for lead leaching; 3) may be less toxic to plants; and 4) are comparable in unit cost.

11. If EDTA is used, consider soil amendments that will adsorb and limit potential migration of EDTA. Such amendments are iron-enriched municipal biosolids or poultry litter. The addition of organic matter will also stimulate microbial population growth and encourage more rapid degradation of EDTA.

12. Consider addition of innocuous basic cation sources, such as calcium sulfate, calcium nitrate, magnesium sulfate, etc., to complex with EDTA and displace and re-precipitate lead in soil to limit potential lead leaching through soil.

13. Develop an analytical method to measure residual EDTA absorbed on soil. This would be EDTA sorbed onto soil in non water-soluble form which is not detectable by current analytical methods, and which affect subsequent crop plantings.

14. Conduct agronomic operations with mechanized agricultural equipment to save on labor costs.

15. Plan on using proven high-yielding, prolific rooting crop varieties, such as silage corn, and maximize vegetative production by high rate use of fertilizers, particularly nitrogen.

16. Employ deep-tilling practices to return lead that has moved out of the root zone to the plant rooting zone.

17. Instigate pest repellent measures (e.g., for birds) before the problem becomes too serious to correct.

18. Carefully consider the time frame for remediation. Indications are that the time required for remediation of appreciable amounts of lead from soil using phytoextraction will be unrealistically long.

# Section 10.0
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# APPENDIX B
## Data Archiving and Demonstration Plans

Copies of the project's Technology Demonstration Plan are available through the USAEC and may be obtained by contacting the USAEC's library, telephone (410) 436-1239, at Aberdeen Proving Ground, Maryland, or by writing to the following address:

Commander
U.S. Army Environmental Center
ATTN: SFIM-AEC-RM (TIC, Ms. Julia Tracy)
5179 Hoadley Road
Aberdeen Proving Ground, Maryland 21010-5401

The Technology Demonstration Plan is entitled "*Technology Demonstration Plan for Phytoremediation of Lead-Contaminated Soil at the Twin Cities Army Ammunition Plant*" USAEC Report No. SFIM-AEC-ET-98008; March 1998.

The project demonstration's raw data may be obtained through the USAEC by contacting Ms. Darlene Bader-Lohn, telephone (410) 436-6861, at Aberdeen Proving Ground, Maryland, or by writing to the following address:

Commander
U.S. Army Environmental Center
ATTN: SFIM-AEC-ETD (Ms. Darlene F. Bader-Lohn)
5179 Hoadley Road
Aberdeen Proving Ground, Maryland 21010-5401

Records of experiments and analyses shall be maintained for a period of three years after the end of the project. This shall include machine printouts of chromatogram traces, logbooks, notebooks, logsheets, standard material use logs, and raw data calculation sheets. Records will be accumulated and stored in a federal agency records center with access control, retrieval, and fire protection, as described in 36 CFR 1228 Subpart K.

Due to the limited lifetime of magnetic computer storage media, critical records shall not be stored in that form. Any computer media utilized to store analytical file backups shall be stored for the lifetime of the project plus one year.

# APPENDIX C
# Quality Assurance

# APPENDIX C
# Quality Assurance Plan

## C.1 Purpose and Scope of the Plan

The purpose of the quality assurance plan was to establish processes to ensure that:

- Demonstration conditions and operations were planned, communicated, and documented.
- Sufficient measurements were made to assess the effectiveness of the treatment methods.
- Samples taken were representative of the conditions in the demonstration.
- Samples were delivered to the laboratory for analysis without deterioration.
- Samples were processed by the laboratory without deterioration prior to analysis.
- Measurement techniques were sufficiently specific to measure the target compounds.
- Data collected or generated were reliable.

The quality assurance plan applied to all activities, including performing experiments, sampling, and laboratory analysis of samples.

TVA's Analytical Laboratory provided analytical chemistry support for the project by performing analyses for metals, nutrients, and soil characteristics. Procedures for extraction and analysis of EDTA were developed and tested for this project.

## C.2 Quality Assurance Responsibilities

The attached organizational chart (Figure C-1) shows the TVA organizations providing support to the project.

Responsibilities of the USAEC project team were as follows:

- The USAEC Program Manager was responsible for ensuring that the USAEC and ESTCP project and program goals were met.

Responsibilities of the TCAAP project team were as follows:

- The ATK Project Manager was responsible for overall direction of project field operations at TCAAP. These responsibilities included oversight and direction of staffing levels; process design, procurement, construction, and maintenance; field process operations; ATK-directed laboratory work; technical reports; preparation and presentation of technical papers; and conducting tours and briefings. The ATK Project Manager provided direction to ATK team members to ensure that project goals were met, reports were delivered on schedule, and that task schedules and costs were met. The ATK Project Manager ensured that any variances related to ATK areas or responsibility were adequately explained and was the primary interface with TVA.

- The ATK Field Operations Staff provided assistance to the ATK Project Manager to assure that ATK responsibilities were met.

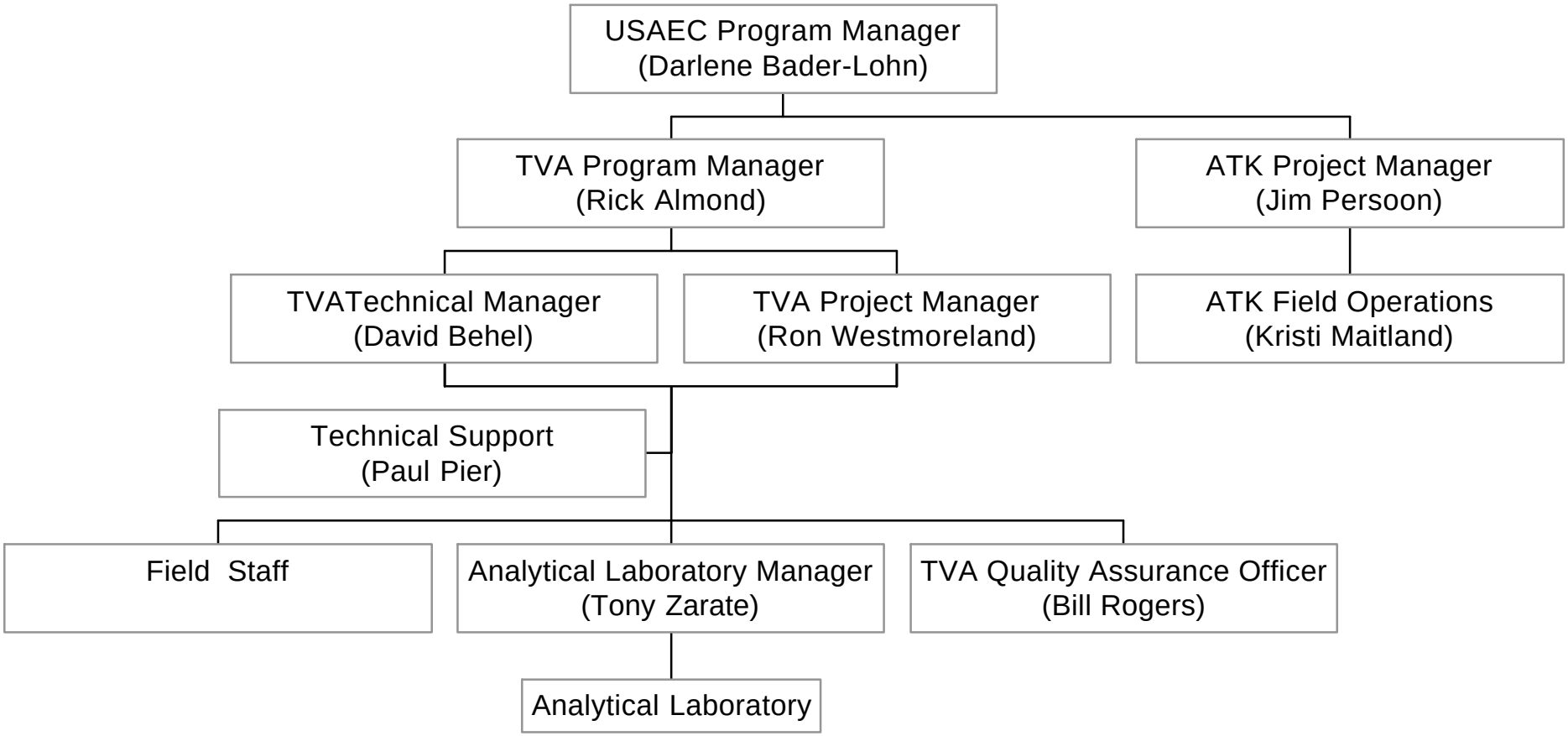


**Figure C-1**

**Project Organization Chart**

Responsibilities of the TVA project team were as follows:

- The TVA Program Manager was responsible for providing guidance to the project and ensuring that program goals were met. The TVA Program Manager was also responsible for resolving any inconsistencies between USAEC, TCAAP, TVA, and ATK mission objectives and those of the project.

- The TVA Project Manager was responsible for overall direction of the project and was responsible for oversight and direction of staffing levels, process design, equipment installation, maintenance, field process operations, technical reports, preparation and presentation of technical papers, and conducting briefings of USAEC personnel. The TVA Project Manager was responsible for providing direction and executing tasks to ensure that project goals were met, reports were delivered on schedule, and that task schedules and costs were met. The TVA Project Manager ensured that any variances were adequately explained.

- TVA's Technical Manager was responsible for planning and implementing the details of the field studies, including experimental design, field process operations, sampling, documentation, maintaining data integrity, data interpretation, providing technical reports to the TVA Project Manager, and preparation and presentation of technical papers. The TVA Technical Manager was available to assist the TVA Project Manager in conducting briefings to Army personnel. The TVA Technical Manager was also the primary interface with ATK field support staff and provided technical direction for field activities.

- The TVA Field Staff reported to the TVA Technical Manager and was responsible for providing assistance in various field tasks during TVA visits to the site.

- The TVA Analytical Laboratory in Muscle Shoals, Alabama, was responsible for providing analytical measurements on soil, plant, and soil solution samples required in the course of the project and was responsible for review of the data produced, documentation of analytical runs, and ensuring data integrity. The laboratory was managed by the Analytical Laboratory Manager. The Analytical Laboratory Manager reported to the TVA Technical Manager and was responsible for providing project analytical oversight and for final analytical data integrity.

- Technical Support Staff provided technical assistance to the TVA Technical Manager in experimental design, data interpretation, troubleshooting, and report writing.

- The TVA QA Officer was responsible for implementing the QA program and for auditing actions and documentation to ensure adherence to this section. The TVA QA Officer was responsible for providing quarterly QC data reports to the TVA Project Manager.

## C.3 Quality Program Procedures and Documents

The Analytical Laboratory activities conducted during this project were carried out in accordance with the laboratory's Quality Assurance Manual which contains the following documents:

QAPLAN - "Quality Assurance Plan"
GLP-0001 - "Procedure Format and Style"
GLP-0002 - "Quality Assurance Records Control"
GLP-0003 - "Procedure Preparation and Distribution"
GLP-0004 - "Training"
GLP-0005 - "Nonconformances and Corrective Actions"
GLP-0006 - "Control of Reagents and Standards"
GLP-0007 - "Analysis Work Plan Preparation"
GLP-0012 - "Treatment of Data"
GLP-0013 - "Instrument Logbook and Control Chart Maintenance"
GLP-0016 - "Sample Receipt, Log-in, and Data Handling"
GLP-0017 - "Control of Changes to Software"
CP-0001 - "Measurement and Test Equipment Control and Calibration"
SP-0001 - "Sample Chain of Custody"

Laboratory analyses were conducted in accordance with written procedures. Modifications to procedures found to be necessary to perform the analyses required in this test plan were noted in equipment operation logs or research notebooks until included in revisions to procedures. Two procedures were developed for this project: AP-0047 "EDTA by High Performance Liquid Chromatography" and AP-0057 "Extraction of EDTA from Soil."

The various quality control samples associated with each analytical run were assessed at the time the data were produced by both analytical staff members and the quality assurance officer. Furthermore, project data from all runs were accumulated and assessed for reasonableness and consistency by the researchers. Consequently, research and quality staff members feel that the quality assurance objectives for the analytical measurement processes associated with this project were met.

The experimental portion of this plan was performed in accordance with the project plan. Data, observations, experimental conditions, and minor modifications to planned activities were recorded in research or field notebooks in a complete enough fashion that all actions, results, and conclusions could be reconstructed.

Sampling was conducted in accordance with written work plans, procedures, or instructions to ensure complete samples were taken at correct times and in a manner which did not invalidate conclusions. All actions in sampling were recorded in research or field notebooks or on forms designed to ensure complete documentation of all experimental parameters. Instructions were provided for proper preservation of samples.

## C.4 Control of Purchased Items

Chemicals, equipment, materials, and other items purchased to conduct this project were of suitable quality to meet the project needs as specified in the written procedures. Purchased items were inspected upon receipt to ensure they met the requirements specified in purchase requests. Nonconforming items were not used. Suitable handling activities, storage conditions, and other controls were utilized to ensure quality of purchased items was not degraded after receipt.

## C.5 Record Control

Records of analysis, records of calibration, research notebooks, chromatograms, sampling logs, custody records, work plans, machine printouts, chromatogram traces, logsheets, standard material use records, raw data calculation sheets, and copies of procedures were maintained as quality assurance records as specified in GLP-0003. Records were accumulated in logical arrangement to facilitate retention and review. In-process records and logbooks were stored in the work area in a safe manner to protect against loss, fire, spills, or other damage.

Records of experiments and analyses will be maintained for a three-year period after the end of the project. This includes machine printouts or chromatogram traces, logbooks, notebooks, logsheets, standard material use logs, and raw data calculation sheets. Due to the limited lifetime of computer storage media, any computer media utilized to store analytical file backups or raw data files will be stored for the lifetime of the project plus one year.

## C.6 Data Quality Parameters

### C.6.1 Accuracy and Precision

Percent recovery, relative percent difference, standard deviation, and other commonly used statistical indicators of accuracy and precision were calculated as defined in Chapter 1 of SW-846, 3rd Edition.

### C.6.2 Method Detection Limit, Method, Quantitation Limit

Method Detection Limits were calculated as defined in Title 40, Code of Federal Regulations, Part 136, Appendix A, "Definition and Procedure for the Determination of the Method Detection Limit" - Revision 1.11.

Method Quantitation Limits were defined as five times the Method Detection Limit as in Chapter 1 of SW-846, 3rd Edition, or as the lowest point used in making the calibration curve, whichever was higher.

## C.7 Calibration Procedures and Quality Control Checks

The precision and accuracy of new or revised analytical procedures were investigated before the procedures were used for analysis of samples.

### C.7.1 Initial Calibration Procedures

#### C.7.1.1 Laboratory Instrumentation

The calibration frequencies and quality control tests required in SW-846 for HPLC methods were used in the HPLC method for EDTA. The calibration frequencies and quality control tests required in SW-846 for metals analysis were used for ICP and AA methods. Guidelines for calibration frequencies and tests, as specified by the manufacturer, were used for flow injection analyzer (FIA) methods.

## C.8 Analytical Laboratory Calibration and Quality Control

### C.8.1 General Quality Control Requirements

The project's analytical data were calculated on vendor-supplied software for the HPLC system, FIA system, and ICP spectrophotometer. These systems typically integrate sample signals, calculate calibration curves automatically, and apply the curves to sample measurements. However, a spreadsheet developed at TVA was used to fit curves and calculate data for the HPLC analysis. Other laboratory calculations were carried out on spreadsheets developed and tested at TVA or on hand-held calculators (e.g., soil moisture). Some devices such as pH meters, give direct readout or printout of analytical data.

### C.8.2 Batch QC

With each batch of 20 samples or subset thereof, one method blank, one matrix spike, and one laboratory control sample were run. In addition, one sample duplicate or one matrix spike duplicate was run with each batch. Note: For some analytical techniques, matrix spikes were not possible.

### C.8.3 Quality Control Requirements for HPLC

Retention time windows were determined and the device was calibrated during development of the procedure. Five calibration standards were used.

At the beginning of each day that analyses were conducted, the midpoint calibration standard was analyzed. Then, every ten samples and at the end of the run, a midpoint calibration standard was run again in accordance with the quality control requirements for HPLC devices.

### C.8.4 Quality Control for Automated Laboratory Instrumentation

Flow Injection Analyzers (FIA) were calibrated before each use following written procedures. For FIA, calibration was performed with standards of five concentrations at the beginning of each day. Concentrations bracketed the range of interest, but were limited to the range of linear response of the device.

For these devices, a midpoint calibration standard was run at least every ten samples and at the end of the run throughout the day. Any group of ten samples preceding and following a midpoint calibration check which fell outside the 15% limit was reanalyzed.

For these devices, a laboratory control sample made from a separate stock than the calibration standards was run with each batch. For any of these devices, samples exhibiting a signal above the linear range of the device were diluted and reanalyzed.

### C.8.5 Definitions

- **Batch** - Usually a group of no more than 20 samples of the same matrix prepared or extracted at the same time with the same reagents.

- **Method Blank** - A sample of clean reagent carried through preparation and extraction in the same manner as samples. One method blank was run with each batch.

- **Matrix Spike** - An aliquot of a sample spiked with a known concentration of all target analytes. Spike concentration was selected to read at five times the Method Quantitation Limit in the sample or about the midpoint of the calibration curve. One matrix spike was run for each batch. Spiking occurred prior to sample preparation and analysis.

- **Matrix Spike Duplicate** - A second aliquot of the same sample treated in the same manner as the matrix spike.

- **Duplicate** - A second aliquot of a sample taken independently through extraction and preparation before analysis.

- **Quality Control Check Sample** - A quality control sample of the same type and matrix as calibration solutions, but made independently from the calibration solutions. This sample is also referred to as a laboratory control sample.

### C.8.6 Data Reduction, Validation, and Reporting

#### C.8.6.1 Data Reduction

The project's analytical data were calculated on vendor-supplied software for the HPLC system, FIA system, and ICP spectrophotometer. These systems typically integrate sample signals, calculate calibration curves automatically, and apply the curves to sample measurements. However, a spreadsheet developed at TVA was used to fit curves and calculate data for the HPLC analysis. Other laboratory calculations were carried out on spreadsheets developed and tested at TVA or on hand-held calculators (e.g. soil moisture). Some devices such as pH meters, give direct readout or printout of analytical data.

The Analytical Laboratory’s Chemical Laboratory Analysts were responsible for calculation and reduction of data.

#### C.8.6.2 Data Validation

Analytical measurements were first reviewed by the chemist producing them and then by another chemist before being interfaced with the laboratory database. If quality control samples fell outside limits, the samples were usually scheduled for reanalysis. After questions were resolved, results were passed on to the Laboratory Manager for final review and validation.

Group supervisors or team leaders were responsible for decisions concerning reanalysis of samples and coordinated with the Project Manager when significant problems were discovered or when resampling was required.

#### C.8.6.3 Data Reporting

Analytical data were reported in units of milligrams per liter for liquid samples. Solid sample results were reported as milligrams per kilogram dry weight unless other units such as percent were more appropriate.

Method Detection Limits and Instrument Detection Limits were reported for each run. Recovery of matrix spikes and recovery of quality control samples were calculated and reported as percentages.

#### C.8.6.4 Corrective Action

Corrective action in accordance with the requirements of GLP-0005 was not identified in the course of this project.

## C.9 Performance and System Audits

### C.9.1 Performance Audits

Analytical Laboratory participated in USEPA Water Pollution Studies twice yearly during this project. The Analytical Laboratory investigated any analyte falling outside control limits and reported its findings to the Quality Assurance Officer in writing. Participation in this cross-checking process provides information on Analytical Laboratory's performance as compared to other laboratories in the nation.

### C.9.2 On-Site System Audits

The Analytical Laboratory's Quality Assurance (QA) Officer periodically inspected logs, records, printouts, results of quality control checks, documentation, case narratives, research notebooks, and other quality-related aspects of the project to ensure detailed compliance.

## C.10 Quality Assurance Reports

### C.10.1 Status Reports

TVA's Project Manager provided periodic progress reports to USAEC which contained a summary of accomplishments and a discussion of significant problems and their resolution.

Quarterly quality control data reports were written by the QA Officer addressing:

- Changes in this QA project plan
- Changes in analytical procedures
- Summary of QC program results
- Summary of training
- Results of audits
- Results of performance sample evaluations

- Data quality assessment in terms of precision, accuracy, and MDLs
- Discussion of whether QA objectives were met

## C.11 Data Management and Analysis

### C.11.1 Analytical Data

Analytical data packages for the project included:

- Sample description or identification information
- Sample analytical results
- Quality control sample results with surrogate recoveries and percent recovery of known compounds

Sufficient data were maintained such that experimental and analytical results could be reconstructed.

Records of all attempts at analysis were maintained whether or not the analysis was successful. However, unusable data were not reported. Data were unusable when quality control samples or quality control checks failed; however, the records for these attempts at analysis were maintained with relevant documentation. Data Qualification Codes in use by the laboratory and which may have been encountered in review of this project's data were as follows:

**NA** - Compound not analyzed

**<MDL** - Compound not detected (value falls less than Method Detection Limit)

**TR or Trace** - Compound present at trace level, indicated but less than MDL

**Q** - "Qualified" - For a sample in which an analyte was quantified, but an associated quality control sample fell outside control limits

## C.12 Contract Laboratory

A contract laboratory was used on two instances in October and November 1998 to perform arsenic analysis by ICP when an instrument failed at TVA. The samples were prepared at TVA with inclusion of laboratory duplicates, matrix spikes, method blanks, and laboratory control samples. The total number of samples involved was 104 for the first set and 95 in the second set. Response on the quality control samples was satisfactory.

# APPENDIX D
# Methods and Procedures

# APPENDIX D-1
# Analytical Procedure for pH: Method ASA 12-2.6

**Soil pH**
ASA 12-2.6

Procedure:

1. Calibrate the pH meter according to manufacturer's instructions using two buffers to bracket the expected range of measurements. Buffers should be approximately three pH units apart.

2. Where available, check the calibration with a third buffer.

3. Prepare a slurry of soil and water in the ratio of 10.0 g to 10.0 ml.

4. Stir the slurry vigorously with a glass rod and place the electrode into the slurry. Allow the electrode to come to equilibrium and measure the pH.

5. Record information about the calibration buffers (manufacturer, expiration date, known value), the check buffer and its measurement, and sample measurements.

References:

"pH, Method 150.1 (Electrometric)," *Methods for Chemical Analysis of Water and Wastes* - Revised March 1983, U. S. Environmental Protection Agency, Cincinnati, OH, PB84-128677.

"Glass Electrode - Calomel Electrode pH Meter Method," Section 12-2.6 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-2
# Analytical Procedure for Total Organic Carbon (TOC): Method ASA 29.3.5.2

**Total Organic Carbon - Rapid Dichromate Oxidation Technique**
**ASA Method 29-3.5.2**

Summary of Method

Organic carbon in soil is oxidized by reacting with potassium dichromate. The heat of dilution of sulfuric acid in water provides heat for the reaction. Excess dichromate is titrated with ferrous ion using *o*-phenanthroline as the indicator. The oxidation reaction is as follows:

$$2\ Cr_2O_7^{2-} + 3\ C + 16\ H^+ = 4\ Cr^{3+} + 3\ CO_2 + 8\ H_2O$$

Reagents

1. 1 *N* Potassium Dichromate Solution. Dissolve 49.04 g of reagent-grade $K_2Cr_2O_7$ (dried at 105°C) in water, and dilute the solution to 1 liter in a volumetric flask.

2. Sulfuric Acid, concentrated (not less than 96%). If chloride is present in soil, add silver sulfate at 15g/l.

3. *o*-Phenanthroline-ferrous complex, 0.025M. Dissolve 14.85 g of *o*-phenanthroline monohydrate and 6.95 g of ferrous sulfate heptahydrate in water. Dilute the solution to a volume of 1,000ml. (This complex is also available under the trade name of Ferroin.)

4. 0.5 *N* Ferrous Sulfate solution. Dissolve 140 g of reagent-grade $FeSO_4$•7H2O in water. Add 15 ml concentrated sulfuric acid. Cool the solution and dilute it to a volume of 1,000ml. Standardize this reagent daily by titrating against 10.0 ml of 1N potassium dichromate.

Or

0.5 *N* Ferrous Ammonium Sulfate Solution. Dissolve 196 g of reagent-grade $(NH_4)_2SO_4$•FeSO4•6H2O in water. and dilute it to a volume of 1,000ml. Standardize this reagent daily by titrating against 10.0 ml of 1N potassium dichromate.

Procedure

1. Grind the soil to pass through a 0.5-mm sieve, avoiding iron or steel mortars.

2. Transfer a weighed sample, containing 10 to 25 mg of organic C, but not in excess of 10g of soil, into a 500-ml wide-mouth flask.

References

"Walkley-Black Procedure" Section 29-3.5.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-3
# Analytical Procedure for Total Kjeldahl Nitrogen (TKN): Lachat Method

QuikChem METHOD 13-107-06-2-D

# DETERMINATION OF TOTAL KJELDAHL NITROGEN IN SOILS AND PLANTS BY FLOW INJECTION ANALYSIS

(Block Digestor Method)

Written by David Diamond

Applications Group

Revision Date:

23 December 1996

ZELLWEGER ANALYTICS, INC.
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zellweger analytics

**QuikChem Method 13-107-06-2-D**

# Total Nitrogen in Kjeldahl Digests of Soils and Plants

(Block Digestor Method)

**1.0 to 100 mg N/L**
**0.03 to 2.50%N in Plant Tissue**
**0.01 to 1.25% N in Soil**

## --Principle--

Samples are digested with sulfuric acid in 75 mL tubes in a block digestor. With a copper sulfate catalyst, the samples' Kjeldahl nitrogen is converted to the ammonium cation. Potassium sulfate is also added to raise the boiling temperature of the digestion and speed the conversion to ammonium. The digest is diluted to a final volume of 50 mL with DI water.

Approximately 0.06 mL of the digested sample is injected onto the chemistry manifold where its pH is controlled by raising it to a known, basic pH with a concentrated buffer. This in-line neutralization converts the ammonium cation to ammonia, and also prevents undue influence of the sulfuric acid matrix on the pH-sensitive color reaction which follows.

The ammonia thus produced is heated with salicylate and hypochlorite to produce blue color which is proportional to the ammonia concentration. The color is intensified by adding sodium nitroprusside. The presence of tartrate in the buffer prevents precipitation of calcium and magnesium.

## --Special Apparatus--

1. Heating Unit
2. Block Digestor/75 mL tubes (Lachat Part No. 1800-000)
3. Vortex Mixer

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# QuikChem Method 13-107-06-2-D

# DETERMINATION OF TOTAL KJELDAHL NITROGEN BY FLOW INJECTION ANALYSIS COLORIMETRY

## 1. SCOPE AND APPLICATION

1.1. This method covers the determination of nitrogen in dried, ground plant or soil samples. Since acid consumption during digestion is proportional to organic matter content, highly organic materials may require less sample. If there is a doubt about the best sample weight, preliminary experiments should be run.

1.3. The applicable range is 1.0 to 100 mg N/L. The method detection limit is 1.0 mg N/L. The method throughput is 72 injections per hour.

## 2. INTERFERENCES

2.1. Samples must not consume more than one fifth of the sulfuric acid during the digestion. The buffer will accomodate a range of 5.6 to 7% (v/v), $H_2SO_4$ in the diluted digestion sample with no change in signal intensity.

## 3. SAFETY

3.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

3.2. Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

3.3. <u>Always</u> wear a full face shield, gloves, and a lab coat when working with hot digest samples.

3.4. The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

3.4.1. Sodium Hydroxide

3.4.2. Sulfuric Acid

3.4.3. Sodium Nitroprusside

3.4.4. Sodium salicylate

3.4.5. Clorox bleach (5.25% sodium hypochlorite)

3.4.6. Copper sulfate

3.4.7. Ammonium chloride

3.4.8. Hydrochloric acid

## 4. EQUIPMENT AND SUPPLIES

4.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

4.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

4.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

4.3.1. Autosampler

4.3.2. Multichannel proportioning pump

4.3.3. Reaction unit or manifold

4.3.4. Colorimetric detector

4.3.5. Data system

4.4. Special Apparatus

4.4.1. Heating unit

4.4.2. Block Digestor/75 mL tubes (Lachat Part No. 1800-000)

4.4.3. Vortex Mixer

## 5. REAGENTS AND STANDARDS

### 5.1. PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

**Degassing with helium:**

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in$^2$) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

**Reagent 1. Buffer**

**By Volume:** In a **1 L volumetric flask** dissolve **65 g sodium hydroxide** (NaOH), **50.0 g sodium potassium tartrate** (potassium sodium tartrate, d,l-$NaKC_4H_4O_6 \cdot H_2O$) and **26.8 g sodium phosphate dibasic heptahydrate** ($Na_2HPO_4 \cdot 7H_2O$), and **950 g water**. Dilute to the mark and invert to mix. Stir or shake until dissolved.

**By Weight:** To a **tared 1 L container** add **65 g sodium hydroxide** (NaOH), **50.0 g sodium potassium tartrate** (potassium sodium tartrate, d,l-$NaKC_4H_4O_6 \cdot H_2O$), **26.8 g sodium phosphate dibasic heptahydrate** ($Na_2HPO_4 \cdot 7H_2O$), and **950 g DI water.** Stir or shake until dissolved.

**Reagent 2. Salicylate Nitroprusside**

**By Volume:** To a **tared 1 L volumetric flask** dissolve **150.0 g sodium salicylate** [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], **1.00 g sodium nitroprusside** [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] and about **800 mL DI water**. Dilute to the mark and invert to mix. Store in a dark bottle and prepare fresh monthly.

**By Weight**: To a **tared 1 L dark container**, add **150.0 g sodium salicylate** [salicylic acid sodium salt $C_6H_4(OH)(COO)Na$], **1.00 g sodium nitroprusside** [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] and **908 g water**. Stir or shake until dissolved. Store in a dark bottle and prepare fresh monthly.

**Reagent 3. Hypochlorite Solution (0.3% NaOCl)**

**By Volume**: In a **1 L volumetric flask**, dilute **60.0 mL Regular Clorox Bleach** (5.25% sodium hypochlorite, The Clorox Company, Oakland, CA) to the mark with **DI water**. Invert to mix. Prepare fresh daily.

**By Weight**: To a **tared 1 L container**, add **64 g of Regular Clorox Bleach** (5.25% sodium hypochlorite, The Clorox Company, Oakland, CA) and **936 g DI water**. Shake to mix. Prepare fresh daily.

**Reagent 4. Matrix Blank/Diluent/Digestion Solution**

**NOTE:** Prepare three liters of this solution.

**By Volume:** In a **1 L volumetric flask**, add approximately **700 mL DI water**, then add **70 mL concentrated sulfuric acid** ($H_2SO_4$). Add **30 g potassium sulfate** ($K_2SO_4$). Add **2.5 g copper sulfate** ($CuSO_4 \cdot 5H_2O$) and dilute to the mark with **DI water**. Mix with a magnetic stirrer and allow the solution to cool. Dilute to the mark with **DI water** after the solution has cooled. Prepare fresh monthly.

**By Weight:** In a **tared 1 L container**, add **915 g DI water**, then add **128.1 g concentrated sulfuric acid** ($H_2SO_4$). Add **30 g potassium sulfate** ($K_2SO_4$). Add **2.5 g copper sulfate** ($CuSO_4 \cdot 5H_2O$). Mix with a magnetic stirrer, or invert to mix, and allow the solution to cool. Prepare fresh monthly.

## 5.2. PREPARATION OF STANDARDS

**Standard 1. Stock Standard 1000 mg N/L**

**By Volume**: In a **1 L volumetric flask** dissolve **4.716 g ammonium sulfate** $(NH_4)_2SO_4$ primary standard in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix.

**Standard 2. Working Stock Standard 100 mg N/L**

**By Volume**: In a **1 L volumetric flask**, add **100.0 mL Standard 1**, **30 g potassium sulfate** ($K_2SO_4$), **2.5 g copper sulfate** ($CuSO_4 \cdot 5H_2O$), and **70 mL sulfuric acid** ($H_2SO_4$). Dilute to the mark with **DI water**. Invert to mix.

| **Working Standards** (Prepare Daily) | A | B | C | D | F |
|---|---|---|---|---|---|
| Concentration mg N/L | 100 | 75.0 | 50.0 | 25.0 | 0.00 |

**By Volume**

| | | | | | |
|---|---|---|---|---|---|
| Volume (mL) of **working stock standard 2** diluted to 100 mL with reagent 4 | 100 | 75.0 | 50.0 | 25.0 | 0.0 |

**By Weight**

| | | | | | |
|---|---|---|---|---|---|
| Weight (g) of **stock standard 2** diluted to final weight (~100 g) multiplied by **factor** below with reagent 4 | 100 | 75.0 | 50.0 | 25.0 | 0.0 |
| **Division Factor**<br>Multiply exact weight of the standard by this **factor** to give final weight | 1.00 | 0.75 | 0.50 | 0.25 | 0 |

## 6. SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1. Plant and soil samples are dried overnight at a temperature less than 100°C. The dried soil is then ground to pass a 20 mesh screen and plant tissue is ground to pass a 40 mesh screen. If this fineness of grind is not achieved, samples may not be homogenous. To verify homogeneity, several of each sample should be digested. Digests may be covered tightly and stored for one week.

## 7. PROCEDURE

### 7.1. DIGESTION PROCEDURE

**NOTE:** Calibration is performed using standards in the digest matrix, i.e., NOT digested. Standards are not digested but are instead synthetic solutions of ammonium-nitrogen prepared in the digest matrix. Instructions for preparing standards in the digest matrix are given in section 5 of this method.

**CAUTION:** Always wear safety goggles, a complete face shield, a labcoat, and acid resistant rubber gloves when carrying out the following procedure. It is also important to follow the safety procedures described in the block digestor manual.

7.1.1. Since standards are not carried through the digestion procedure, a sample with known concentration of total nitrogen should be included with each digestion set to verify complete digestion.

7.1.2. Start with a clean, dry set of digestion tubes. To each tube, add 0.2 g of plant tissue or 0.4 g of soil. If weighing papers are used, a blank should be carried through the digestion and the sample results should be corrected for the blank. If the complete set of tubes is not being used, remove the empty tubes prior to digestion.

7.1.3. To each tube add 1.50 g of potassium sulfate ($K_2SO_4$) and 0.125 g of copper sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$) This can be accomplished by adding a commercially available salt catalyst mixture in tablet form. (Available from SCT Sales, Inc. Littleton, CO., (303-730-0084, cat no. KC-C1).

7.1.4. Add 2-4 boiling stones to each tube. Hengar (Alundum) granules are effective for smooth boiling. They are available from Fisher Scientific, cat. no. S145-500.

7.1.5. To each tube add 3.5 mL of concentrated sulfuric acid ($H_2SO_4$). This is efficiently accomplished using an acid resistant repipet device (EM Science, 108033-1).

7.1.6. Place tubes in block digestor which has been preheated to 160°C. On the block digestor controller, set Temp 1 to 390°C and Time 1 to 180 minutes. If the block temperature is greater than 180°C, cool the block before inserting tubes. If using the Lachat BD-46 or BD-26, the entire digestion can be done with cold fingers in place.

3. Add 10 ml of 1N $K_2Cr_2O_7$ with a volumetric pipette. Swirl the flask gently to disperse the soil in the solution.

4. Rapidly add 20 ml concentrated sulfuric acid, directing the stream into the suspension. Immediately swirl the flask gently until soil and reagents are mixed, then more vigorously for a total of 1 minute.

5. Allow the flask to stand on a heat-impervious surface for about 30 minutes.

6. Add 200 ml water to the flask, and filter the suspension if experience with the particular soil shows that the endpoint of the titration cannot be otherwise be clearly discerned.

7. Add three drops o-phenanthroline indicator and tirate the solution with 0.5N $FeSO_4$. As the endpoint is approached, the solution takes on a greenish cast and then changes to a dark green. At this point, add the ferrous sulfate solution drop by drop until the color changes sharply to blue to red (maroon in reflected light against a white background.)

8. To standardize the dichromate, make a blank determination without soil.

9. Repeat the determination with less soil if greater than 75% of the dichromate is reduced.

10. Calculate the results as follows:

Organic C % $=(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4)(0.003)(100)(1.30)/(\text{g water-free soil})$

$=(10.0 - \text{meq Fe } SO_4)(0.003)(100)(1.30)/(\text{g water-free soil})$

Note: 1.30 is an empirically obtained correction factor.

11. Calculate the normality of the ferrous sulfate solution as follows:

Normality = 10/(vol)

where vol is the volume of ferrous ion solution required to titrate 10.0 ml 1 *N* $K_2Cr_2O_7$.

Note: Ferrous ammonium sulfate may be substituted for ferrous sulfate in this procedure.

7.1.7. Continue to digest for three hours. During the first two hours the temperature will ramp to 390°C and then during the third hour the temperature should hold at 390+/- 5°C. It is critical that the digestion's remain at 390°C for one full hour.

7.1.8. Remove the samples from the block and allow about 10 minutes for cooling.

7.1.9. Add 46.5 mL of DI water to each tube. Carefully vortex to mix, pointing the tube away in case of splashing. The final volume should be 50 mL.

7.1.10. If digests are not run immediately they should be covered with Parafilm or capped tightly.

## 7.2. SYSTEM START-UP AND CALIBRATION PROCEDURE

7.2.1. Prepare reagent and standards as described in section 5.

7.2.2. Set up manifold as shown in section 11.1.

7.2.3. Input peak timing and integration window parameters as specified in section 11.

7.2.4. Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

7.2.5. Place standards in the autosampler, and fill the sample tray. Input the information required by data system, such as concentration, replicates and QC scheme.

7.2.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with responses for each standard.

7.2.7. After a stable baseline has been obtained, start the sampler and perform analysis.

## 7.3. SYSTEM NOTES

7.3.1. Allow at least 15 minutes for the heating unit to warm up to 60°C.

7.3.2. Upon system start up it is crucial to establish good flow before the salicylate reagent is added. If the salicylate reagent merges with the acid sample prior to neutralization, it will precipitate. Always add the salicylate reagent last. When in doubt, check that the flowcell waste stream is alkaline (with litmus paper) before adding that salicylate reagent.

7.3.3 If basline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure:

Place all reagent transmission lines in water and pump to clear reagents (2-5 minutes).

Place reagent lines and carrier in a **1 N hydrochloric acid** (1 volume of HCl added to 11 volumes of water) and pump for several minutes.

Place all transmission lines in water and pump for several minutes.

Resume pumping reagents.

At the end of the run place all transmission lines **except the buffer** in water and flush system for two minutes. Place buffer transmission in water, flush system, then pump all lines dry.

7.3.4. In normal operation nitroprusside gives a yellow background color which combines with the blue indosalicylate to give an emerald green color. This is the normal color of the solution in the waste container.

7.3.5. With most block digesters, about 3% of the original concentration of sulfuric acid is lost during digestion. However, large variations in residual acid concentration will result in poor accuracy and abnormal peak shapes.

7.3.6. Digestion efficiency may be better with a mercury catalyst.

7.3.7. The percent nitrogen can be calculated by the formula:

$$\%N = [(V_D/W_S) \times C_D]/10{,}000$$

where:

$V_D$ = Total digest volume (mL), Default = 50 mL

$W_S$ = Weight of sample (g), Default = 0.2 g (Plant), 0.4 g (Soil)

$C_D$ = Concentration in the digest (mg N/L)

## 8. DATA ANALYSIS AND CALCULATIONS

8.1. Calibration is done by injecting standards. The data system will the prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

8.2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted with matrix blank and reanalyzed.

8.3. Report results in % nitrogen.

## 9. METHOD PERFORMANCE

9.1. The method support data are presented in section 11. This data was generated according to Lachat Work Instruction J01002, Procedure for Generating Method Support Data on the QuikChem 8000.

## 10. REFERENCES


10.1. Lachat Instruments Inc., QuikChem Method 13-107-06-2-D written by David Diamond on 28 Dec 1992.

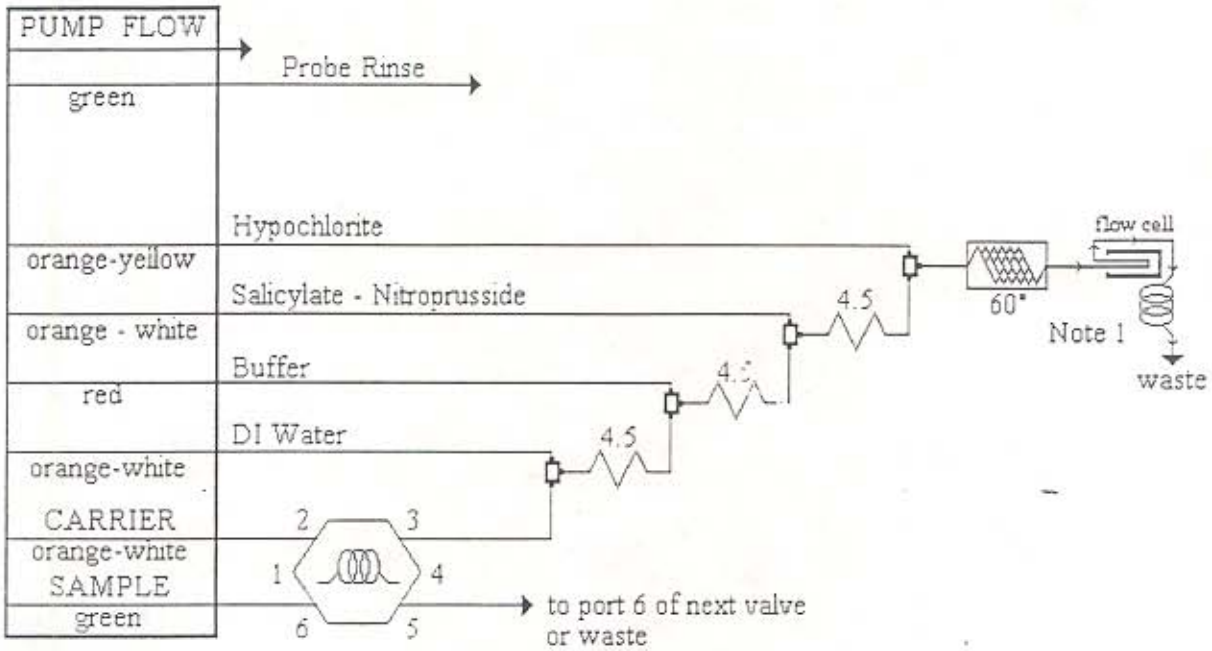
10.2. Correspondence, Allen Doyle, University of Alaska, Fairbanks, Institute for Arctic Biology, 4/20/92.

10.3. Jones, N.M. and H.D. Bradshaw, Copper: An Alternative to Mercury; more effective than zirconium in Kjeldahl Digestion of Ecological material. Communications in Soil and Plant Analysis, 20:1513-1524, 1989.

10.4. Kaltra, Y.P. and D.G. Maynard, Methods Manual for Forest Soil and Plant Analysis, Information Report NOR-X-39, Forestry Canada, Ontario Canada, 1991.

# 11. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

## 11.1. TOTAL KJELDAHL NITROGEN MANIFOLD DIAGRAM




Sample Loop = Microloop  Interference Filter = 660 nm

**CARRIER is DI Water.**

Manifold tubing is **0.5 mm (0.022 in) i.d.** This is **2.5 uL/cm.**

| | | | |
|---|---|---|---|
| **4.5** | is | 70 | cm of tubing on a 4.5 cm coil support |

**APPARATUS**: An injection valve, a 10 mm path length flow cell, and a colorimeter detector module are required. The shows 650 cm of tubing wrapped around the heater block at the specified temperature.

**Note 1:** 200 cm back pressure loop, 0.5 mm (0.022 in) i.d. tubing

## 11.2. DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

| | |
|---|---|
| Sample throughput: | 72 samples/h, 50 s/sample |
| Pump Speed: | 35 |
| Cycle Period: | 50 |

**Analyte Data:**

| | |
|---|---|
| Concentration Units: | mg N/L |
| Peak Base Width: | 17.2 s |
| % Width Tolerance: | 100 |
| Threshold: | 20000 |
| Inject to Peak Start: | 45 s |
| Chemistry: | Direct |

**Calibration Data:**

| Level | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Concentration mg N/L | 100 | 75.0 | 50.0 | 25.0 | 0.00 |

| | |
|---|---|
| Calibration Fit Type: | 2nd Order Polynomial |
| Calibration Rep.Handling: | Average |
| Weighting Method: | None |
| Concentration Scaling: | None |
| Force Through Zero: | No |

**Sampler Timing:**

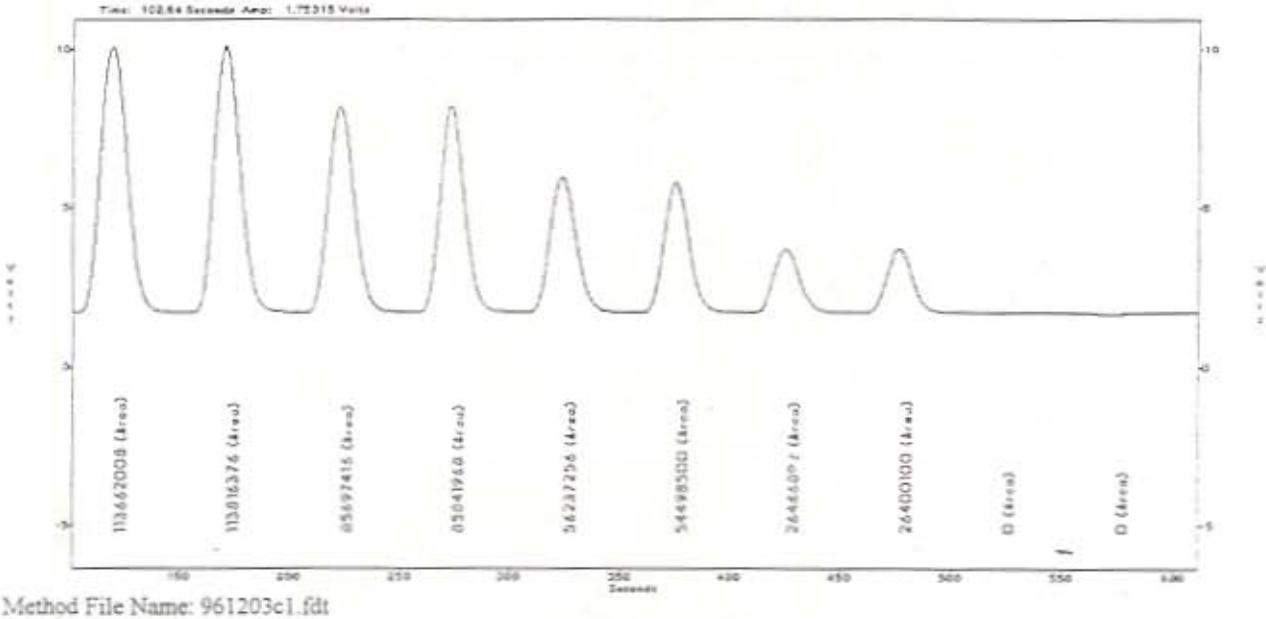
| | |
|---|---|
| Min Probe in Wash Period: | 5 s |
| Probe in Sample Period: | 30 s |

**Valve Timing:**

| | |
|---|---|
| Load Time: | 0.0 s |
| Load Period: | 20 s |
| Inject Period: | 30 s |

## 11.3. SUPPORT DATA FOR QUIKCHEM 8000

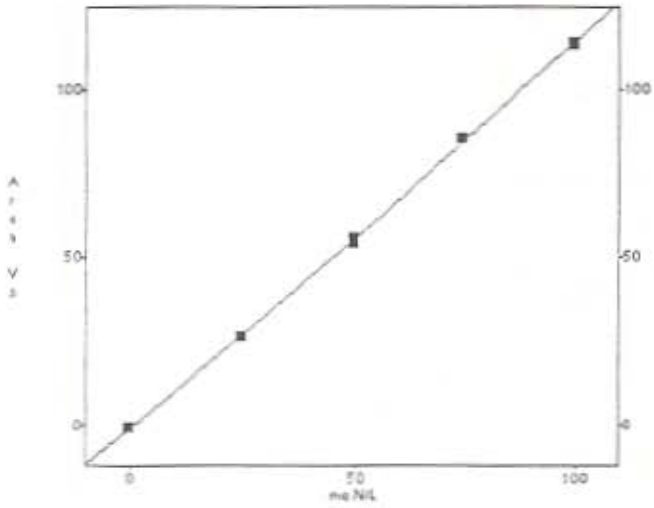
Calibration Data for Total Kjeldahl Nitrogen



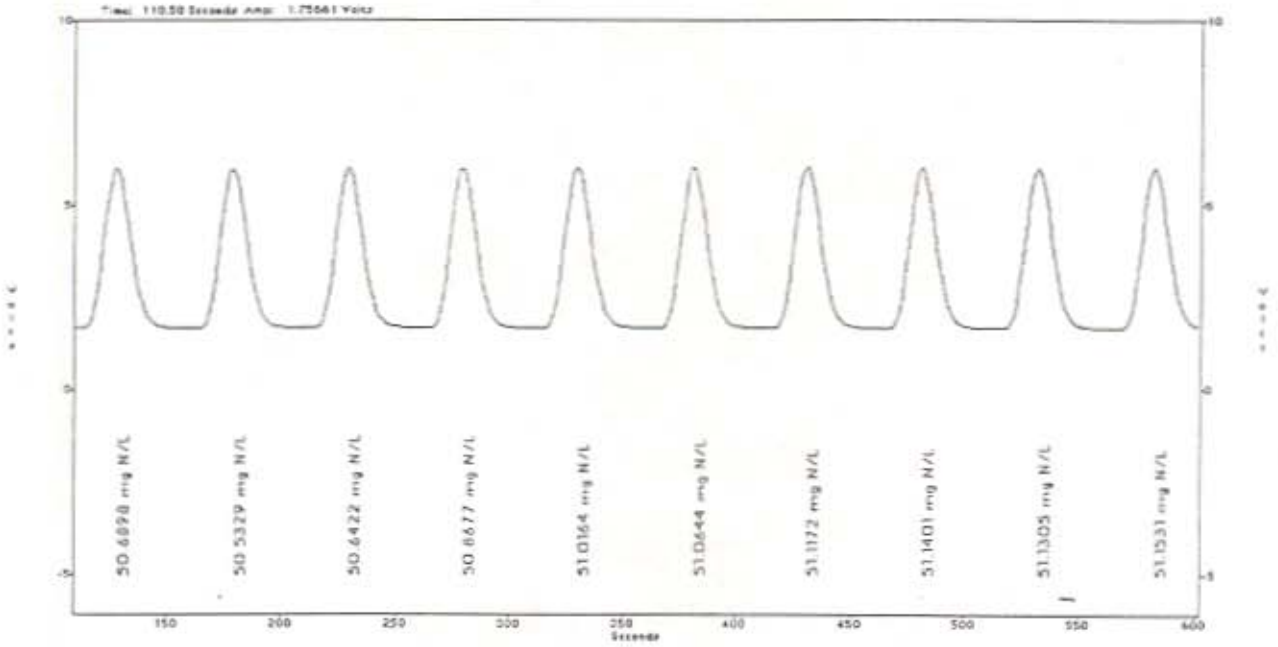
Method File Name: 961203c1.fdt
Acq. Date: 03 December 1996

Calibration Graph and Statistics

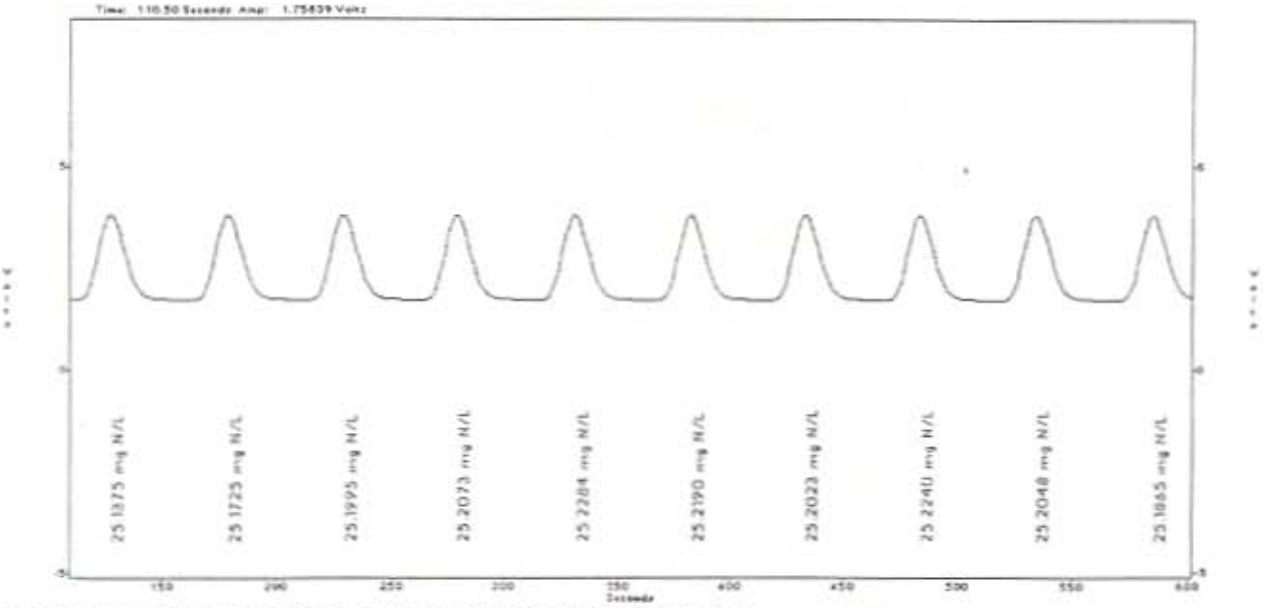
| Level | Area | mg N/L | Determined | Replicate %RSD | % residual |
|---|---|---|---|---|---|
| 1 | 113739192 | 100. | 99.5 | 0.1 | 0.5 |
| 2 | 85769696 | 75.0 | 76.0 | 0.1 | -1.3 |
| 3 | 55367880 | 50.0 | 49..8 | 2.2 | 0.4 |
| 4 | 26433496 | 25.0 | 24.3 | 0.2 | 3.0 |
| 5 | 0 | 0.0 | 0.0 | 0.0 | — |



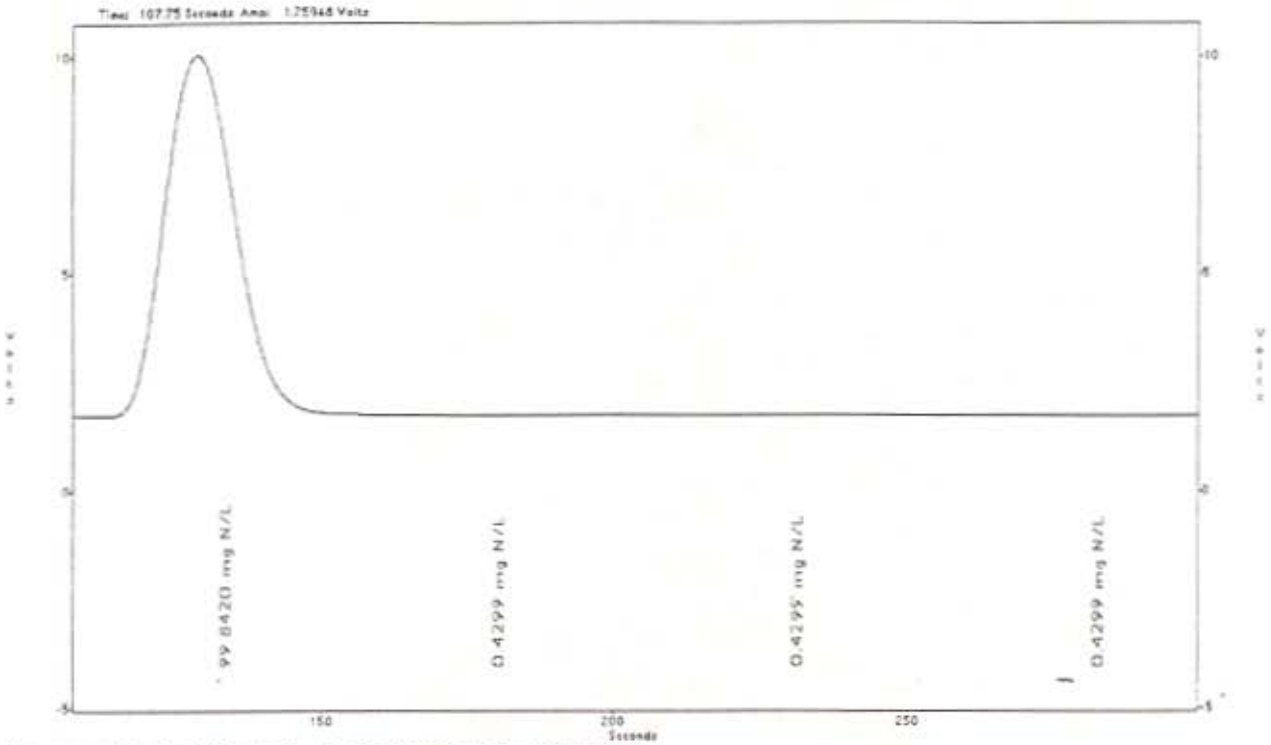

Scaling: None
Weighting: None
2nd Order Poly
Conc = -3.473e-016 Area² + 9.108e-007 Area + 4.299e-001
$R^2$ = 0.9997




Precision data for total kjeldahl nitrogen using 50.0 mg N/L standard
**%RSD = 0.46**
Standard Deviation (s) =0.235, Mean (x) = 50.9 mg/L, Known value = 50.0 mg/L
Data File name 961203p2.fdt
Acq. Date: 03 December 1996

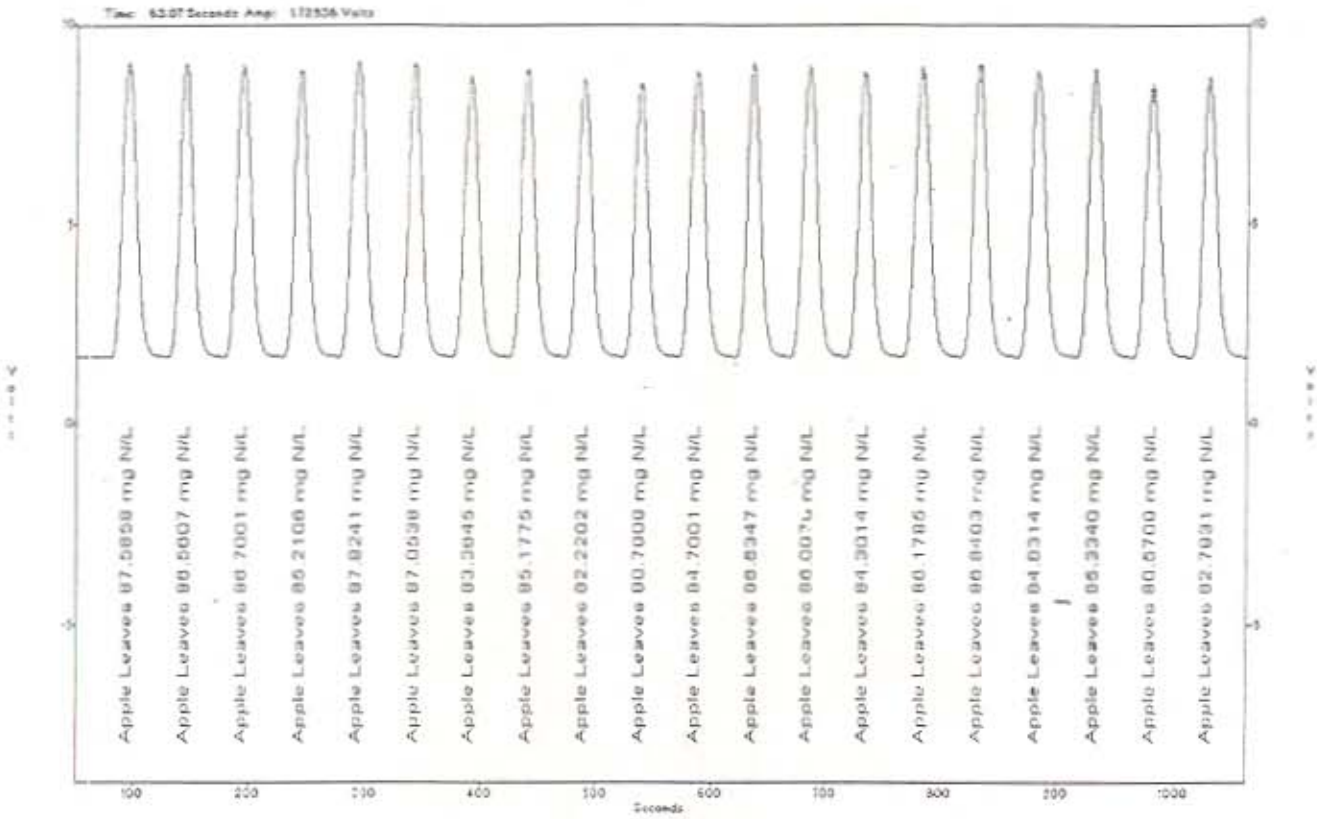



Precision data for total kjeldahl nitrogen using 25.0 mg N/L standard
**% RSD = 0.11**
Standard Deviation (s) = 0.027, Mean (x) = 25.20, Known value = 25.0 mg/L
Data File name 961203m1.fdt
Acq. Date: 03 December 1996




Carryover Study: 100 mg/L standard followed by 3 blanks
**Carryover Passed**
Data File name 931203r1.fdt
Acq. Date: 03 December 1996

**APPLE LEAVES:** National Institute of Standards and Technology Certified Standard




Ten digested samples of NIST certified apple leaves, run in duplicate. Each duplicate pair represents a separate weighing and digestion.

**Digestion %RSD = 1.40, n = 10**

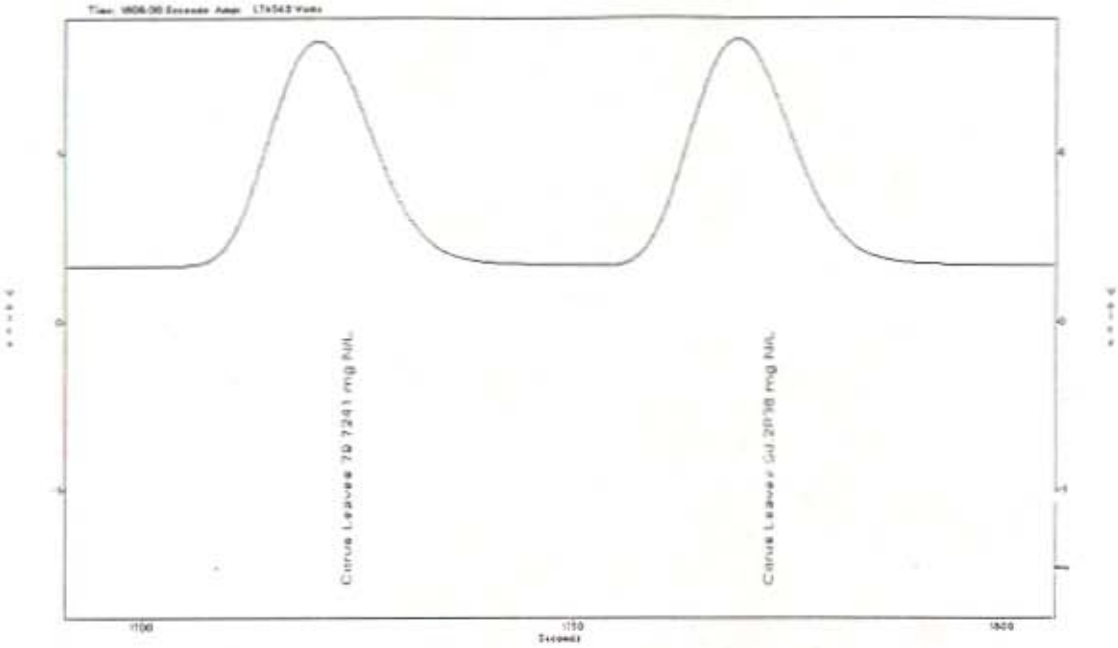
Mean (x) = 2.09 % N, Standard Deviation (s) = 0.0293, Known Value = 2.31 % N

Datafile Name: 961205s2.fdt

Acq. date: 5 December 1996

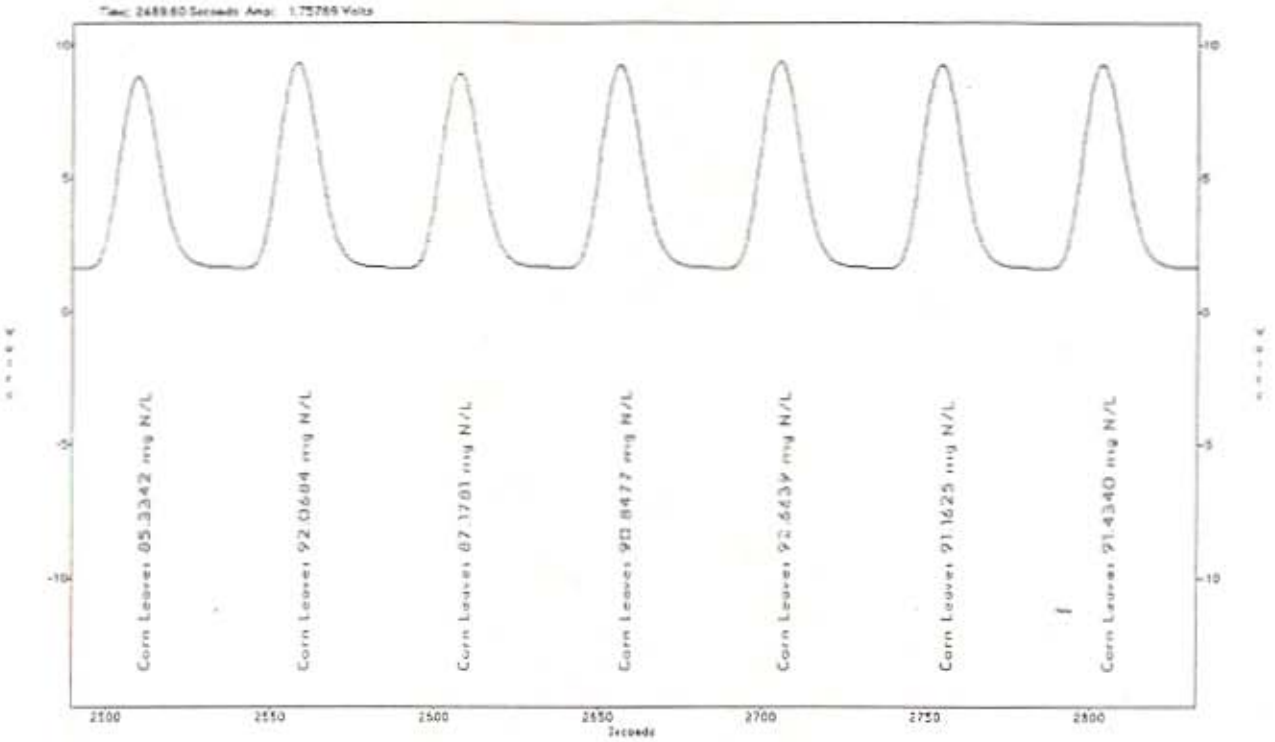
| Tube Number | Mean conc. of 2 reps (mg N/L) | Mean conc. of 2 reps (% N) | Recovery (%) |
|---|---|---|---|
| 1 | 87.1 | 2.05 | 88.8 |
| 2 | 86.0 | 2.11 | 91.5 |
| 3 | 87.4 | 2.13 | 92.0 |
| 4 | 84.3 | 2.08 | 89.9 |
| 5 | 81.5 | 2.08 | 90.0 |
| 6 | 85.7 | 2.09 | 90.6 |
| 7 | 85.2 | 2.10 | 90.8 |
| 8 | 86.5 | 2.10 | 91.1 |
| 9 | 85.1 | 2.12 | 91.9 |
| 10 | 81.7 | 2.04 | 88.2 |

**CITRUS LEAVES:** National Institute of Standards and Technology Certified Standard




One digested sample of NIST certified citrus leaves, run in duplicate.
Mean (x) = 2.63 % N, Known Value = 2.86 % N, Standard Deviation (s) = 0.0129
Datafile Name: 961205s2.fdt
Acq. date: 5 December 1996

## CORN LEAVES



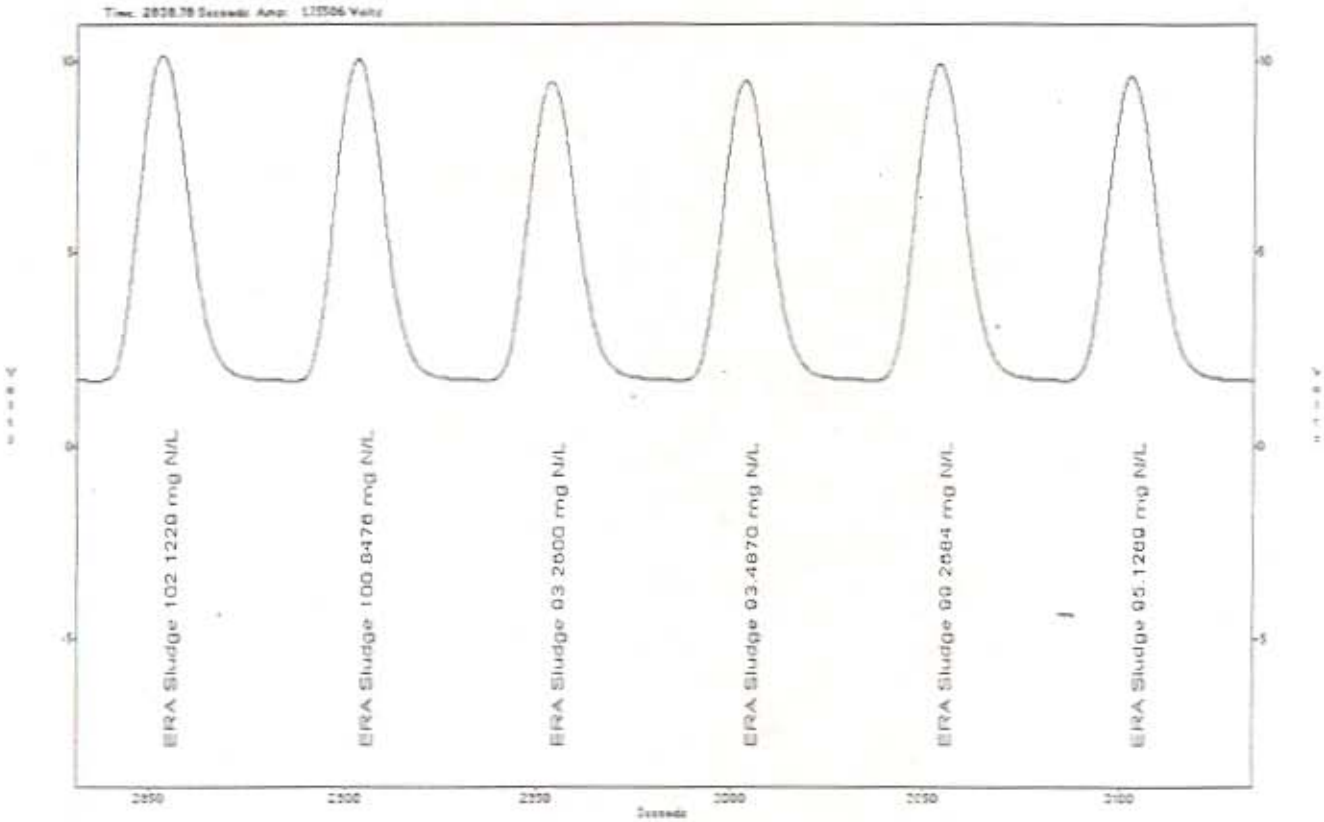

Four digested samples of corn leaves, run in duplicate. Each duplicate pair represents a separate weighing and digestion.

**Digestion % RSD = 3.03, n = 4**

Mean (x) = 2.48 % N, Standard Deviation (s) = 0.0754, Known Value = 2.71 % N
Datafile Name: 961205s2.fdt
Acq. date: 5 December 1996

| Tube Number | Mean Conc. of 2 reps (mg N/L) | Mean Conc. of 2 reps (% N) | Recovery (%) |
|---|---|---|---|
| 1 | 85.8 | 2.38 | 87.7 |
| 2 | 89.6 | 2.49 | 91.9 |
| 3 | 91.8 | 2.54 | 93.6 |
| 4 | 91.3 | 2.53 | 93.5 |

## ERA SLUDGE




Three digested samples of ERA* Sludge, run in duplicate. Each duplicate pair represents a separate weighing and digestion.

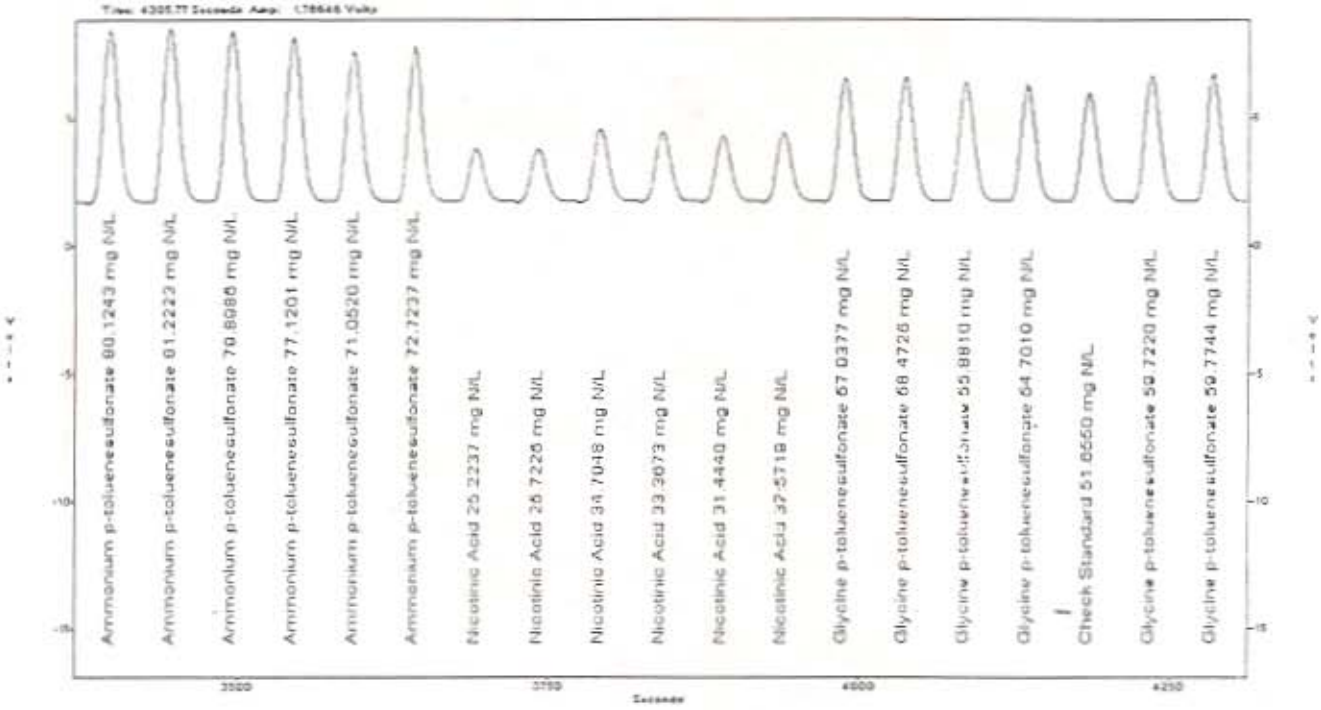
**Digestion %RSD = 1.41, n = 3**

Mean (x) = 4.77 % N, Standard Deviation (s) = 0.0673, Known Value = 4.75 % N,
Acceptable range = 3.04 - 6.46 % N
Datafile Name: 961205s2.fdt
Acq. date: 5 December 1996

| Tube Number | Mean Conc. of 2 reps (mg N/L) | Mean Conc. of 2 reps (% N) | Within Acceptable Range (Y/N) |
|---|---|---|---|
| 1 | 101.5 | 4.70 | Yes |
| 2 | 93.4 | 4.83 | Yes |
| 3 | 97.2 | 4.77 | Yes |

*** Environmental Resource Associates, Arvada Colorado, 303-431-8454. Catalog no. 545, lot. no. 23016**

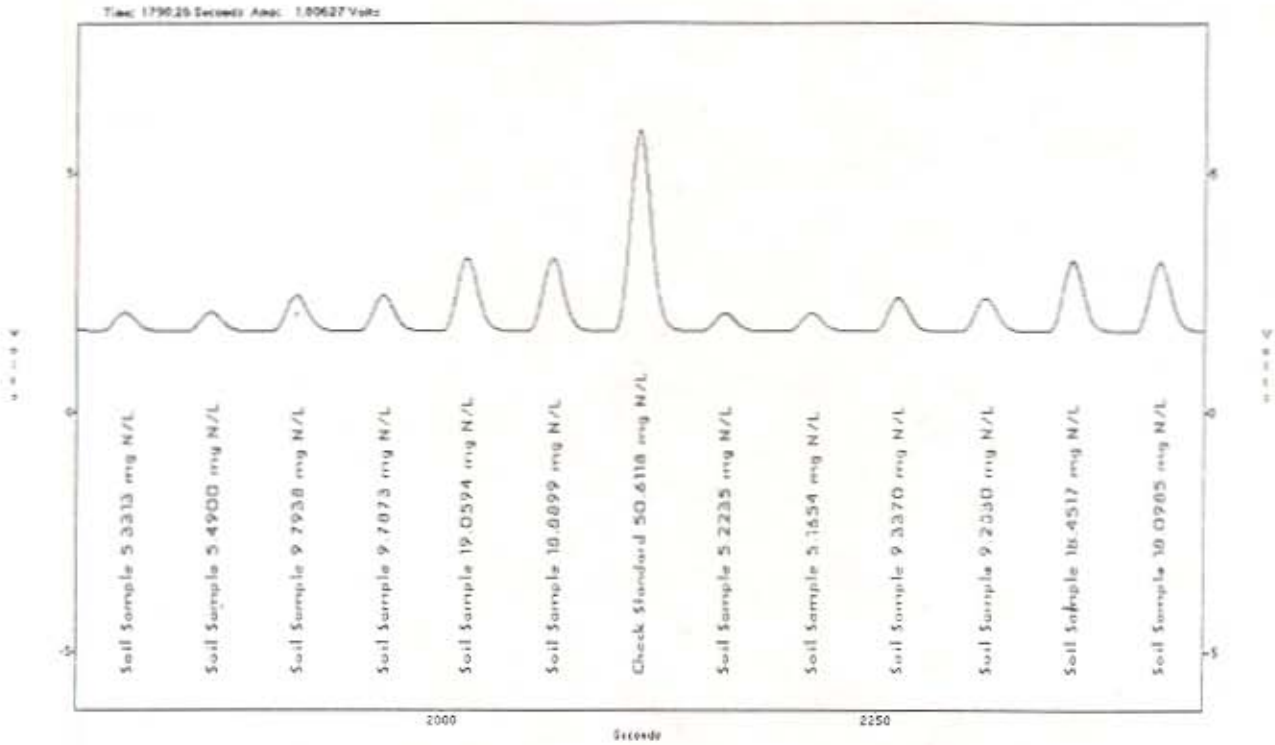
## PRIMARY STANDARDS




Three sets of digested primary standards, run in duplicate. Each duplicate pair represents a separate weighing and digestion.
Datafile Name: 961205s2.fdt
Acq. date: 5 December 1996

| Primary Standard | Known Value (% N) | Mean (x) (% N) | Standard Deviation (s) | Digestion % RSD, n = 3 |
|---|---|---|---|---|
| Ammonium p-toluenesulfonate | 7.40 | 7.27 | 0.144 | 1.98 |
| Nicotinic acid | 4.74 | 1.50 | 0.234 | 15.6 |
| Glycine p-toluenesulfonate | 5.67 | 5.56 | 0.180 | 3.24 |

## UNKNOWN SOIL SAMPLE



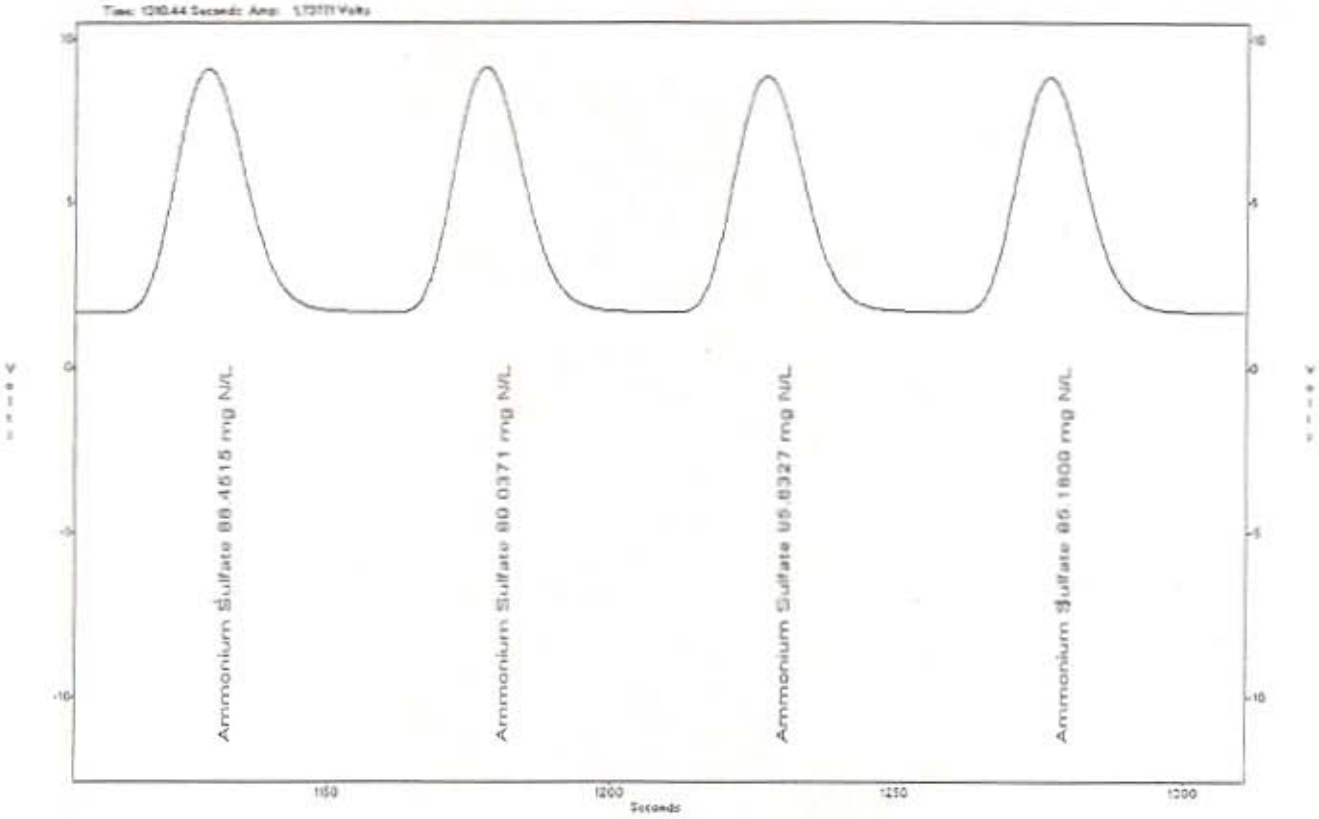

Six unknown soil samples, digested using different starting weights: 0.1, 0.2, and 0.4 g, run in duplicate. Each duplicate pair represents a separate weighing and digestion. Results show a digestion precision of 5.91%. The determined concentration is independent of sample weight from 0.1 to 0.4 g.

**Digestion %RSD = 5.91, n = 6**

Mean (x) = 0.243 % N, Standard Deviation (s) = 0.014
Datafile Name: 961205s2.fdt
Acq. date: 5 December 1996

| Tube Number | Sample Weight (g) | Mean conc. of 2 reps (mg N/L) | Mean conc. of 2 reps (% N) |
|---|---|---|---|
| 1 | 0.1 | 5.41 | 0.27 |
| 2 | 0.2 | 9.79 | 0.24 |
| 3 | 0.4 | 18.97 | 0.24 |
| 4 | 0.1 | 5.19 | 0.25 |
| 5 | 0.2 | 9.31 | 0.23 |
| 6 | 0.4 | 18.28 | 0.23 |

## AMMONIUM SULFATE RECOVERY




Two digested samples of primary standard ammonium sulfate, run in duplicate. Each duplicate pair represents a separate weighing and digestion.

**Digestion % RSD = 0.97, n = 2**

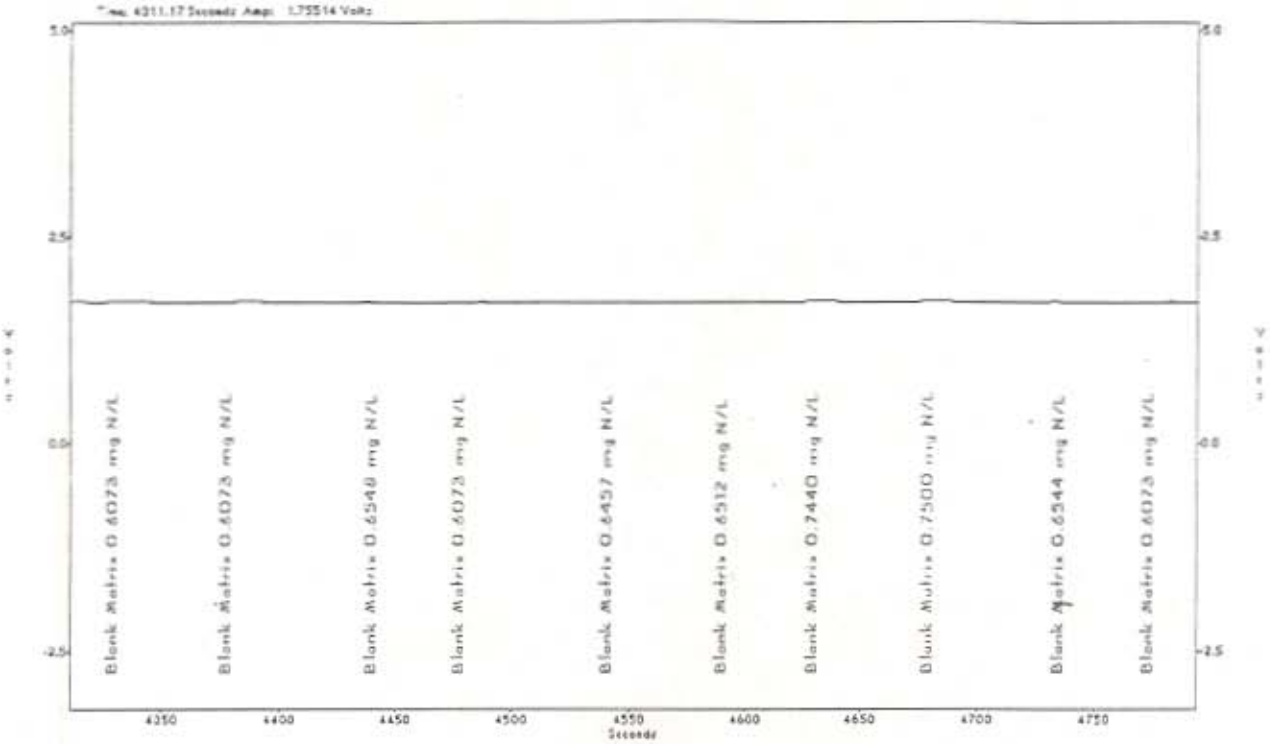
Mean (x) = 20.59 % N, Standard Deviation (s) = 0.199, Known Value = 21.26 % N

Datafile Name: 961205s2.fdt

Acq. date: 5 December 1996

| Tube Number | Mean Conc. of 2 reps (mg N/L) | Mean Conc. of 2 reps (% N) | Recovery (%) |
|---|---|---|---|
| 1 | 88.74 | 20.45 | 96.2 |
| 2 | 85.41 | 20.73 | 97.5 |

## DIGESTION BLANKS




Five digestion blanks containing the weighing paper, copper sulfate, potassium sulfate, and sulfuric acid only, digested and run in duplicate. Each duplicate pair represents a separate digestion. All results are less than 1 mg N/L.

Datafile Name: 961205s2.fdt

Acq. date: 5 December 1996

# APPENDIX D-4
## Preparation Procedure for Exchangeable P: Method ASA 24-5.2

**Preparation Procedure for Exchangeable P**

ASA 24-5.2

Phosphorus Soluble in Dilute Hydrochloric Acid and Sulfuric Acid
or
Mehlich I (North Carolina Double Acid) P Determination in Soil

Reagents:

1. Extraction Solution: Add 12 ml of concentrated $H_2SO_4$ and 73 ml of concentrated HCl to approximately 15 liters of deionized water. Make to 18 liters. This solution is approximately 0.05 N HCl and 0.025 N $H_2SO_4$. Smaller quantities may be made in the same ratio.

Procedure:

1. Weigh 12.5 g of soil to a 125-ml Erlenmeyer flask.

2. Add 50.0 ml of extracting solution.

3. Shake on oscillating shaker at 180 oscillations per minute for exactly 5 minutes.

4. Filter through Whatman 42 filter paper into a 50-ml Erlenmeyer flask.

5. Submit the filtrates for analysis by inductively coupled plasma (ICP), atomic absorption, or spectrometric methods.

References:

"Phosphorus Soluble in Dilute Hydrochloric Acid and Sulfuric Acid," Section 24-5.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-5
# Preparation Procedure for Exchangeable K, Ca, and Mg: Method ASA 9-3.1

**Determination of Exchangeable Cations in Soils Without Determining Total CEC**

Ammonium Acetate Extraction

ASA 9-3.1

Reagent:

1. 1N Ammonium Acetate - Dissolve 231.34 g of reagent grade ammonium acetate in 2 liters of deionized water. Make to a 3 liter volume. Place beaker on a stirrer, insert electrodes in the solution and adjust pH to 7.0 with concentrated ammonium hydroxide or glacial acetic acid. For an 18 liter volume dissolve 1388.04 g of ammonium acetate. (Other volumes may be made in the same ratio.)

Procedure:

1. Weigh 5 g of soil (-2 mm, which is -9 mesh) into 125 ml Erlenmeyer flask.

2. Add 50 ml of 1N ammonium acetate, shake for 30 minutes on oscillating shaker on low setting (180/min).

3. Let stand at least 6 hours, preferably overnight, occasionally swirling the flasks.

4. Filter through Whatman 40 filter paper into 50 ml Erlenmeyer flask.

5. Submit the filtrates for analysis by inductively coupled plasma (ICP) or atomic absorption.

6. Convert soil ppm to centimols (cmol) per kg (report to a hundredth of a cmol).

Examples:

| Cation | Divide soil ppm by |
|---|---|
| Ca | 400 |
| Mg | 242 |
| K | 391 |
| Mn | 549 |

References:

"Replacement of Exchangeable Cations, Ammonium Acetate Method" Section 9-3.1 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-6
## Preparation Procedure for Exchangeable Al: Method ASA 9-4.2

**Exchangeable Aluminum by One Normal Potassium Chloride Extraction**
ASA 9-4.2

Reagents: 1N KCl - Dissolve 74.0 grams potassium chloride in about 800 ml of deionized water. Dilute to 1 liter.

Procedure:

1. Weigh 5 grams soil into a 250 ml centrifuge tube.
2. Add 50 ml 1N KCl to each sample.
3. Shake for 30 minutes at 180/min setting.
4. Centrifuge for 5 minutes at 1500 rpm.
5. Filter through Whatman 42 filter paper into a 50ml Erlenmeyer flask.
6. Submit the sample for aluminum analysis by ICP.

References:

Can. J. Soil Sci. 70:263-275

"Exchangeable Acidity, Potassium Chloride Method," Section 9-4.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-7
# Analytical Procedure for Total Metals; Exchangeable P, K, Ca, Mg, and Al; and DTPA-Extractable Fe and Mn: Method 6010B

METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

## 1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Chapter Three for the appropriate digestion procedures.

1.2 Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements and matrices other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 8.0) is demonstrated.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

## 2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background

intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

## 3.0 INTERFERENCES

3.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

3.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

3.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

3.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement

correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

3.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.

3.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

3.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

3.1.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

3.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

3.1.9 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

3.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

3.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

3.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is ≥ 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate

and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 8.5.1 will help determine if a physical interference is present.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

3.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/l and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

3.6 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

## 4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio-frequency generator compliant with FCC regulations.

4.1.3 Optional mass flow controller for argon nebulizer gas supply.

4.1.4 Optional peristaltic pump.

4.1.5 Optional Autosampler.

4.1.6 Argon gas supply - high purity.

4.2 Volumetric flasks of suitable precision and accuracy.

4.3 Volumetric pipets of suitable precision and accuracy.

5.0 REAGENTS

5.1 Reagent or trace metals grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.1.3 Nitric acid (conc), $HNO_3$.

5.1.4 Nitric acid (1:1), $HNO_3$. Add 500 mL concentrated $HNO_3$ to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

Note: This section does not apply when analyzing samples that have been prepared by Method 3040.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1:1) HCl and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-liter flask, add an additional 10.0 mL of (1:1) HCl and dilute to volume with reagent water.

NOTE: Weight of analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4 % error for some of the compounds.

5.3.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 2.6673 g $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.3203 g of $As_2O_3$ (element fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.5163 g $BaCl_2$ (element fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 µg Be: Do not dry. Dissolve 19.6463 g $BeSO_4 4H_2O$ (element fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated $HNO_3$, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Boron solution, stock, 1 mL = 1000 µg B: Do not dry. Dissolve 5.716 g anhydrous $H_3BO_3$ (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

5.3.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.1423 g CdO (element fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a

minimum amount of (1:1) $HNO_3$. Heat to increase rate of dissolution. Add 10.0 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.4969 g $CaCO_3$ (element Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) $HNO_3$. Add 10.0 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.9231 g $CrO_3$ (element fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) $HNO_3$. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.2564 g CuO (element fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) $HNO_3$. Add 10.0 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.4298 g $Fe_2O_3$ (element fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated $HNO_3$. Cool, add an additional 5.0 mL of concentrated $HNO_3$, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.5985 g $Pb(NO_3)_2$ (element fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) $HNO_3$. Add 10 mL (1:1) $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.3248 g lithium carbonate (element fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.6584 g MgO (element fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) $HNO_3$. Add 10.0 mL (1:1) concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated $HNO_3$) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Mercury solution, stock, 1 mL = 1000 µg Hg: Do not dry, highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated $HNO_3$ and dilute to volume in 1-L volumetric flask with reagent water.

5.3.18 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.7325 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (element fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated $HNO_3$, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Phosphate solution, stock, 1 mL = 1000 µg P: Dissolve 4.3937 g anhydrous $KH_2PO_4$ (element fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.9069 g KCl (element fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Selenium solution, stock, 1 mL = 1000 µg Se: Do not dry. Dissolve 1.6332 g $H_2SeO_3$ (element fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Silica solution, stock, 1 mL = 1000 µg $SiO_2$: Do not dry. Dissolve 2.964 g $NH_4SiF_6$, weighed accurately to at least four significant figures, in 200 mL (1:20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

5.3.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.5748 g $AgNO_3$ (element fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated $HNO_3$. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.5419 g NaCl (element fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.27 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.3034 g $TlNO_3$ (element fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.28 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least 4 significant figures, in 200 mL (1:1) HCl with heating to effect dissolution. Let solution cool and dilute with (1:1) HCl in a 1-L volumetric flask.

5.3.29 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 2.2957 g $NH_4VO_3$ (element fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated $HNO_3$. Heat to increase rate of dissolution. Add 10.0 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.30 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.2447 g ZnO (element fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute $HNO_3$. Add 10.0 mL concentrated $HNO_3$ and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations (see Sections 7.3 and 7.4).

5.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The Initial Calibration Verification (ICV) is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (see Section 8.6.1 for use).

5.7 The Continuing Calibration Verification (CCV)) should be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve (see Section 8.6.1 for use).

5.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

## 7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).

7.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.

7.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

7.2.2 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for

a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100-1500 watts forward power, 15-19 liters/min argon coolant flow, 0.6-1.5 L/min argon nebulizer flow, 1-1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

7.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

7.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

7.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

7.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, Tl or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least

sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

7.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

7.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

7.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.

7.2.3.7 Before daily calibration and after the instrument warmup period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (< 2% change) from day to day.

7.2.4 For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements.

7.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

7.2.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. Refer to Chapter One for additional guidance on the performance of MDL studies.

7.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

7.2.5.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using method of standard additions can give confidence in the method detection limit values determined in reagent water.

7.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. For those analytes that are known interferences, and are present at above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

7.2.6 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (Section 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

7.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 5.6), a calibration blank (Section 5.5.1), and a continuing calibration verification (CCV) (Section 5.7) immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of

the check standard and calibration verification must verify that the instrument is within ± 10% of calibration with relative standard deviation < 5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

7.5 Rinse the system with the calibration blank solution (Section 5.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

7.7 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution.

NOTE: Refer to Method 7000 for a more detailed discussion of the MSA.

7.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

## 8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. All quality control measures described in Chapter One should be followed.

8.2 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample (refer to Chapter One).

8.4 Analyze matrix spiked duplicate samples at a frequency of one per matrix batch. A matrix duplicate sample is a sample brought through the entire sample preparation and analytical process in duplicate.

8.4.1.1 The relative percent difference between spiked matrix duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
$D_1$ = first sample value.
$D_2$ = second sample value (replicate).

(A control limit of ± 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.)

8.4.1.2 The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 8.5.1 and 8.5.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate QC samples as follows.

8.6.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 5.6). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV should be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 5.5.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

8.6.1.1 The results of the ICV and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.2 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.3 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

8.6.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 5.8). Results should be within ± 20% of the true value.

## 9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 Performance data for aqueous solutions and solid samples from a multilaboratory study (9) are provided in Tables 5 and 6.

## 10.0 REFERENCES

1. Boumans, P.W.J.M. Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry, 2nd Edition. Pergamon Press, Oxford, United Kingdom, 1984.

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4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

5. Jones, C.L. et al. An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050. EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.

TABLE 1
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

| Detection Element | Wavelength[a] (nm) | Estimated IDL[b] (µg/L) |
|---|---|---|
| Aluminum | 308.215 | 30 |
| Antimony | 206.833 | 21 |
| Arsenic | 193.696 | 35 |
| Barium | 455.403 | 0.87 |
| Beryllium | 313.042 | 0.18 |
| Boron | 249.678x2 | 3.8 |
| Cadmium | 226.502 | 2.3 |
| Calcium | 317.933 | 6.7 |
| Chromium | 267.716 | 4.7 |
| Cobalt | 228.616 | 4.7 |
| Copper | 324.754 | 3.6 |
| Iron | 259.940 | 4.1 |
| Lead | 220.353 | 28 |
| Lithium | 670.784 | 2.8 |
| Magnesium | 279.079 | 20 |
| Manganese | 257.610 | 0.93 |
| Mercury | 194.227x2 | 17 |
| Molybdenum | 202.030 | 5.3 |
| Nickel | 231.604x2 | 10 |
| Phosphorus | 213.618 | 51 |
| Potassium | 766.491 | See note c |
| Selenium | 196.026 | 50 |
| Silica ($SiO_2$) | 251.611 | 17 |
| Silver | 328.068 | 4.7 |
| Sodium | 588.995 | 19 |
| Strontium | 407.771 | 0.28 |
| Thallium | 190.864 | 27 |
| Tin | 189.980x2 | 17 |
| Titanium | 334.941 | 5.0 |
| Vanadium | 292.402 | 5.0 |
| Zinc | 213.856x2 | 1.2 |

[a]The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL[c]

| Analyte | Wavelength (nm) | Interferant[a,b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Al | Ca | Cr | Cu | Fe | Mg | Mn | Ni | Ti | V |
| Aluminum | 308.215 | -- | -- | -- | -- | -- | -- | 0.21 | -- | -- | 1.4 |
| Antimony | 206.833 | 0.47 | -- | 2.9 | -- | 0.08 | -- | -- | -- | 0.25 | 0.45 |
| Arsenic | 193.696 | 1.3 | -- | 0.44 | -- | -- | -- | -- | -- | -- | 1.1 |
| Barium | 455.403 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Beryllium | 313.042 | -- | -- | -- | -- | -- | -- | -- | -- | 0.04 | 0.05 |
| Cadmium | 226.502 | -- | -- | -- | -- | 0.03 | -- | -- | 0.02 | -- | -- |
| Calcium | 317.933 | -- | -- | 0.08 | -- | 0.01 | 0.01 | 0.04 | -- | 0.03 | 0.03 |
| Chromium | 267.716 | -- | -- | -- | -- | 0.003 | -- | 0.04 | -- | -- | 0.04 |
| Cobalt | 228.616 | -- | -- | 0.03 | -- | 0.005 | -- | -- | 0.03 | 0.15 | -- |
| Copper | 324.754 | -- | -- | -- | -- | 0.003 | -- | -- | -- | 0.05 | 0.02 |
| Iron | 259.940 | -- | -- | -- | -- | -- | -- | 0.12 | -- | -- | -- |
| Lead | 220.353 | 0.17 | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Magnesium | 279.079 | -- | 0.02 | 0.11 | -- | 0.13 | -- | 0.25 | -- | 0.07 | 0.12 |
| Manganese | 257.610 | 0.005 | -- | 0.01 | -- | 0.002 | 0.002 | -- | -- | -- | -- |
| Molybdenum | 202.030 | 0.05 | -- | -- | -- | 0.03 | -- | -- | -- | -- | -- |
| Nickel | 231.604 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Selenium | 196.026 | 0.23 | -- | -- | -- | 0.09 | -- | -- | -- | -- | -- |
| Sodium | 588.995 | -- | -- | -- | -- | -- | -- | -- | -- | 0.08 | -- |
| Thallium | 190.864 | 0.30 | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Vanadium | 292.402 | -- | -- | 0.05 | -- | 0.005 | -- | -- | -- | 0.02 | -- |
| Zinc | 213.856 | -- | -- | -- | 0.14 | -- | -- | -- | 0.29 | -- | -- |

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

| | | | |
|---|---|---|---|
| Al - | 1000 mg/L | Mg - | 1000 mg/L |
| Ca - | 1000 mg/L | Mn - | 200 mg/L |
| Cr - | 200 mg/L | Ti - | 200 mg/L |
| Cu - | 200 mg/L | V - | 200 mg/L |
| Fe - | 1000 mg/L | | |

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3
MIXED STANDARD SOLUTIONS

| Solution | Elements |
|---|---|
| I | Be, Cd, Mn, Pb, Se and Zn |
| II | Ba, Co, Cu, Fe, and V |
| III | As, Mo |
| IV | Al, Ca, Cr, K, Na, Ni,Li, and Sr |
| V | Ag (see "NOTE" to Section 5.4), Mg, Sb, and Tl |
| VI | P |

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

| Element | Sample No. 1 | | | | Sample No. 2 | | | | Sample No. 3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | True Conc. (ug/L) | Mean Conc. (ug/L) | RSD[b] (%) | Accuracy[d] (%) | True Conc. (ug/L) | Mean Conc. (ug/L) | RSD[b] | Accuracy[d] (%) | True Conc. (ug/L) | Mean Conc. (ug/L) | RSD[b] (%) | Accuracy[d] (%) |
| Be | 750 | 733 | 6.2 | 98 | 20 | 20 | 9.8 | 100 | 180 | 176 | 5.2 | 98 |
| Mn | 350 | 345 | 2.7 | 99 | 15 | 15 | 6.7 | 100 | 100 | 99 | 3.3 | 99 |
| V | 750 | 749 | 1.8 | 100 | 70 | 69 | 2.9 | 99 | 170 | 169 | 1.1 | 99 |
| As | 200 | 208 | 7.5 | 104 | 22 | 19 | 23 | 86 | 60 | 63 | 17 | 105 |
| Cr | 150 | 149 | 3.8 | 99 | 10 | 10 | 18 | 100 | 50 | 50 | 3.3 | 100 |
| Cu | 250 | 235 | 5.1 | 94 | 11 | 11 | 40 | 100 | 70 | 67 | 7.9 | 96 |
| Fe | 600 | 594 | 3.0 | 99 | 20 | 19 | 15 | 95 | 180 | 178 | 6.0 | 99 |
| Al | 700 | 696 | 5.6 | 99 | 60 | 62 | 33 | 103 | 160 | 161 | 13 | 101 |
| Cd | 50 | 48 | 12 | 96 | 2.5 | 2.9 | 16 | 116 | 14 | 13 | 16 | 93 |
| Co | 700 | 512 | 10 | 73 | 20 | 20 | 4.1 | 100 | 120 | 108 | 21 | 90 |
| Ni | 250 | 245 | 5.8 | 98 | 30 | 28 | 11 | 93 | 60 | 55 | 14 | 92 |
| Pb | 250 | 236 | 16 | 94 | 24 | 30 | 32 | 125 | 80 | 80 | 14 | 100 |
| Zn | 200 | 201 | 5.6 | 100 | 16 | 19 | 45 | 119 | 80 | 82 | 9.4 | 102 |
| Se[c] | 40 | 32 | 21.9 | 80 | 6 | 8.5 | 42 | 142 | 10 | 8.5 | 8.3 | 85 |

[a] Not all elements were analyzed by all laboratories.
[b] RSD = relative standard deviation.
[c] Results for Se are from two laboratories.
[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

| Element | Mean Conc. (mg/L) | N[b] | RSD[b] (%) | Accuracy[c] (%) |
|---|---|---|---|---|
| Al | 14.8 | 8 | 6.3 | 100 |
| Sb | 15.1 | 8 | 7.7 | 102 |
| As | 14.7 | 7 | 6.4 | 99 |
| Ba | 3.66 | 7 | 3.1 | 99 |
| Be | 3.78 | 8 | 5.8 | 102 |
| Cd | 3.61 | 8 | 7.0 | 97 |
| Ca | 15.0 | 8 | 7.4 | 101 |
| Cr | 3.75 | 8 | 8.2 | 101 |
| Co | 3.52 | 8 | 5.9 | 95 |
| Cu | 3.58 | 8 | 5.6 | 97 |
| Fe | 14.8 | 8 | 5.9 | 100 |
| Pb | 14.4 | 7 | 5.9 | 97 |
| Mg | 14.1 | 8 | 6.5 | 96 |
| Mn | 3.70 | 8 | 4.3 | 100 |
| Mo | 3.70 | 8 | 6.9 | 100 |
| Ni | 3.70 | 7 | 5.7 | 100 |
| K | 14.1 | 8 | 6.6 | 95 |
| Se | 15.3 | 8 | 7.5 | 104 |
| Ag | 3.69 | 6 | 9.1 | 100 |
| Na | 14.0 | 8 | 4.2 | 95 |
| Tl | 15.1 | 7 | 8.5 | 102 |
| V | 3.51 | 8 | 6.6 | 95 |
| Zn | 3.57 | 8 | 8.3 | 96 |

[a]these performance values are independent of sample preparation because the labs analyzed portions of the same solutions

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

TABLE 6

ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS[a]

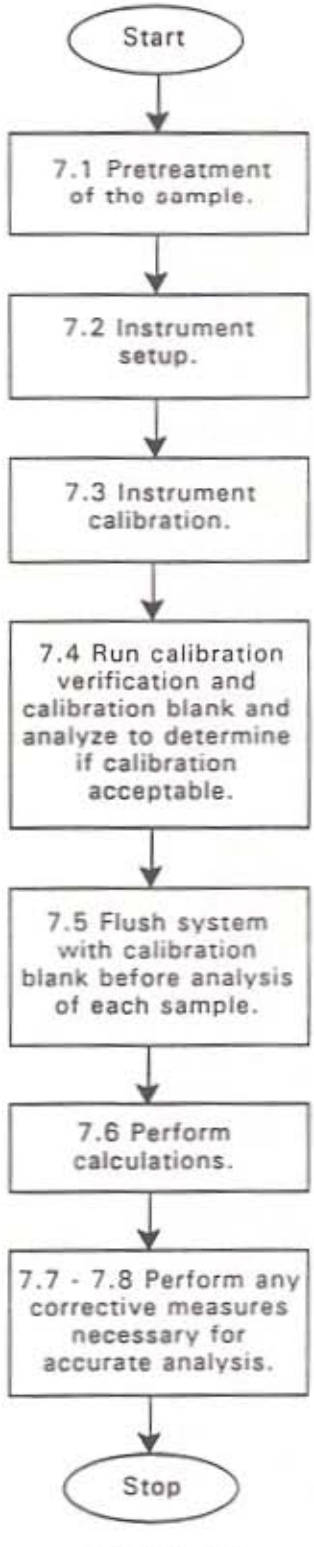
| Element | Spiked Coal Fly Ash (NIST-SRM 1633a) Mean Conc. (mg/L) | N[b] | RSD[b] (%) | Bias[c] (%AAS) | Spiked Electroplating Sludge Mean Conc. (mg/L) | N[b] | RSD[b] (%) | Bias[c] (%AAS) |
|---|---|---|---|---|---|---|---|---|
| Al | 330 | 8 | 16 | 104 | 127 | 8 | 13 | 110 |
| Sb | 3.4 | 6 | 73 | 96 | 5.3 | 7 | 24 | 120 |
| As | 21 | 8 | 83 | 270 | 5.2 | 7 | 8.6 | 87 |
| Ba | 133 | 8 | 8.7 | 101 | 1.6 | 8 | 20 | 58 |
| Be | 4.0 | 8 | 57 | 460 | 0.9 | 7 | 9.9 | 110 |
| Cd | 0.97 | 6 | 5.7 | 101 | 2.9 | 7 | 9.9 | 90 |
| Ca | 87 | 6 | 5.6 | 208 | 954 | 7 | 7.0 | 97 |
| Cr | 2.1 | 7 | 36 | 106 | 154 | 7 | 7.8 | 93 |
| Co | 1.2 | 6 | 21 | 94 | 1.0 | 7 | 11 | 85 |
| Cu | 1.9 | 6 | 9.7 | 118 | 156 | 8 | 7.8 | 97 |
| Fe | 602 | 8 | 8.8 | 102 | 603 | 7 | 5.6 | 98 |
| Pb | 4.6 | 7 | 22 | 94 | 25 | 7 | 5.6 | 98 |
| Mg | 15 | 8 | 15 | 110 | 35 | 8 | 20 | 84 |
| Mn | 1.8 | 7 | 14 | 104 | 5.9 | 7 | 9.6 | 95 |
| Mo | 891 | 8 | 19 | 105 | 1.4 | 7 | 36 | 110 |
| Ni | 1.6 | 6 | 8.1 | 91 | 9.5 | 7 | 9.6 | 90 |
| K | 46 | 8 | 4.2 | 98 | 51 | 8 | 5.8 | 82 |
| Se | 6.4 | 5 | 16 | 73 | 8.7 | 7 | 13 | 101 |
| Ag | 1.4 | 3 | 17 | 140 | 0.75 | 7 | 19 | 270 |
| Na | 20 | 8 | 49 | 130 | 1380 | 8 | 9.8 | 95 |
| Tl | 6.7 | 4 | 22 | 260 | 5.0 | 7 | 20 | 180 |
| V | 1010 | 5 | 7.5 | 100 | 1.2 | 6 | 11 | 80 |
| Zn | 2.2 | 6 | 7.6 | 93 | 266 | 7 | 2.5 | 101 |

[a]These performance values are independent of sample preparation because the labs analyzed portions of the same digests.

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY



# APPENDIX D-8
# Preparation Procedure for DTPA-Extractable Fe and Mn: Method ASA 17-4.3

**DTPA Extraction of Soils for Fe and Mn**
ASA 17-4.3

Reagent:

DTPA Extraction Solution (0.005M DTPA, 0.01M Calcium Chloride, 0.1M TEA)

1. Add 600 ml deionized water to a 1 liter volumetric flask.
2. Add 14.9 g TEA (Triethanolamine) and dissolve (add 16.5 ml if liquid form used).
3. Add 1.970 g of diethylene triamine pentaacetic acid and dissolve.
4. Add 1.470 g of calcium chloride and dissolve.
5. Bring volume to about 970 ml with deionized water.
6. Transfer to a beaker and adjust to pH of 7.3 with 6N HCl (about 13 ml required).
7. Return to volumetric flask and bring to volume.

Procedure:

1. Place 10 g dry soil in 125 ml Erlenmeyer flask.
2. Add 20 ml of DTPA extracting solution.
3. Shake for 2 hours on an oscillating shaker on low setting (180/min).
4. Filter extract through previously folded Whatman 42 filter paper into a 50 ml Erlenmeyer flask.
5. Submit the filtrates for analysis of iron and manganese by inductively coupled plasma (ICP), atomic absorption, or spectrometric methods.

References:

"Availability Indices," Section 17-4.3 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-9
# Preparation Procedure for Total Metals in Soils and Plants: Method 3050B

METHOD 3050B

# ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

## 1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detecion limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

| FLAA/ICP-AES | | GFAA/ICP-MS |
|---|---|---|
| Aluminum | Magnesium | Arsenic |
| Antimony | Manganese | Beryllium |
| Barium | Molybdenum | Cadmium |
| Beryllium | Nickel | Chromium |
| Cadmium | Potassium | Cobalt |
| Calcium | Silver | Iron |
| Chromium | Sodium | Lead |
| Cobalt | Thallium | Molybdenum |
| Copper | Vanadium | Selenium |
| Iron | Zinc | Thallium |
| Lead | | |
| Vanadium | | |

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

## 2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid ($HNO_3$) and hydrogen peroxide ($H_2O_2$).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first

with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

## 3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

## 4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain 30°C ± 4°C.

4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

## 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), $HNO_3$. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%), $H_2O_2$. Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

## 7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

> NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1 $HNO_3$, mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated $HNO_3$, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by $HNO_3$, repeat this step (addition of 5 mL of conc. $HNO_3$) over and over until no brown fumes are given off by the sample indicating the complete reaction with $HNO_3$. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 $HNO_3$, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated $HNO_3$, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by $HNO_3$, repeat this step (addition of 5 mL concentrated $HNO_3$) until no brown fumes are given off by the sample indicating the complete reaction with $HNO_3$. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% $H_2O_2$. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% $H_2O_2$. Care must be taken to ensure that losses do not occur due to excessive vigorous effervesence. Go to Section 7.2.3.

7.2.2 Continue to add 30% $H_2O_2$ in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% $H_2O_2$.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) $HNO_3$. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL $H_2O$ to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

**NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.**

7.5 Add 2.5 mL conc. $HNO_3$ and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

## 8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

| | |
|---|---|
| Ag | 2,000 mg/kg |
| As | 1,000,000 mg/kg |
| Ba | 2,500 mg/kg |
| Be | 1,000,000 mg/kg |
| Cd | 1,000,000 mg/kg |
| Co | 1,000,000 mg/kg |
| Cr | 1,000,000 mg/kg |
| Cu | 1,000,000 mg/kg |
| Mo | 1,000,000 mg/kg |
| Ni | 1,000,000 mg/kg |
| Pb | 200,000 mg/kg |
| Sb | 200,000 mg/kg |
| Se | 1,000,000 mg/kg |
| Tl | 1,000,000 mg/kg |
| V | 1,000,000 mg/kg |
| Zn | 1,000,000 mg/kg |

NOTE: These ranges will vary with sample matrix, molecular form, and size.

## 9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

## 10.0 REFERENCES


1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Edgell, K.; USEPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988.

4. Kimbrough, David E., and Wakakuwa, Janice R. Acid Digestion for Sediments, Sludges, Soils, and Solid Wastes. A Proposed Alternative to EPA SW 846 Method 3050. Environmental Science and Technology, Vol. 23, Page 898, July 1989.

5. Kimbrough, David E., and Wakakuwa, Janice R. Report of an Interlaboratory Study Comparing EPA SW 846 Method 3050 and an Alternative Method from the California Department of Health Services, Fifth Annual Waste Testing and Quality Assurance Symposium, Volume I, July 1989. Reprinted in Solid Waste Testing and Quality Assurance: Third Volume, ASTM STP 1075, Page 231, C.E. Tatsch, Ed., American Society for Testing and Materials, Philadelphia, 1991.

6. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Environmental Science and Technology, Vol. 26, Page 173, January 1992. Presented Sixth Annual Waste Testing and Quality Assurance Symposium, July 1990.

7. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Sixth Annual Waste Testing and Quality Assurance Symposium, Reprinted in Solid Waste Testing and Quality Assurance: Fourth Volume, ASTM STP 1076, Ed., American Society for Testing and Materials, Philadelphia, 1992.

8. NIST published leachable concentrations. Found in addendum to certificate of analysis for SRMs 2709, 2710, 2711 - August 23, 1993.

9. Kingston, H.M. Haswell, S.J. ed., Microwave Enhanced Chemistry, Professional Reference Book Series, American Chemical Society, Washington, D.C., Chapter 3, 1997.

TABLE 1

STANDARD RECOVERY (%) COMPARISON FOR METHODS 3050A AND 3050B[a]

| Analyte | METHOD 3050A[a] | METHOD 3050B w/option[a] |
|---|---|---|
| Ag | 9.5 | 98 |
| As | 86 | 102 |
| Ba | 97 | 103 |
| Be | 96 | 102 |
| Cd | 101 | 99 |
| Co | 99 | 105 |
| Cr | 98 | 94 |
| Cu | 87 | 94 |
| Mo | 97 | 96 |
| Ni | 98 | 92 |
| Pb | 97 | 95 |
| Sb | 87 | 88 |
| Se | 94 | 91 |
| Tl | 96 | 96 |
| V | 93 | 103 |
| Zn | 99 | 95 |

[a] All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2

PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

| | Percent Recovery[a,c] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Analyte | Sample 4435 | | Sample 4766 | | Sample HJ | | Average | |
| | 3050A | 3050B | 3050A | 3050B | 3050A | 3050B | 3050A | 3050B |
| Ag | 9.8 | 103 | 15 | 89 | 56 | 93 | 27 | 95 |
| As | 70 | 102 | 80 | 95 | 83 | 102 | 77 | 100 |
| Ba | 85 | 94 | 78 | 95 | b | b | 81 | 94 |
| Be | 94 | 102 | 108 | 98 | 99 | 94 | 99 | 97 |
| Cd | 92 | 88 | 91 | 95 | 95 | 97 | 93 | 94 |
| Co | 90 | 94 | 87 | 95 | 89 | 93 | 89 | 94 |
| Cr | 90 | 95 | 89 | 94 | 72 | 101 | 83 | 97 |
| Cu | 81 | 88 | 85 | 87 | 70 | 106 | 77 | 94 |
| Mo | 79 | 92 | 83 | 98 | 87 | 103 | 83 | 98 |
| Ni | 88 | 93 | 93 | 100 | 87 | 101 | 92 | 98 |
| Pb | 82 | 92 | 80 | 91 | 77 | 91 | 81 | 91 |
| Sb | 28 | 84 | 23 | 77 | 46 | 76 | 32 | 79 |
| Se | 84 | 89 | 81 | 96 | 99 | 96 | 85 | 94 |
| Tl | 88 | 87 | 69 | 95 | 66 | 67 | 74 | 83 |
| V | 84 | 97 | 86 | 96 | 90 | 88 | 87 | 93 |
| Zn | 96 | 106 | 78 | 75 | b | b | 87 | 99 |

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.

Table 3
Results of Analysis of Nist Standard Reference Material 2704
"River Sediment" Using Method 3050B (µg/g ± SD)

| Element | Atm. Pressure Microwave Assisted Method with Power Control | Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb) | Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor) | Hot-Plate | NIST Certified Values for Total Digestion (µg/g ±95% CI) |
|---|---|---|---|---|---|
| Cu | 101 ± 7 | 89 ± 1 | 98 ± 1.4 | 100 ± 2 | 98.6 ± 5.0 |
| Pb | 160 ± 2 | 145 ± 6 | 145 ± 7 | 146 ± 1 | 161 ± 17 |
| Zn | 427 ± 2 | 411 ± 3 | 405 ± 14 | 427 ± 5 | 438 ± 12 |
| Cd | NA | 3.5 ± 0.66 | 3.7 ± 0.9 | NA | 3.45 ± 0.22 |
| Cr | 82 ± 3 | 79 ± 2 | 85 ± 4 | 89 ± 1 | 135 ± 5 |
| Ni | 42 ± 1 | 36 ± 1 | 38 ± 4 | 44 ± 2 | 44.1 ± 3.0 |

NA - Not Available

Table 4
Results of Analysis of NIST Standard Reference Material 2710
"Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

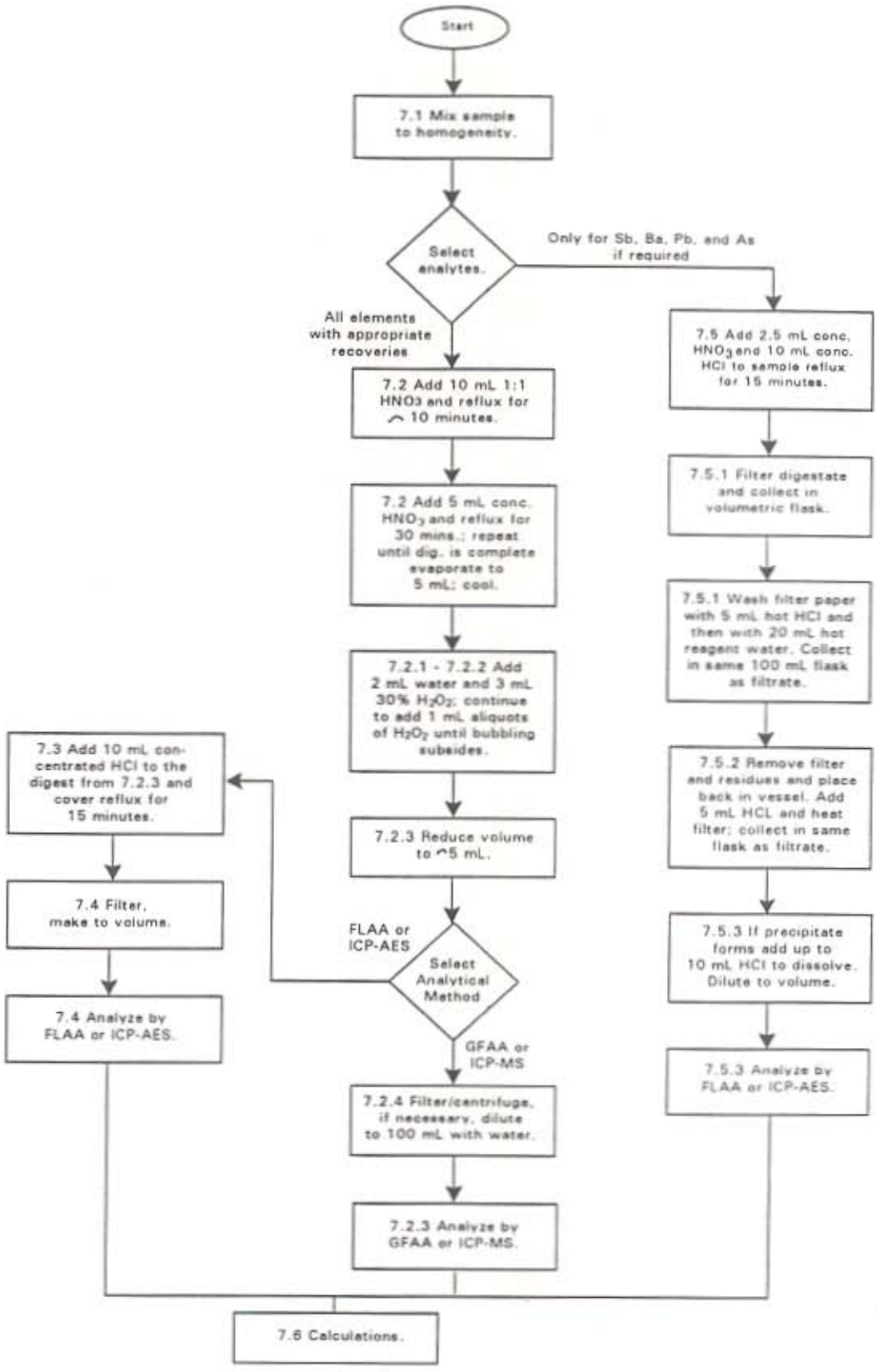
| Element | Atm. Pressure Microwave Assisted Method with Power Control | Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb) | Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor) | Hot-Plate | NIST Leachable Concentrations Using Method 3050 | NIST Certified Values for Total Digestion (µg/g ±95% CI) |
|---|---|---|---|---|---|---|
| Cu | 2640 ± 60 | 2790 ± 41 | 2480 ± 33 | 2910 ± 59 | 2700 | 2950 ± 130 |
| Pb | 5640 ± 117 | 5430 ± 72 | 5170 ± 34 | 5720 ± 280 | 5100 | 5532 ± 80 |
| Zn | 6410 ± 74 | 5810 ± 34 | 6130 ± 27 | 6230 ± 115 | 5900 | 6952 ± 91 |
| Cd | NA | 20.3 ± 1.4 | 20.2 ± 0.4 | NA | 20 | 21.8 ± 0.2 |
| Cr | 20 ± 1.6 | 19 ± 2 | 18 ± 2.4 | 23 ± 0.5 | 19 | 39* |
| Ni | 7.8 ± 0.29 | 10 ± 1 | 9.1 ± 1.1 | 7 ± 0.44 | 10.1 | 14.3 ± 1.0 |

NA - Not Available * Non-certified values, for information only.

Table 5
Results of Analysis of NIST Standard Reference Material 2711
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

| Element | Atm. Pressure Microwave Assisted Method with Power Control | Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb) | Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor) | Hot-Plate | NIST Leachable Concentrations Using Method 3050 | NIST Certified Values for Total Digestion (µg/g ±95% CI) |
|---|---|---|---|---|---|---|
| Cu | 107 ± 4.6 | 98 ± 5 | 98 ± 3.8 | 111 ± 6.4 | 100 | 114 ± 2 |
| Pb | 1240 ± 68 | 1130 ± 20 | 1120 ± 29 | 1240 ± 38 | 1100 | 1162 ± 31 |
| Zn | 330 ± 17 | 312 ± 2 | 307 ± 12 | 340 ± 13 | 310 | 350.4 ± 4.8 |
| Cd | NA | 39.6 ± 3.9 | 40.9 ± 1.9 | NA | 40 | 41.7 ± 0.25 |
| Cr | 22 ± 0.35 | 21 ± 1 | 15 ± 1.1 | 23 ± 0.9 | 20 | 47* |
| Ni | 15 ± 0.2 | 17 ± 2 | 15 ± 1.6 | 16 ± 0.4 | 16 | 20.6 ± 1.1 |

NA - Not Available
* Non-certified values, for information only.


Start
7.1 Mix sample to homogeneity.
Select analytes.
Only for Sb, Ba, Pb, and As if required
All elements with appropriate recoveries
7.2 Add 10 mL 1:1 HNO3 and reflux for ~ 10 minutes.
7.2 Add 5 mL conc. HNO3 and reflux for 30 mins.; repeat until dig. is complete evaporate to 5 mL; cool.
7.2.1 - 7.2.2 Add 2 mL water and 3 mL 30% H2O2; continue to add 1 mL aliquots of H2O2 until bubbling subsides.
7.2.3 Reduce volume to ~5 mL.
FLAA or ICP-AES
Select Analytical Method
GFAA or ICP-MS
7.2.4 Filter/centrifuge, if necessary, dilute to 100 mL with water.
7.2.3 Analyze by GFAA or ICP-MS.
7.3 Add 10 mL concentrated HCl to the digest from 7.2.3 and cover reflux for 15 minutes.
7.4 Filter, make to volume.
7.4 Analyze by FLAA or ICP-AES.
7.5 Add 2.5 mL conc. HNO3 and 10 mL conc. HCl to sample reflux for 15 minutes.
7.5.1 Filter digestate and collect in volumetric flask.
7.5.1 Wash filter paper with 5 mL hot HCl and then with 20 mL hot reagent water. Collect in same 100 mL flask as filtrate.
7.5.2 Remove filter and residues and place back in vessel. Add 5 mL HCL and heat filter; collect in same flask as filtrate.
7.5.3 If precipitate forms add up to 10 mL HCl to dissolve. Dilute to volume.
7.5.3 Analyze by FLAA or ICP-AES.
7.6 Calculations.

# APPENDIX D-10
# Analytical Procedure for Arsenic: Method 7060A

METHOD 7060A

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

## 1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

## 2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration. Other modifiers may be used in place of nickel nitrate if the analyst documents the chemical and concentration used.

2.3 The typical detection limit for water samples using this method is 1 ug/L. This detection limit may not be achievable when analyzing waste samples.

## 3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A matrix modifier such as nickel nitrate must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using $D_2$ arc background

correction. Although Zeeman background correction is very useful in this situation, use of any appropriate background correction technique is acceptable.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

## 4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker or equivalent: 250 mL.

4.2 Class A Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a suitable recording device.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Data systems recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

## 5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the $H_2O_2$ is <MDL, the reagent can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide ($As_2O_3$, analytical reagent grade) or equivalent in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated $HNO_3$ and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in reagent water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with reagent water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated $HNO_3$, 30% $H_2O_2$, and 5% nickel nitrate solution or other appropriate matrix modifier. Amounts added should be representative of the concentrations found in the samples. Dilute to 100 mL with reagent water.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid and refrigerated prior to analysis.

6.5 Although waste samples do not need to be refrigerated sample handling and storage must comply with the minimum requirements established in Chapter One.

## 7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050A. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer a known volume of well-mixed sample to a 250-mL Griffin beaker or equivalent; add 2 mL of 30% $H_2O_2$ and sufficient concentrated $HNO_3$ to result in an acid concentration of 1% (v/v). Heat, until digestion is complete, at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool, transfer to a volumetric flask, and bring back to 50 mL with reagent water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution or other appropriate matrix modifier, and dilute to 10 mL with reagent water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

## 8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

## 9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for aqueous samples using this method is 5-100 ug/L. Concentration ranges for non-aqueous samples will vary with matrix type.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

## 10.0 REFERENCES

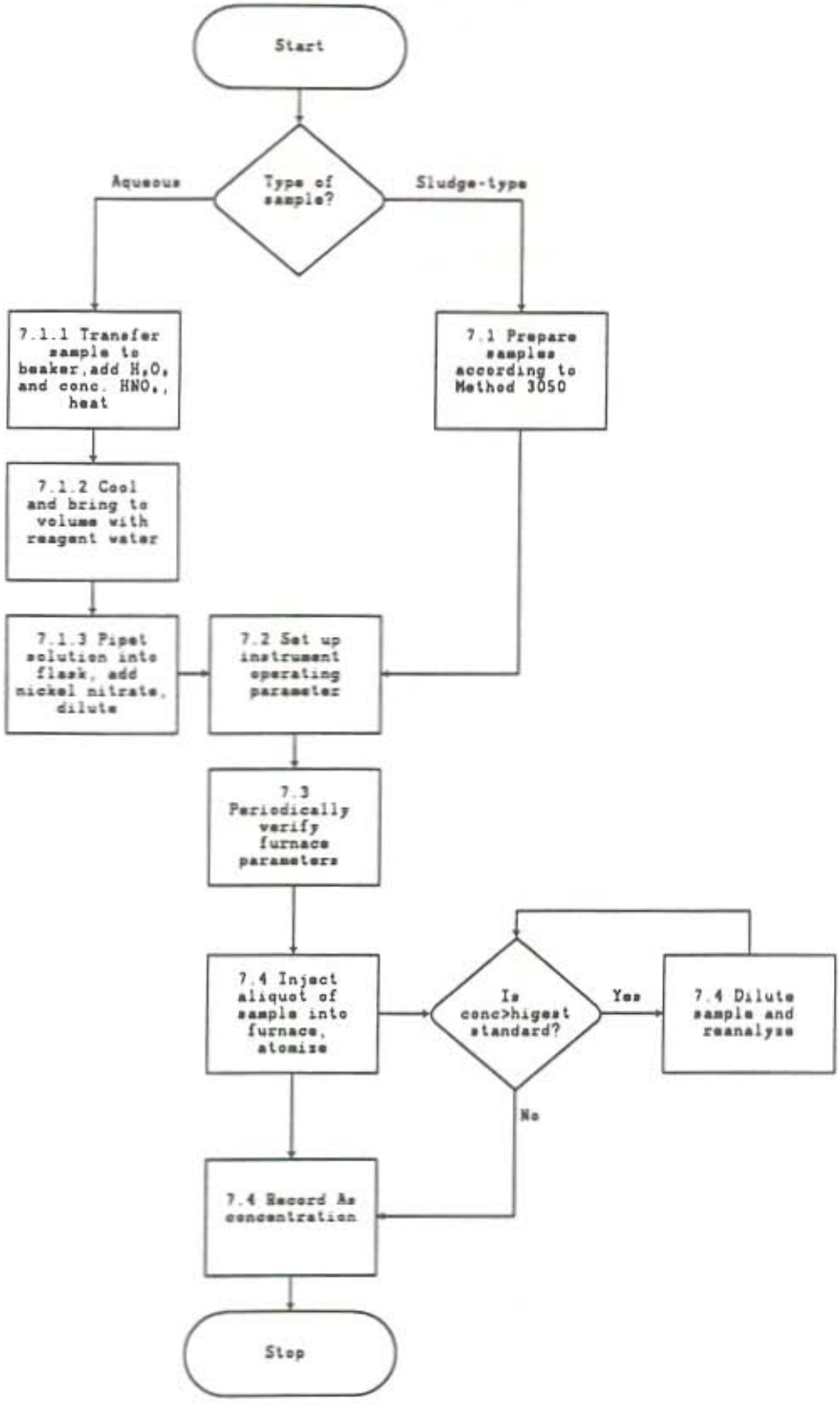
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

| Sample Matrix | Preparation Method | Laboratory Replicates |
|---|---|---|
| Contaminated soil | 3050 | 2.0, 1.8 ug/g |
| Oily soil | 3050 | 3.3, 3.8 ug/g |
| NBS SRM 1646 Estuarine sediment | 3050 | 8.1, 8.33 ug/g[a] |
| Emission control dust | 3050 | 430, 350 ug/g |

[a]Bias of -30 and -28% from expected, respectively.


Start
Type of sample?
Aqueous
Sludge-type
7.1.1 Transfer sample to beaker, add $H_2O_2$ and conc. $HNO_3$, heat
7.1 Prepare samples according to Method 3050
7.1.2 Cool and bring to volume with reagent water
7.1.3 Pipet solution into flask, add nickel nitrate, dilute
7.2 Set up instrument operating parameter
7.3 Periodically verify furnace parameters
7.4 Inject aliquot of sample into furnace, atomize
Is conc>higest standard?
Yes
7.4 Dilute sample and reanalyze
No
7.4 Record As concentration
Stop

# APPENDIX D-11
# Preparation Procedure for Bio-Available Lead (Pb): Method ASA 21-5

**Bio-Available Lead**
**(Water Extractable Lead)**
**ASA Method 21-5**

1.0 Procedure

Extract 5.0 grams (dry weight) soil with 50 ml water for three hours on a reciprocating shaker at 180 cycles per minute. Centrifuge the sample as needed and then filter the supernatant through a 1-micron syringe filter. Acidify a 10-ml portion of the filtered sample with 10 ml nitric acid and dilute to 50 ml.

Submit for lead analysis by inductively coupled plasma (ICP). Report sample weight, percent moisture, extraction volume and dilution factor to the metals workgroup so that analytical values may be calculated.

2.0 Recordkeeping

Retain all worksheets, calculations, graphs, and notes.

3.0 Quality Control Samples

Duplicate samples may be extracted as quality control samples. Other quality control samples such as matrix spikes may be performed on extracts as required by the metals analytical procedure.

4.0 References

"Selective Extraction," Section 21-5 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-12
# Analytical Procedure for Chelator (EDTA): Method AP-0047

## 1.0 PURPOSE

This procedure provides instructions to perform (Ethylene dinitrilo)tetraacetic Acid (EDTA) determinations by high performance liquid chromatography (HPLC). See note 9.1.

## 2.0 SCOPE

This procedure is applicable to aqueous samples or liquid extracts from soil samples.

## 3.0 SUMMARY

Reagent containing ferric ion ($Fe^{3+}$) is added to all samples and standards. The EDTA forms a complex with the ferric ion to form a UV-absorbing chromophore. The analysis is accomplished using ion-pair HPLC with a diode array detector.

## 4.0 REFERENCES

4.1 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 3rd Edition, Most Recent Update (July 1992 with proposed methods dated November 1992)

4.1.1 Chapter 1, "Quality Assurance"

4.1.2 Chapter 4, "Organic Analysis"

4.1.3 Method 8000A, "Gas Chromatography"

4.2 "Extraction of EDTA from Soils", AP-0057, Environmental Applications, Tennessee Valley Authority, Muscle Shoals, Alabama

## 5.0 RESPONSIBILITIES

5.1 The Specialty Laboratory supervisor, or his designee, shall ensure that this procedure is followed during the determination of EDTA.

5.2 The laboratory group leader, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure. The group leader is responsible for reviewing all data generated. The group leader is responsible for training new personnel on this procedure.

5.3 The chemist or analyst shall follow this procedure, shall ensure the accuracy of all calculations, and shall report any abnormal results or nonconformances to the laboratory group leader.

6.0 **REQUIREMENTS**

6.1 Prerequisites

6.1.1 All soil samples must be extracted by the method: "Extraction of EDTA from Soils" AP-0057 before analysis.

6.2 Limitations and Actions

6.2.1 High levels of EDTA (>500 ppm) affect the response to EDTA in subsequent samples. Samples following those with high levels of EDTA shall be carefully reviewed and reanalyzed as needed.

6.2.2 All samples reading higher than the calibration curve shall be diluted into the range of the calibration curve.

6.3 Apparatus/Equipment

6.3.1 Analytical balance, capable of reading to 0.1 mg.

6.3.2 HPLC system with diode array detector.

6.3.3 HPLC column, Supelco LC-8DB, 5 micron, 15 cm x 4.6 mm.

6.3.4 Guard column, Supelco LC-ABZ.

6.3.5 Sand bath, constant temperature at approximately 90-95 degrees C.

6.3.6 0.2 micron nylon syringe filter.

6.3.7 0.45 micron, type HA Millipore filter.

6.4 Reagents and Standards

6.4.1 Tetrabutylammonium (dihydrogen) Phosphate (TBAP), reagent grade.

6.4.2 Sodium Hydroxide, NaOH, approximately 25% solution, reagent grade.

6.4.3 Sodium phosphate monobasic, monohydrate, reagent grade.

6.4.4 Phosphoric acid, approximately 40 % solution, reagent grade.

6.4.5 Methanol, HPLC grade.

6.4.6 Ethylenediaminetetraacetic acid, disodium salt, dihydrate (EDTA) reagent grade. Formula weight 372.24 g/mole. Correct all weights of the dihydrate to the anhydrous basis by multiplying by the ratio 336.21/372.24 (0.90321).

6.4.7 Water, HPLC grade.

6.4.8 HPLC Mobile Phase

6.4.8.1 To 400 ml of HPLC grade water, add 1.69g tetrabutylammonium phosphate (TBAP).

6.4.8.2 Add 6.9 g of sodium phosphate monobasic, monohydrate. The pH will be approximately 4.5.

6.4.8.3 Add 100 ml HPLC grade methanol. Mix well.

6.4.8.4 Filter solution through a 0.45 micron type HA millipore filter.

6.4.8.5 Dilute to 1 L with HPLC grade water.

6.4.9 Iron Reagent

6.4.9.1 To 40 ml of HPLC grade water, add 1.69 g of tetrabutylammonium phosphate (TBAP).

6.4.9.2 Add 0.69 g sodium phosphate monobasic, monohydrate.

6.4.9.3 Adjust pH to 3.0 with 0.05 M phosphoric acid.

6.4.9.4 Add 0.5 g ferric nitrate.

6.4.9.5 Mix and allow to stand for 1 hour.

6.4.9.6 Centrifuge solution and decant aqueous phase.

6.4.9.7 Filter the solution through a 0.45 micron type HA millipore filter.

6.4.9.8 Dilute to 100 ml with HPLC grade water.

6.4.10 EDTA, disodium salt, 1000 ppm cal stock. Weigh approximately 0.1 g of EDTA (weighed to the nearest 0.1 mg) and dilute to 100 ml with HPLC grade water. J.T. Baker ultrapure bioreagent.

6.4.11 EDTA, disodium salt, calibration standards. Dilute the 1000 ppm stock standard to produce the following calibration standards: 1 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm calibration standards.

6.4.12 EDTA, disodium salt, lab control sample and spiking solution 1000 ppm stock. Weigh approximately 0.1 g of EDTA (weighed to the nearest 0.1 mg) and dilute to 100 ml with HPLC grade water. Reagents, Inc.

6.4.13 EDTA, disodium salt, secondary QC standard. Dilute the 1000 ppm QC stock to produce the following QC standards: 75 ppm spiking solution and 15 ppm QC check standard.

6.5 Quality Control Sample Requirements

6.5.1 Each batch of samples must have the following quality control samples: One spiked sample, one duplicate spike sample, one sample duplicate, one laboratory control sample and one method blank.

6.5.2 The accuracy of the calibration curve is checked on a daily basis with a midpoint check standard analyzed once per every 10 samples analyzed and at the end of the analysis. Recalibration is not required with subsequent analysis unless the midpoint check falls outside the 85 to 115 percent range.

7.0 **PROCEDURE**

7.1 Calibration

7.1.1 Calibrate the instrument with the following standards: 1 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm.

7.1.2 Pipette 1 ml of each known standard into an HPLC sample vial.

7.1.3 Add 0.1 ml of the iron reagent.

7.1.4 Mix thoroughly.

7.1.5 Analyze standards with parameters as in 7.2.3. Utilize vendor-supplied chromatography workstation software to fit the calibration data. Inspect the curve for goodness of fit of 0.99 or better.

7.2 Procedure Instructions

7.2.1 Sample Preparation

7.2.1.1 Filter the aqueous sample through a 0.2 micron nylon syringe filter.

7.2.1.2 Pipette 1 ml of the sample into an HPLC vial.

7.2.1.3 Add 0.1 ml of the iron reagent.

7.2.1.4 Mix thoroughly by shaking.

7.2.3 Instrument Parameters

7.2.3.1 Detector: Photodiode array.

7.2.3.2 Wavelength: 254 nm.

7.2.3.3 Column: Supelcosil LC-8DB; 15 cm x 4.6 mm with guard, LC-ABZ, 2 cm.

7.2.3.4 Flow rate: 1.5 ml/min.

7.2.3.5 Analysis time: 10 minutes.

7.2.3.6 Injection volume: 50 microliters

7.2.4 HPLC Sample Analysis

7.2.4.1 Turn the detector on, allow approximately 1 hour for lamp to warm up.

7.2.4.2 Turn the pump on; 60/40 methanol/water and allow the system to stabilize. NOTE: Prime the pump before operation.

7.2.4.3 Change the composition of the pump to 100% water and allow the system to stabilize.

7.2.4.4 Change the mobile phase of the system to 100% iron reagent mobile phase and allow the system to stabilize.

7.2.4.5 Place the samples on the autosampler and create a sample list. Activate the newly created sample list.

7.2.4.6 Activate the analysis.

7.2.5 Cleaning Column After Analysis

7.2.5.1 Change the mobile phase of the system to 100% water and allow the system to stabilize after the analysis is complete.

7.2.5.2 Change the mobile phase of the system to 60/40 methanol/water and allow the system to stabilize.

7.3 Calculations and Recording Data

7.3.1 The percent recovery for spikes are to be calculated as follows:

$$\% \text{ SPREC} = \frac{\text{SP - SAMP}}{\text{SP1}} \times 100\%$$

where:

SPREC = Percent spike recovery
SP = Actual spike read
SAMP = Spike's corresponding sample read
SP1 = Theoretical value of spike

7.3.2 The percent recovery for control samples and checks are to be calculated as follows:

$$\% CK = \frac{C1}{C2} \times 100$$

where:

CK = Percent recovery for control sample or check standard.
C1 = Actual known value reading
C2 = Theoretical value of known

7.3.3 Utilize commercial chromatography workstation software or a suitable spreadsheet to apply calibration curve factors to peak heights to calculate concentration in samples

Example: When a calibration curve has been fit to the equation $C = A + Bx$ (where x is observed peak height), the concentration would be calculated as:

Conc = (A + Bx) * Volume / Weight * DF

For a soil sample:

A, B = fit parameters of calibration curve
x = observed peak height
Volume = final extraction volume
Weight = weight of soil extracted, corrected for moisture
DF = dilution factor (when sample was diluted) or 1.000

Reporting units would be mg Disodium EDTA/kg soil

(However, see Note 9.2)

For a liquid sample (direct injection):

A, B = fit parameters of calibration curve
x = observed peak height
Volume = 1.000
Weight = 1.000
DF = dilution factor (when sample was diluted) or 1.000

Reporting units would be mg Disodium EDTA/Liter

7.3.4 File all original data, preparation worksheets, chromatograms, calculations, quality control summary sheets, and printouts with the workorder as quality assurance records.

## 8.0 SAFETY

8.1 Read Material Safety Data Sheets (MSDS).

8.2 Wear gloves when handling chemicals. Avoid inhalation of dust.

8.3 Wear lab coat and safety glasses while performing this procedure.

8.4 Material Safety Data Sheets (MSDS) are available for tetrabutyl ammonium phosphate, methanol, sodium hydroxide, EDTA, ferric nitrate and sodium phosphate monobasic, monohydrate.

## 9.0 NOTES

9.1 The chemical names Ethylenediamine tetraacetic acid and (Ethylenedinitrilo)tetraacetic acid are synonyms.

9.2 For the Lead Phytoremediation project, report values as milligrams Disodium EDTA per liter in the extract. Also report sample weight and percent moisture separately.

In this case: Conc = (A + Bx) * Volume / Weight * DF

Where

A, B = fit parameters of calibration curve
x = observed peak height
Volume = final extraction volume
Weight = 1.000
DF = dilution factor (when sample was diluted) or 1.000

## 10.0 ATTACHMENTS AND APPENDICES

None

**End of Procedure**

# APPENDIX D-13
# Analytical Procedure for Soil Moisture: Method ASA 21-2.2.2

**Soil Moisture, Oven Drying Method**
ASA Physical Method 21-2.2.2

1.0 Purpose

To determine the moisture loss of a soil sample by oven drying overnight at 105 °C.

2.0 Scope

This procedure applies to soil, sand, silt, rock, and soil organic matter.

3.0 Summary

A sample is dried overnight at 105 °C. Moisture content is determined by weight loss.

4.0 References

Chapter 21-2.2 "Gravimetry With Oven Drying." *Methods of Soil Analysis, Part I, Physical and Mineralogical Methods*, Second Edition, 1986. Arnold Klute, Editor. American Society of Agronomy, Inc. Soil Science Society of America Inc. Publisher, Madison, Wisconsin, USA.

ASTM D 2216-92, "Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock"

ASTM D 2974-87 (Reapproved 1995) "Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils"

5.0 Responsibilities

5.1 The Laboratory Manager shall ensure that this procedure is followed during the analysis of samples.

5.2 The Laboratory Group Leader shall review and approve data produced under this procedure.

5.3 The laboratory analyst shall follow this procedure and laboratory safety guidelines. The analyst shall record all data, calculate results, and sign a written report of the analysis.

6.0 Requirements

6.1 Prerequisites

None

6.2 Limitations and Actions

For extremely dry soils, the quantity weighed should be increased in step 7.1.3 to 50g.

6.3 Requirements

6.3.1 Apparatus/Equipment

6.3.1.1 Laboratory oven with forced air, thermostatted to control temperature to plus or minus 5 °C.

6.3.1.2 Desiccator with active dessicant (Drierite, or Anhydrone)

6.3.1.3 Tongs or insulated gloves

6.3.1.4 Analytical Balance - capable of weighing to 0.0001 g.

6.3.2 Reagents and Standards

None

6.4 Quality Control Sample Requirements

Run a duplicate sample and method blank for every batch of 20 samples or subset thereof.

7.0 Procedure

7.1 Procedure Instructions

7.1.1 Thoroughly mix a portion of soil. Remove stones larger than 1 cm diameter. Remove roots and leaves. Break up any lumps or adhesions.

7.1.2 Dry a beaker or weighing dish for 30 minutes at 105 °C. Allow to cool in a desiccator with active dessicant.

7.1.3 Obtain the tare weight of the container then the weight plus 10 to 20g soil (record weight to 0.0001g).

7.1.4 Place the moist sample and container in the drying oven overnight (approximately 16 hours) at 105 °C uncovered.

7.1.5 Remove the container from the oven and place it in a desiccator with active dessicant to cool.

7.1.6 Weigh the dried sample and container.

7.2 Calculations and Recording Data

7.2.1 Calculate the water content of the material to the nearest 0.1% as follows:

$$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)] * 100$$

where

$w$ = water content, %
$M_{cws}$ = mass of container and wet specimen in grams
$M_{cs}$ = mass of container and dry specimen in grams
$M_c$ = mass of container

7.2.2 Calculate the percent solids to the nearest 0.1% as follows:

Percent solids = 100 - w

7.2.3 Record data on the form provided in 10.1.

Note: A spreadsheet may be used to calculate the data.

8.0 Safety

8.1 Follow general laboratory safety rules. Exercise care in removing hot items from the oven. Use tongs or insulated gloves.

8.2 Excercise caution to not spill hot soil containing organic matter into Anhydrone (magnesium perchlorate) which is a strong oxidizing agent.

9.0 Notes

None

## 10.0 Attachments and Appendices

### 10.1 Soil Percent Moisture Worksheet

Percent Moisture
Oven Drying Water Worksheet

Initial Date/Time _____ Initial Oven Temp _____
Final Date/Time _____ Final Oven Temp _____

| | | | | | | |
|---|---|---|---|---|---|---|
| Workorder | | | | | | |
| Fraction | | | | | | |
| Gross Wt | | | | | | |
| Tare Wt | | | | | | |
| Dried Wt | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Wt sample | | | | | | |
| Wt loss | | | | | | |
| % Moisture | | | | | | |
| %Solid | | | | | | |

Entered by _____ Date _____

Reviewed by _____ Date _____

END OF PROCEDURE

# APPENDIX D-14
# Preparation Procedure for Total Metals in Soil Solution: Method 3005A

METHOD 3005A

# ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

## 1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

| | |
|---|---|
| Aluminum | Magnesium |
| Antimony** | Manganese |
| Arsenic* | Molybdenum |
| Barium | Nickel |
| Beryllium | Potassium |
| Cadmium | Selenium* |
| Calcium | Silver |
| Chromium | Sodium |
| Cobalt | Thallium |
| Copper | Vanadium |
| Iron | Zinc |
| Lead | |

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

## 2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-$\mu$m filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

## 3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

## 4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

## 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), $HNO_3$. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with $HNO_3$ (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-$\mu$m filter and then acidified at the time of collection with $HNO_3$ (5 mL/L).

## 7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated $HNO_3$ and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute $HNO_3$.

7.4 Adjust the final volume to 100 mL with reagent water.

## 8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

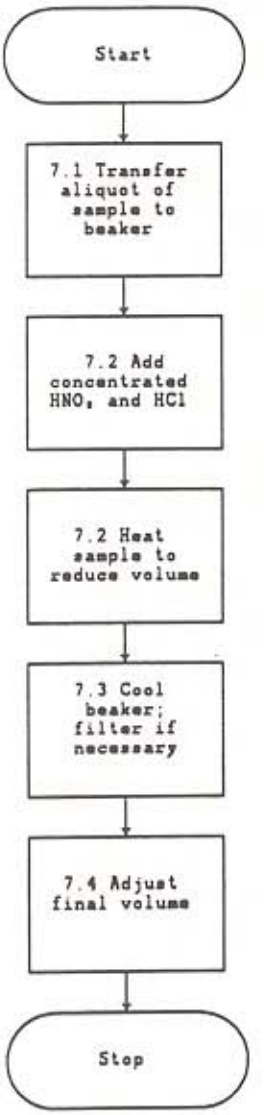
## 9.0 METHOD PERFORMANCE

9.1 No data provided.

## 10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO, and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

# APPENDIX D-15
# Analytical Procedure for Trichloroethylene: Method 8021B

# AROMATIC AND HALOGENATED VOLATILES BY GAS CHROMATOGRAPHY USING PHOTOIONIZATION AND/OR ELECTROLYTIC CONDUCTIVITY DETECTORS

## 1.0 SCOPE AND APPLICATION

1.1 Method 8021 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

| | | Appropriate Technique | | | |
|---|---|---|---|---|---|
| Analyte | CAS No.[a] | Purge-and -Trap | Direct Injection | Vac Distln | Head Space |
| Allyl chloride | 107-05-1 | b | b | nd | nd |
| Benzene | 71-43-2 | b | b | b | b |
| Benzyl chloride | 100-44-7 | pp | b | nd | nd |
| Bis(2-chloroisopropyl) ether | 108-60-1 | b | b | nd | nd |
| Bromoacetone | 598-31-2 | pp | b | nd | nd |
| Bromobenzene | 108-86-1 | b | nd | nd | nd |
| Bromochloromethane | 74-97-5 | b | b | nd | b |
| Bromodichloromethane | 75-27-4 | b | b | b | b |
| Bromoform | 75-25-2 | b | b | b | b |
| Bromomethane | 74-83-9 | b | b | b | b |
| Carbon tetrachloride | 56-23-5 | b | b | b | b |
| Chlorobenzene | 108-90-7 | b | b | b | b |
| Chlorodibromomethane | 124-48-1 | b | b | b | b |
| Chloroethane | 75-00-3 | b | b | b | b |
| 2-Chloroethanol | 107-07-03 | pp | b | nd | nd |
| 2-Chloroethyl vinyl ether | 110-75-8 | b | b | b | nd |
| Chloroform | 67-66-3 | b | b | b | b |
| Chloromethyl methyl ether | 107-30-2 | pp | pc | nd | nd |
| Chloroprene | 126-99-8 | b | nd | nd | nd |
| Chloromethane | 74-87-3 | b | b | b | b |
| 4-Chlorotoluene | 106-43-4 | b | b | nd | nd |
| 1,2-Dibromo-3-chloropropane | 96-12-8 | pp | b | nd | b |
| 1,2-Dibromoethane | 106-93-4 | b | nd | nd | b |
| Dibromomethane | 74-95-3 | b | b | b | b |
| 1,2-Dichlorobenzene | 95-50-1 | b | nd | nd | b |
| 1,3-Dichlorobenzene | 541-73-1 | b | nd | nd | b |
| 1,4-Dichlorobenzene | 106-46-7 | b | nd | nd | b |
| Dichlorodifluoromethane | 75-71-8 | b | b | b | b |
| 1,1-Dichloroethane | 75-34-3 | b | b | b | b |
| 1,2-Dichloroethane | 107-06-2 | b | b | b | b |

| Analyte | CAS No.[a] | Appropriate Technique | | | |
|---|---|---|---|---|---|
| | | Purge-and -Trap | Direct Injection | Vac Distln | Head Space |
| 1,1-Dichloroethene | 75-35-4 | b | b | b | b |
| cis-1,2-Dichloroethene | 156-59-2 | b | nd | nd | nd |
| trans-1,2-Dichloroethene | 156-60-5 | b | b | b | b |
| 1,2-Dichloropropane | 78-87-5 | b | nd | b | b |
| 1,3-Dichloro-2-propanol | 96-23-1 | pp | b | nd | nd |
| cis-1,3-dichloropropene | 10061-01-5 | b | b | b | nd |
| trans-1,3-dichloropropene | 10061-02-6 | b | b | b | nd |
| Epichlorhydrin | 106-89-8 | pp | b | nd | nd |
| Ethylbenzene | 100-41-4 | b | b | b | b |
| Hexachlorobutadiene | 87-68-3 | b | nd | nd | b |
| Methylene chloride | 75-09-2 | b | b | b | b |
| Naphthalene | 91-20-3 | b | nd | nd | b |
| Styrene | 100-42-5 | b | b | b | b |
| 1,1,1,2-Tetrachloroethane | 630-20-6 | b | nd | nd | b |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | b | b | b | b |
| Tetrachloroethene | 127-18-4 | b | b | b | b |
| Toluene | 108-88-3 | b | b | b | b |
| 1,2,4-Trichlorobenzene | 120-82-1 | b | nd | nd | b |
| 1,1,1-Trichloroethane | 71-55-6 | b | b | b | b |
| 1,1,2-Trichloroethane | 79-00-5 | b | b | b | b |
| Trichloroethene | 79-01-6 | b | b | b | b |
| Trichlorofluoromethane | 75-69-4 | b | b | b | b |
| 1,2,3-Trichloropropane | 96-18-4 | b | b | b | b |
| Vinyl chloride | 75-01-4 | b | b | b | b |
| o-Xylene | 95-47-6 | b | b | b | b |
| m-Xylene | 108-38-3 | b | b | b | b |
| p-Xylene | 106-42-3 | b | b | b | b |

[a] Chemical Abstract Service Registry Number.
b Adequate response by this technique.
i Inappropriate technique for this analyte.
nd Not Determined
pc Poor chromatographic behavior.
pp Poor purging efficiency resulting in high EQLs. May require heated purge (e.g., 40°C) or a more appropriate sample preparation technique, e.g., azeotropic distillation, equilibrium headspace or vacuum distillation, for good method performance.

1.2 Method detection limits (MDLs) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some structural isomers (i.e., xylenes) may be hampered by coelution.

1.3 The estimated quantitation limit (EQL) of Method 8021A for an individual compound is approximately 1 µg/kg (wet weight) for soil/sediment samples, 0.1 mg/kg (wet weight) for wastes, and 1 µg/L for ground water (see Table 3). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs for measurement of purgeable organics at low µg/L concentrations and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst (References 4 and 6).

1.6 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

1.7 Other non-RCRA compounds which are amenable to analysis by Method 8021 include:

| Analyte | CAS No.[a] |
|---|---|
| n-Butylbenzene | 104-51-8 |
| *sec*-Butylbenzene | 135-98-8 |
| *tert*-Butylbenzene | 98-06-6 |
| 2-Chlorotoluene | 95-49-8 |
| 1,3-Dichloropropane | 142-28-9 |
| 2,2-Dichloropropane | 594-20-7 |
| 1,1-Dichloropropene | 563-58-6 |
| Isopropylbenzene | 98-82-8 |
| p-Isopropyltoluene | 99-87-6 |
| n-Propylbenzene | 103-65-1 |
| 1,2,3-Trichlorobenzene | 87-61-6 |
| 1,2,4-Trimethylbenzene | 95-63-6 |
| 1,3,5-Trimethylbenzene | 108-67-8 |

[a] Chemical Abstract Service Registry Number

## 2.0 SUMMARY OF METHOD

2.1 Method 8021 provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. Samples can be analyzed using direct injection (Method 3585 for oily matrices) or purge-and-trap (Method 5030/5035), headspace (Method 5021), or vacuum distillation (Method 5032). Groundwater samples may be analyzed using Method 5030, Method

5021, or Method 5032. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series. The GC system may also be set up to use a single detector when an analyst is looking for only halogenated compounds (HECD) or aromatic compounds (PID).

2.2 Tentative identifications are obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Confirmatory information can be gained by comparing the relative response from the two detectors. Concentrations of the identified components are measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

## 3.0 INTERFERENCES

3.1 Refer to the appropriate 5000 Series method and Method 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.3 Sulfur dioxide is a potential interferant in the analysis for vinyl chloride.

## 4.0 APPARATUS AND MATERIALS

4.1 Sample introduction apparatus - Refer to Sec. 4.0 of the appropriate 5000 Series method for a listing of the equipment for each sample introduction technique.

4.2 Gas Chromatograph - capable of temperature programming; equipped with variable-constant differential flow controllers, subambient oven controller, photoionization and electrolytic conductivity detectors connected with a short piece of uncoated capillary tubing, 0.32-0.5 mm ID, and data system.

4.2.1 Primary Column - 60-m x 0.75 mm ID VOCOL wide-bore capillary column with 1.5-µm film thickness (Supelco) or equivalent.

4.2.2 Confirmation column - 60-m x 0.53 ID SPB-624 wide-bore capillary column with 3.0-µm film thickness (Supelco) has been suggested as one possible option. Other columns that will provide appropriate resolution of the target compoundsmay also be employed for confirmation, or confirmation may be performed using GC/MS.

4.2.3 Photoionization detector (PID) (Tracor Model 703, or equivalent).

4.2.4 Electrolytic conductivity detector (HECD) (Tracor Hall Model 700-A, or equivalent).

4.3 Syringes - 5 mL glass hypodermic with Luer-Lok tips.

4.4 Syringe valves - 2-way with Luer ends [polytetrafluoroethylene (PTFE) or Kel-F].

4.5 Microsyringe - 25-µL with a 2-in. x 0.006-in. ID, 22° bevel needle (Hamilton #702N or equivalent).

4.6 Microsyringes - 10-, 100-µL.

4.7 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.8 Bottles - 15-mL, PTFE-lined with screw-cap or crimp top.

4.9 Analytical balance - 0.0001 g.

4.10 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

## 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, $CH_3OH$ - Pesticide quality or equivalent, demonstrated to be free of analytes. Store away from other solvents.

5.4 Vinyl chloride, (99.9% pure), $CH_2$=CHCl. Vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey, as well as from other sources. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

5.5 Stock standards - Stock solutions may either be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials of the toxicity should be prepared in a hood.

NOTE: If direct injection is used, the solvent system of standards must match that of the sample. It is not necessary to prepare high concentration aqueous mixed standards when using direct injection.

5.5.1 Place about 9.8 mL of methanol in a 10-mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material, as described below.

5.5.2.1 Liquids: Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5-mL valved gas-tight syringe with the

reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.5.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap or crimp top. Store, with minimal headspace, at -10°C to -20°C and protect from light. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.5.5 Frequency of Standard Preparation

5.5.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.5.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.6 Prepare secondary dilution standards, using stock standard solutions, in methanol, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 5.8 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.5.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.7 Calibration standards - There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.7.1 Initial calibration standards should be prepared at a minimum of five concentrations from the secondary dilution of stock standards (see Secs. 5.5 and 5.6) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve. See Sec. 7.0 of Method 8000 for guidance on initial calibration.

5.7.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.5 and 5.6) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.0 of Method 8000 for guidance on calibration verification.

5.7.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.7.4 The calibration standards should also contain the internal standards chosen for the analysis if internal standard calibration is used.

5.8 In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

NOTE: Prepare calibration solutions for use with direct injection analyses in water at the concentrations required.

5.8.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.8.2 Use a 25-µL Hamilton 702N micro syringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.8.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.8.4 Mix aqueous standards by inverting the flask three times.

5.8.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.8.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.8.7 Standards should be stored and handled according to guidance in Secs. 5.5.4 and 5.5.5.

5.9 Internal standards - It is recommended that a spiking solution containing fluorobenzene and 2-bromo-1-chloropropane in methanol be prepared, using the procedures described in Secs. 5.5

and 5.6. It is further recommended that the secondary dilution standard be prepared at a concentration of 5 mg/L of each internal standard compound. The addition of 10 µL of such a standard to 5.0 mL of sample calibration standard would be equivalent to 10 µg/L. External standard quantitation may also be used.

5.10 Surrogate standards -The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with two or more surrogate compounds. A combination of 1,4-dichlorobutane and bromochlorobenzene is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Sec. 5.5, add a volume to give 750 µg of each surrogate to 45 mL of organic-free reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Sec. 5.9).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

## 7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection (Method 3585 for oily matrices) or purge-and-trap (Methods 5030/5035), headspace (Method 5021), or by vacuum distillation (Method 5032). Methods 5030, 5021, or 5032 may be used directly on groundwater samples. Methods 5035, 5021, or 5032 may be used for low-concentration contaminated soils and sediments. For high-concentration soils or sediments (>200 µg/kg), methanolic extraction, as described in Method 5035, may be necessary prior to purge-and-trap analysis. For guidance on the dilution of oily waste samples for direct injection refer to Method 3585.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Set up the gas chromatograph system so that the photoionization detector (PID) is in series with the electrolytic conductivity detector (HECD). It may be helpful to contact the manufacturer of the GC for guidance on the proper installation of dual detector systems.

NOTE: Use of the dual detector system is not a requirement of the method. The GC system may also be set up to use a single detector when the analyst is looking for just halogenated compounds (using the HECD) or for just aromatic compounds (using the PID).

7.2.2 Oven settings:

| | |
|---|---|
| Carrier gas (Helium) Flow rate: | 6 mL/min. |
| Temperature program | |
| Initial temperature: | 10°C, hold for 8 minutes at |
| Program: | 10°C to 180°C at 4°C/min |
| Final temperature: | 180°C, hold until all expected compounds have eluted. |

7.2.3 The carrier gas flow is augmented with an additional 24 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors.

7.2.4 These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data presented in Table 2. The operating conditions used to collect these data are:

| | |
|---|---|
| Reactor tube: | Nickel, 1/16 in OD |
| Reactor temperature: | 810°C |
| Reactor base temperature: | 250°C |
| Electrolyte: | 100% n-Propyl alcohol |
| Electrolyte flow rate: | 0.8 mL/min |
| Reaction gas: | Hydrogen at 40 mL/min |
| Carrier gas plus make-up gas: | Helium at 30 mL/min |

7.2.5 A sample chromatogram obtained with this column is presented in Figure 1. This column was used to develop the method performance statements in Sec. 9.0. Estimated retention times and MDLs that can be achieved under these conditions are given in Table 1. Other columns or element specific detectors may be used if the requirements of Sec. 8.0 are met.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Sec. 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Methods 5030/5035 (purge-and-trap method) or the direct injection method (see Sec. 7.4.1.1), by Method 5021 (headspace) or by Method 5032 (vacuum distillation). If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g., aqueous process wastes) direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L), therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.1.2 Refer to Method 3585 for guidance on the dilution and direct injection of waste oil samples.

7.4.1.3 Samples may be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature and acceptable method performance is demonstrated.

7.4.2 Follow Sec. 7.0 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, identification criteria, and calibration verification. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two detectors for a number of organic compounds analyzable using this method.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 Second column confirmation

A 60-m x 0.53 ID SPB-624 wide-bore capillary column with 3.0-µm film thickness (Supelco) has been suggested as one possible option for confirming compound identifications. Other columns that will provide appropriate resolution of the target compoundsmay also be employed for confirmation, or confirmation may be performed using GC/MS.

7.4.7 If the response for a peak is off-scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

7.4.8 For target compounds that boil below 30°C at 1 atm pressure (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and vinyl chloride), analysts may use a calibration verification acceptance criteria of within ± 20% difference from the initial calibration response.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and includes evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy,

and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 Calibration verification acceptance criteria - For target compounds that boil below 30°C at 1 atm pressure (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and vinyl chloride), analysts may use a calibration verification acceptance criteria of within ± 20% difference from the initial calibration response.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

9.1 Method detection limits for these analytes have been calculated from data collected by spiking organic-free reagent water at 0.1 µg/L. These data are presented in Table 1.

9.2 This method was tested in a single laboratory using organic-free reagent water spiked at 10 µg/L. Single laboratory precision and accuracy data for each detector are presented for the method analytes in Table 2.

## 10.0 REFERENCES

1. "Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series",

Method 502.2, Rev. 2.0 (1989); Methods for the Determination of Organic Compounds in Drinking Water", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, EPA/600/4-88/039, December, 1988.

2. "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method", Method 502.1; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH 45268, September, 1986.

3. "Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography", Method 503.1; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, September, 1986.

4. Glaser, J.A., Forest, D.L., McKee, G.D., Quave, S.A., Budde, W.L. "Trace Analyses for Wastewaters", Environ. Sci. Technol., 1981, 15, 1426.

5. Bellar, T.A., Lichtenberg, J.J. "The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 45268.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS WITH PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

| Analyte | PID Ret. Time[a] minute | HECD Ret. Time minute | PID MDL µg/L | HECD MDL µg/L |
|---|---|---|---|---|
| Dichlorodifluoromethane | -[b] | 8.47 | | 0.05 |
| Chloromethane | - | 9.47 | | 0.03 |
| Vinyl Chloride | 9.88 | 9.93 | 0.02 | 0.04 |
| Bromomethane | - | 11.95 | | 1.1 |
| Chloroethane | - | 12.37 | | 0.1 |
| Trichlorofluoromethane | - | 13.49 | | 0.03 |
| 1,1-Dichloroethene | 16.14 | 16.18 | ND[c] | 0.07 |
| Methylene Chloride | - | 18.39 | | 0.02 |
| trans-1,2-Dichloroethene | 19.30 | 19.33 | 0.05 | 0.06 |
| 1,1-Dichloroethane | - | 20.99 | | 0.07 |
| 2,2-Dichloropropane | - | 22.88 | | 0.05 |
| cis-1,2-Dichloroethane | 23.11 | 23.14 | 0.02 | 0.01 |
| Chloroform | - | 23.64 | | 0.02 |
| Bromochloromethane | - | 24.16 | | 0.01 |
| 1,1,1-Trichloroethane | - | 24.77 | | 0.03 |
| 1,1-Dichloropropene | 25.21 | 25.24 | 0.02 | 0.02 |
| Carbon Tetrachloride | - | 25.47 | | 0.01 |
| Benzene | 26.10 | - | 0.009 | |
| 1,2-Dichloroethane | - | 26.27 | | 0.03 |
| Trichloroethene | 27.99 | 28.02 | 0.02 | 0.01 |
| 1,2-Dichloropropane | - | 29.66 | | 0.006 |
| Bromodichloromethane | - | 29.43 | | 0.02 |
| Dibromomethane | - | 29.59 | | 2.2 |
| Toluene | 31.95 | - | 0.01 | |
| 1,1,2-Trichloroethane | - | 33.21 | | ND |
| Tetrachloroethene | 33.88 | 33.90 | 0.05 | 0.04 |
| 1,3-Dichloropropane | - | 34.00 | | 0.03 |
| Dibromochloromethane | - | 34.73 | | 0.03 |
| 1,2-Dibromoethane | - | 35.34 | | 0.8 |
| Chlorobenzene | 36.56 | 36.59 | 0.003 | 0.01 |
| Ethylbenzene | 36.72 | - | 0.005 | |
| 1,1,1,2-Tetrachloroethane | - | 36.80 | | 0.005 |
| m-Xylene | 36.98 | - | 0.01 | |
| p-Xylene | 36.98 | - | 0.01 | |
| o-Xylene | 38.39 | - | 0.02 | |
| Styrene | 38.57 | - | 0.01 | |
| Isopropylbenzene | 39.58 | - | 0.05 | |
| Bromoform | - | 39.75 | | 1.6 |
| 1,1,2,2-Tetrachloroethane | - | 40.35 | | 0.01 |
| 1,2,3-Trichloropropane | - | 40.81 | | 0.4 |

TABLE 1(cont.)

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS WITH PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

| Analyte | PID Ret. Time[a] minute | HECD Ret. Time minute | PID MDL µg/L | HECD MDL µg/L |
|---|---|---|---|---|
| n-Propylbenzene | 40.87 | - | 0.004 | |
| Bromobenzene | 40.99 | 41.03 | 0.006 | 0.03 |
| 1,3,5-Trimethylbenzene | 41.41 | - | 0.004 | |
| 2-Chlorotoluene | 41.41 | 41.45 | ND | 0.01 |
| 4-Chlorotoluene | 41.60 | 41.63 | 0.02 | 0.01 |
| tert-Butylbenzene | 42.92 | - | 0.06 | |
| 1,2,4-Trimethylbenzene | 42.71 | - | 0.05 | |
| sec-Butylbenzene | 43.31 | - | 0.02 | |
| p-Isopropyltoluene | 43.81 | - | 0.01 | |
| 1,3-Dichlorobenzene | 44.08 | 44.11 | 0.02 | 0.02 |
| 1,4-Dichlorobenzene | 44.43 | 44.47 | 0.007 | 0.01 |
| n-Butylbenzene | 45.20 | - | 0.02 | |
| 1,2-Dichlorobenzene | 45.71 | 45.74 | 0.05 | 0.02 |
| 1,2-Dibromo-3-Chloropropane | | 48.57 | | 3.0 |
| 1,2,4-Trichlorobenzene | 51.43 | 51.46 | 0.02 | 0.03 |
| Hexachlorobutadiene | 51.92 | 51.96 | 0.06 | 0.02 |
| Naphthalene | 52.38 | - | 0.06 | |
| 1,2,3-Trichlorobenzene | 53.34 | 53.37 | ND | 0.03 |
| Internal Standards | | | | |
| Fluorobenzene | 26.84 | - | | |
| 2-Bromo-1-chloropropane | - | 33.08 | | |

[a] Retention times determined on 60 m x 0.75 mm ID VOCOL capillary column. Program: Hold at 10°C for 8 minutes, then program at 4°C/min to 180°C, and hold until all expected compounds have eluted.

[b] Dash (-) indicates detector does not respond.

[c] ND = Not determined

TABLE 2

SINGLE LABORATORY ACCURACY AND PRECISION DATA
FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

| Analyte | Photoionization Detector | | Hall Electrolytic Conductivity Detector | |
|---|---|---|---|---|
| | Standard Recovery,[a] % | Deviation of Recovery | Standard Recovery,[a] % | Deviation of Recovery |
| Benzene | 99 | 1.2 | -[b] | - |
| Bromobenzene | 99 | 1.7 | 97 | 2.7 |
| Bromochloromethane | - | - | 96 | 3.0 |
| Bromodichloromethane | - | - | 97 | 2.9 |
| Bromoform | - | - | 106 | 5.5 |
| Bromomethane | - | - | 97 | 3.7 |
| n-Butylbenzene | 100 | 4.4 | - | - |
| sec-Butylbenzene | 97 | 2.6 | - | - |
| tert-Butylbenzene | 98 | 2.3 | - | - |
| Carbon tetrachloride | - | - | 92 | 3.3 |
| Chlorobenzene | 100 | 1.0 | 103 | 3.7 |
| Chloroethane | - | - | 96 | 3.8 |
| Chloroform | - | - | 98 | 2.5 |
| Chloromethane | - | - | 96 | 8.9 |
| 2-Chlorotoluene | ND[c] | ND | 97 | 2.6 |
| 4-Chlorotoluene | 101 | 1.0 | 97 | 3.1 |
| 1,2-Dibromo-3-chloropropane | - | - | 86 | 9.9 |
| Dibromochloromethane | - | - | 102 | 3.3 |
| 1,2-Dibromoethane | - | - | 97 | 2.7 |
| Dibromomethane | - | - | 109 | 7.4 |
| 1,2-Dichlorobenzene | 102 | 2.1 | 100 | 1.5 |
| 1,3-Dichlorobenzene | 104 | 1.7 | 106 | 4.3 |
| 1,4-Dichlorobenzene | 103 | 2.2 | 98 | 2.3 |
| Dichlorodifluoromethane | - | - | 89 | 5.9 |
| 1,1-Dichloroethane | - | - | 100 | 5.7 |
| 1,2-Dichloroethane | - | - | 100 | 3.8 |
| 1,1-Dichloroethene | 100 | 2.4 | 103 | 2.9 |
| cis-1,2 Dichloroethene | ND | ND | 105 | 3.5 |
| trans-1,2-Dichloroethene | 93 | 3.7 | 99 | 3.7 |
| 1,2-Dichloropropane | - | - | 103 | 3.8 |
| 1,3-Dichloropropane | - | - | 100 | 3.4 |
| 2,2-Dichloropropane | - | - | 105 | 3.6 |
| 1,1-Dichloropropene | 103 | 3.6 | 103 | 3.4 |
| Ethylbenzene | 101 | 1.4 | - | - |
| Hexachlorobutadiene | 99 | 9.5 | 98 | 8.3 |
| Isopropylbenzene | 98 | 0.9 | - | - |
| p-Isopropyltoluene | 98 | 2.4 | - | - |

TABLE 2 (cont.)

SINGLE LABORATORY ACCURACY AND PRECISION DATA
FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

| Analyte | Photoionization Detector | | Hall Electrolytic Conductivity Detector | |
|---|---|---|---|---|
| | Standard Recovery,[a] % | Deviation of Recovery | Standard Recovery,[a] % | Deviation of Recovery |
| Methylene chloride | - | - | 97 | 2.8 |
| Naphthalene | 102 | 6.3 | - | - |
| n-Propylbenzene | 103 | 2.0 | - | - |
| Styrene | 104 | 1.4 | - | - |
| 1,1,1,2-Tetrachloroethane | - | - | 99 | 2.3 |
| 1,1,2,2-Tetrachloroethane | - | - | 99 | 6.8 |
| Tetrachloroethene | 101 | 1.8 | 97 | 2.4 |
| Toluene | 99 | 0.8 | - | - |
| 1,2,3-Trichlorobenzene | 106 | 1.9 | 98 | 3.1 |
| 1,2,4-Trichlorobenzene | 104 | 2.2 | 102 | 2.1 |
| 1,1,1-Trichloroethane | - | - | 104 | 3.4 |
| 1,1,2-Trichloroethane | - | - | 109 | 6.2 |
| Trichloroethene | 100 | 0.78 | 96 | 3.5 |
| Trichlorofluoromethane | - | - | 96 | 3.4 |
| 1,2,3-Trichloropropane | - | - | 99 | 2.3 |
| 1,2,4-Trimethylbenzene | 99 | 1.2 | - | - |
| 1,3,5-Trimethylbenzene | 101 | 1.4 | - | - |
| Vinyl chloride | 109 | 5.4 | 95 | 5.6 |
| o-Xylene | 99 | 0.8 | - | |
| m-Xylene | 100 | 1.4 | - | - |
| p-Xylene | 99 | 0.9 | - | - |

[a] Recoveries and standard deviations were determined from seven samples and spiked at 10 µg/L of each analyte. Recoveries were determined by internal standard method using a purge-and-trap. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for HECD.

[b] Detector does not respond

[c] ND = Not determined

[d] This method was tested in a single laboratory using water spiked at 10 µg/L (see Reference 8).

TABLE 3

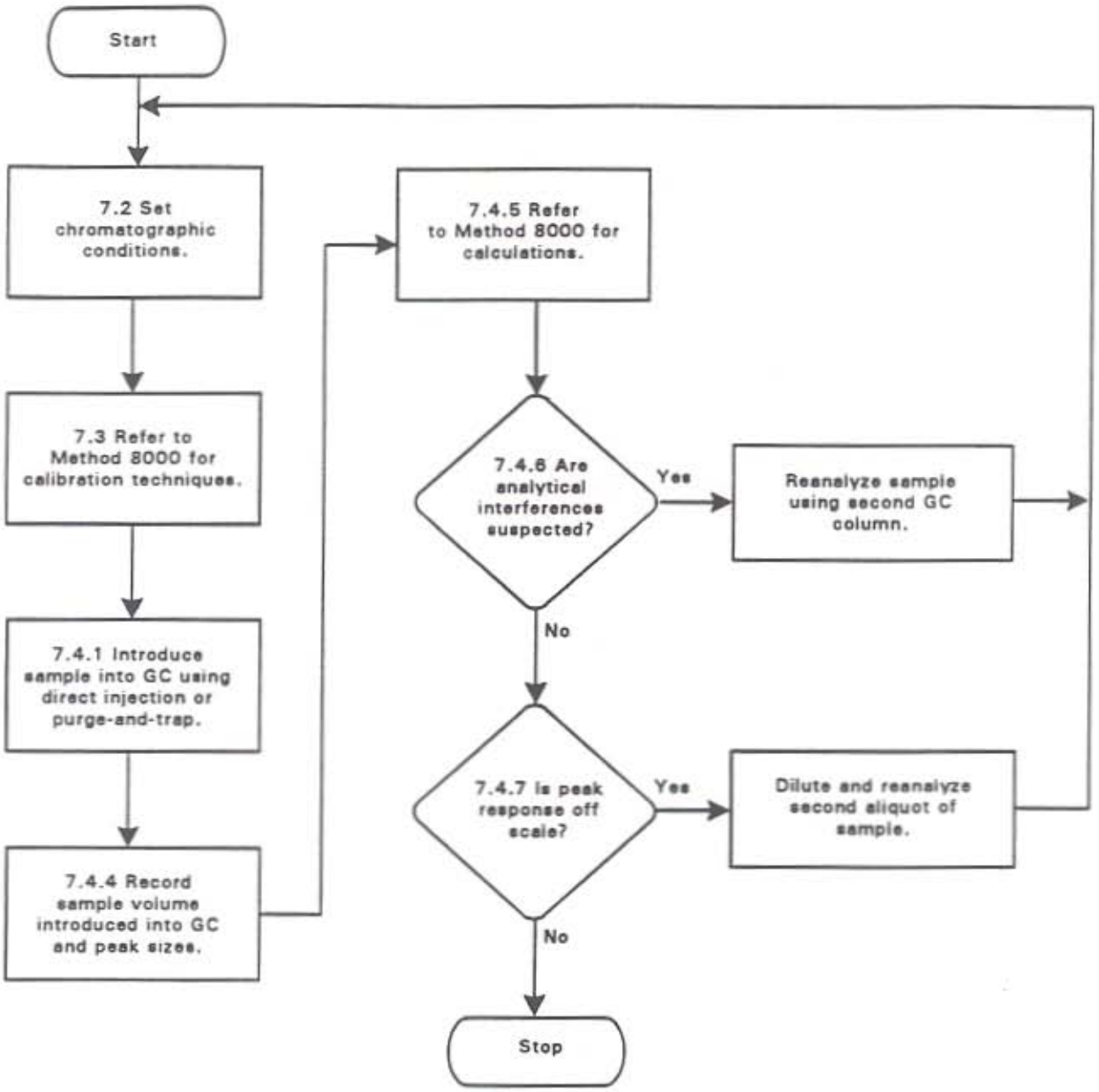
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

| Matrix | Factor[b] |
|---|---|
| Ground water | 10 |
| Low-concentration soil | 10 |
| Water miscible liquid waste | 500 |
| High-concentration soil and sludge | 1250 |
| Non-water miscible waste | 1250 |

[a] Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS


Start
7.2 Set chromatographic conditions.
7.3 Refer to Method 8000 for calibration techniques.
7.4.1 Introduce sample into GC using direct injection or purge-and-trap.
7.4.4 Record sample volume introduced into GC and peak sizes.
7.4.5 Refer to Method 8000 for calculations.
7.4.6 Are analytical interferences suspected?
Yes
Reanalyze sample using second GC column.
No
7.4.7 Is peak response off scale?
Yes
Dilute and reanalyze second aliquot of sample.
No
Stop

# APPENDIX D-16
# Chain of Custody Procedure: SP-0001

# APPENDIX D-17
# Preparation Procedure for EDTA in Soil: AP-0057

"Sample Chain of Custody"

1.0 PURPOSE

This procedure provides instructions for sample custody from collection to final disposition.

2.0 SCOPE

This procedure applies to all samples collected under a sampling plan which requires documentation of sample custody.

3.0 SUMMARY

Requirements for documentation of sample collection and sample custody are specified.

4.0 REFERENCES

4.1 U. S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, 3rd Edition, Most Recent Update (September 1994)

4.2 "Preparation Aids for the Development of Category II Quality Assurance Project Plans," EPA/600/8-91/004, February 1991, Guy F. Simes, Risk Reduction Engineering Laboratory, Office of Research and Developent, U.S. Environmental Protection Agency, Cincinnati, OH 45268

4.3 "Preparation Aids for the Development of Category III Quality Assurance Project Plans," EPA/600/8-91/005, February 1991, Guy F. Simes, Risk Reduction Engineering Laboratory, Office of Research and Development, U.S. Enviromental Protection Agency, Cincinnati, OH 45268

4.4 "Sample Receipt, Log-in, and Data Handling", GLP-0016, Tennessee Valley Authority, Analytical Laboratory of Environmental Applications, Muscle Shoals, AL.

5.0 RESPONSIBILITIES

5.1 The laboratory team leader shall ensure that this procedure is followed.

5.2 The sampler shall follow this procedure to ensure sample integrity in the field.

5.3 The person transporting the samples shall follow the procedure to ensure sample integrity in transit.

5.4 The person receiving the samples shall follow this procedure to ensure sample integrity upon receipt and immediately following.

5.5 Laboratory analysts shall follow this procedure during sample analysis.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sample containers shall be cleaned to specifications of the sampling plan, or in their absence, to good commercial practice.

6.1.2 Sample containers shall have preservative added before sampling as required by the sampling plan.

6.2 Limitations and Actions

6.2.1 If the sampling organization has its own sampling procedure, sample custody procedure, labels, or custody forms, they may be substituted for the contents of this procedure as permitted by the sampling plan.

6.2.2 The number of persons handling samples from the time of sampling to receipt by the laboratory should be held to a minimum.

6.2.3 Sample containers shall be labeled by attaching tie-on tags, adhesive labels, or by writing on sample containers with indelible markers. Sample containers shall be labeled with sufficient information that they may be traced to sample collection logs, field sheets, or custody records. Choice of adhesive labels or indelible ink should take into consideration that samples may come into contact with melted ice or condensed moisture during shipment or storage.

6.2.4 Individual samples shall be sealed or sample shipping containers shall be sealed with a tamper-proof seal when they will be relinquished by TVA to a common carrier or if the sampling plan requires it. If the samples will remain in the custody of TVA employees from the time of sampling through transport to the laboratory or under lock and key (as in a locked vehicle or storage container) during this time, use of seals is not required. However, even if seals are not required, their use is strongly urged on shipping containers if the sample is to change hands several times in transport.

6.3 Requirements

6.3.1 Apparatus/Equipment

This procedure specifies no additional apparatus or equipment in addition to any sampling plan.

6.3.2 Materials

6.3.2.1 Sample containers specified in the sampling plan shall be utilized.

6.3.2.2 Labels - Samples labels shall have an adhesive which does not readily release when containers become damp.

6.3.2.3 Custody Forms - Sample chain of custody forms shall be used to record custody of samples after sampling from relinquishment by the sampling organization through transport to receipt by the laboratory. The following information shall be supplied on the custody form:

a. Project identification
b. Sample collection date
c. Sample identification
d. Collection time
e. Number of containers per sample identification code
f. Requested analysis
g. Sampling location
h. Comments
i. Signature of sample collector.

In addition the form shall contain an area so that each relinquishment and receipt of samples may be documented.

"Sample Chain of Custody"

Example custody forms are attached as appendices 10.1 and 10.2. Other forms specific to a given project may be developed as long as they contain the minimum information specified above.

Note: If sample collection time and location are already recorded on a field sheet or sampling log, that information need not be repeated on this form provided a copy of the sampling information is transmitted to the laboratory with the custody sheet.

6.3.2.4 Tamper-evident seals - These seals shall be individually numbered or otherwise marked so that they could not be removed and replaced without it being detected. Two styles have been useful for samples or sample containers.

6.3.2.4.1 Adhesive seals advertised as meeting forensic science requirements, such as Kapak brand seals.

6.3.2.4.2 Padlock-style plastic seals for hasps.

6.3.2.5 Field Logbooks or Field Sheets - Sampling activities may be documented in field logbooks or field sheets designed for that purpose. When these are used, they shall contain:

a. Project identification
b. Sample collection date
c. Sample identification
d. Collection time
e. Number of containers per sample identification code
f. Reference to the sampling procedure
g. Sampling location
h. Comments
i. Signature of sample collector.

7.0 PROCEDURE

7.1 Field Operations

7.1.1 Prior to sampling, label sample containers with an adhesive label or with indelible marker. (Note: If the sampling conditions require it, labels may be affixed after sampling and cleaning the outside of the container.)

"Sample Chain of Custody"

7.1.2 Document sample information in a field log, field sheet, or the custody sheet if the first two are not provided.

7.1.3 Seal the sample container with an adhesive seal if the sampling plan requires it.

7.1.4 Complete a "Sample Chain of Custody" form.

7.1.4.1 If field logs or field sheets contain collection time and location, these items may be omitted from the form. In that case, draw a diagonal line in that column and attach a copy of the field logs or sheet so that the laboratory may have pertinent sampling information.

7.1.4.2 If a numbered seal is to be used on the shipping container, note that number in the comments section of the custody form.

7.1.4.3 If the shipping container is to be sealed, sign and date the "relinquished" area of the form.

7.1.5 Place the original copy of the paperwork in a plastic bag inside the shipping container. Retain one copy for field files. Transmit a third copy by separate courier, mail or fax to the laboratory.

7.1.6 Place the samples in a shipping container. As required by the sampling plan, place ice (or commercial substitute) and a temperature test bottle in the container as well. Seal the shipping container if the sampling plan requires it. See also 6.2.4.

7.1.7 Deliver the container to be transported to the laboratory.

7.2 Laboratory Receipt (Reference also GLP-0016)

7.2.1 Inspect the seals. Open the shipping container. Inspect the sample custody form to ensure that it is correctly completed. Sign as receiver. Compare the shipping container contents to the information on the form.

7.2.2 If the "relinquished" blank is not completed and the person delivering the samples is present, have that person sign the "relinquished by." Otherwise write "Not completed", date and initial. If a person signs "relinquished by," provide that person a copy of the paperwork.

7.2.2 As required by the sampling plan, measure the temperature of any samples or temperature blanks and record that information on the custody sheet.

7.2.3 Communicate any errors, broken seals, missing seals, broken samples, differing identification numbers, extra samples, missing samples or misidentification to field personnel. Document all discussions by memorandum or database sample comment file. Document all problems and their resolution by memorandum or database sample comment file. If seals show signs of tampering, bring this to the attention of the group leader or team leader.

7.2.4 Refer to GLP-0016 for further sample receipt and log-in instructions.

7.2.6 Following logging, store the samples in a locked, refrigerated storage area as required by the sampling plan or project plan.

7.3 Laboratory Custody

7.3.1 Samples in locked storage areas, being prepared, being processed, or in autosampler trays are considered to be in the custody of the laboratory. When sampling plans require it, laboratory work areas shall be locked when unattended.

7.4 Sample Disposal

7.4.1 When customers request it, samples shall be returned to them following analysis.

7.4.2 Otherwise, dispose of samples after the time period specified in the sampling plan or project plan. If these do not specify a date, samples should be kept no longer than three months after all analyses are complete.

7.4.3 If the sampling plan requires it, document sample disposal in the workorder file, or custody records.

8.0 SAFETY

8.1 Wear rubber gloves and protective eyewear when handling samples unless it is known that the samples are innocuous.

8.2 Avoid contact with samples. Be aware of broken containers, corrosives, irritants, biohazards, flammability, pyrophoricity, reactivity, radioactivity

and toxicity. Inspect labels and shipping information for warnings. When hazards are known, label samples with hazard information if that is not already provided by the customer.

8.3 In case of skin contact, wash thoroughly with soap and water.

8.4 In case of eye contact, hold the eyes open and wash for at least 15 minutes in an eyewash. Call for help.

8.5 Flammable liquids must be refrigerated only in explosion-proof refrigerators to avoid the risk of explosion caused by sparks in the electrical contacts of the compressor.

8.6 In handling samples, be aware of spills on outside of containers. Clean the exterior of containers as needed.

9.0 NOTES

None

"Sample Chain of Custody"

## 10.0 ATTACHMENTS AND APPENDICES

### 10.1 Chain of Custody Record - TVA 29203 B (RC-CTR 4-94)

**CHAIN OF CUSTODY RECORD**

Environmental Site Remediation • TVA Environmental Research Center • Muscle Shoals, Alabama 35660

SWMU NO. | SWMU SEQUENCE | SWMU NAME | SWMU LOCATION | PROJECT

SAMPLERS (SIGNATURE)

| SAMPLE NO. | DATE | TIME | COMP / GRAB (C/G) | SAMPLE LOCATION | NO. OF CONTAINERS | ANALYTES | | |

"Sample Chain of Custody"

10.2 Sample custody form - General

**Sample Chain of Custody**
**Tennessee Valley Authority**
**Environmental Appliations CTR-1K Muscle Shoals, AL**

Project

Date of Collection

| | Sample ID | Collection Time* | Number of Containers | Analyses Requested | Location* | Comments |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | | | | | | |
| 7 | | | | | | |
| 8 | | | | | | |
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| 26 | | | | | | |
| 27 | | | | | | |
| 28 | | | | | | |
| 29 | | | | | | |
| 30 | | | | | | |

| Signatures | Date and Time |
|---|---|
| Collector | |
| Relinquishing | |
| Receiving | |

* These columns need not be completed if field sampling sheets containing the same information are attached

END OF PROCEDURE

# APPENDIX D-17
# Preparation Procedure for EDTA in Soil: AP-0057

1.0 PURPOSE

This procedure describes a water extraction method to extract EDTA from soil for subsequent analysis by HPLC.

2.0 SCOPE

Soil samples prepared by this procedure can be analyzed by HPLC.

3.0 SUMMARY

A representative sample not exceeding 30g (wet weight) is stirred vigorously on a magnetic stirrer with an appropriate measured volume of deionized water for two hours. The concentration of EDTA in the liquid portion of the slurry must be less than 200 mg/L to ensure solubility of EDTA complexes. The slurry is then centrifuged and filtered through a 0.2 micron filter. The pH of this solution is then adjusted to 4.5 - 5.0 and then analyzed by HPLC.

4.0 REFERENCES

4.1 ASTM D1193-91, "Standard Specification for Reagent Water," American Society for Testing and Materials.

4.2 AP-0047, "Determination of EDTA by High Performance Liquid Chromatography," Tennessee Valley Authority, Muscle Shoals, Alabama.

5.0 RESPONSIBILITIES

5.1 The Analytical Laboratory Supervisor, or his designee, shall ensure that this procedure is followed during the water extraction of EDTA from soils.

5.2 The Laboratory Group Leader, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure and is responsible for the training of new personnel on this procedure.

5.3 The analyst shall follow this procedure and report any abnormal results or nonconformance to the Laboratory Group Leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 All sample containers must be prewashed with detergents, acids and ASTM Type II water. Plastic and glass containers are both suitable.

6.1.2 Samples shall be refrigerated upon receipt and analyzed as soon as possible.

6.2 Limitations and Actions

6.2.1 In step 7.2 the EDTA concentration in the aqueous extract must be less than 200 mg/L.

6.3 Requirements

6.3.1 Apparatus/Equipment

6.3.1.1 Erlenmeyer flasks: 50, 125, 250 and 500 ml

6.3.1.2 Watch glasses: 50 and 65 mm

6.3.1.3 Analytical balance: capable of weighing to 0.1 mg

6.3.1.4 Magnetic stirrers and magnetic stirring bars

6.3.1.5 Centrifuge and centrifuge tubes

6.3.1.6 Filter syringes and syringe filters: 0.45 and 0.2 micron nylon syringe filters

6.3.1.7 pH meter and appropriate buffers or short range pH paper (for the range 4.5 - 5)

6.3.2 Reagents and Standards

6.3.2.1 Reagents

6.3.2.1.1 ASTM Type II water (ASTM D1193): Water shall be monitored for impurities by conductivity (conductivity of less than 1.0 umho/cm at 25°C).

6.3.2.1.2 0.2% Nitric acid: Pipet 0.2 ml reagent grade concentrated nitric acid to a 100 ml volumetric flask and dilute to volume with ASTM Type II water.

6.3.2.2 Standards

None

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity.

7.2 For each sample weigh an appropriate sized sample (not exceeding 30 g wet weight) into an appropriate sized Erlenmeyer flask such that the final concentration of EDTA in the extract is less than 200 mg/L and the resulting slurry fills approximately two-thirds of the volume of the flask.

7.3 Add a measured volume of ASTM Type II water. (From this volume of water plus the water from the moisture analysis of the sample, a total water volume can be calculated.)

7.4 Cover with a watch glass, place sample on a magnetic stirrer and stir vigorously for 2 hours.

7.5 After stirring, pour the slurry (or a portion of the slurry) into a centrifuge tube and centrifuge for 15 minutes at greater than 3000 rpm.

7.6 Using a syringe and syringe filter, filter a portion of the aqueous extract.

7.6 Adjust the pH of the extract to 4.5 - 5.0 with 0.2% nitric acid using a pH meter or short range pH paper.

7.7 Submit for analysis of EDTA by HPLC.

8.0 SAFETY

8.1 General laboratory safety rules shall be observed.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICIES

None

**End of Procedure**

# APPENDIX D-18
# CEC Method 9-3.1/9.4.2

**Exchangeable Cation Determination with Total Cation Exchange Capacity**

**Method ASA 9-3.1/9-4.2**

Summary of Method

A soil is extracted with 1 *N* Ammonium Acetate to replace and release exchangeable cations which are then determined by metals analysis. A second extraction with 10% potassium chloride replaces and releases the ammonium ion. Ammonium ion concentration is determined colorimetrically and is equal to the Cation Exchange Capacity (CEC).

Reagents

1. 1*N* Ammonium Acetate - Dilute 1035 ml of glacial acetic acid to 14 liters with water. Add 1200 ml concentration ammonium hydroxide. Dilute to 18 liters with deionized water. Adjust to pH 7.0 with acetic acid or ammonium hydroxide. Smaller volumes may be prepared in the same ratios.

1.1 Ammonium Hydroxide - Concentrated, reagent grade

1.2 Acetic Acid - Glacial, reagent grade

2. 95% Ethanol - reagent grade

3. 10% KCl - Add 100g of potassium chloride to 900 ml water. Adjust to pH 2.5 with hydrochloric acid. Dilute to 1 liter with deionized water.

Procedure

ASA 9-3.1 - Exchangeable Cations - Ammonium Acetate Method

1. Sieve an air-dried soil sample through a 2 mm sieve (9 mesh).

2. Weigh 20 g of soil ( < 2 mm fraction) into an extraction flask. Weigh the soil to 0.0001 g on an analytical balance. Record the weight.

3. Add 50 ml 1*N* ammonium acetate.

4. Shake for 30 minutes and allow to stand at least 6 hours, preferably overnight.

5. Swirl sample. Transfer the entire sample to a Buchner funnel fitted with Whatman #42 filter paper (or equivalent).

6. Filter, then leach the soil with 200 ml of additional ammonium acetate in four increments of 50 ml each.

   Note: Do not allow the soil to dry or crack.

7. Transfer the leachate to a 250 ml volumetric flask and make to volume. Keep the soil in the funnel to determine CEC in step 9.

8. Submit the leachate for metals analysis (Na, K, Ca, Fe, etc.) for exchangeable cations by means of atomic absorption or inductively coupled plasma.

ASA 9.4.2 Cation Exchange Capacity - Potassium Chloride Method

9. Wash the soil with 200 ml of 95% ethanol in four 50 ml increments.

   Note: Do not allow soil to dry or crack.

10. Using a clean suction flask, leach soil with 200 ml of 10% KCl in four 50 ml increments.

11. Transfer the leachate to a 250 ml volumetric flask and make to volume with 10% KCl.

12. Submit the leachate for ammonium analysis using a flow injection analyzer or other autoanalyzer.

13. Report results of CEC and exchangeable cations in centimole per kilogram.

$$\text{Capacity (centimoles/kg)} = \frac{X \text{ mg/L} * 0.25 * 100}{MW * WT}$$

Where X is the liquid concentration of the analyte in mg/L, WT is the weight of soil in grams and MW is the molecular weight.

Or

$$\text{Capacity (centimoles/kg)} = \frac{Y \text{ mg/kg}}{MW * 10}$$

Where Y is the concentration of the analyte in soil in mg/kg.

| Analyte | MW | Factor |
|---|---|---|
| Na | 22.99 | 1 |
| Ca | 40.08 | 2 |
| K | 39.10 | 1 |
| Mg | 24.31 | 2 |
| Al | 26.98 | 3 |
| Ammonia N | 14.01 | 1 |

Note: Some researchers request the capacity in centiequivalents/kg. In that case, multiply by the factor in the table above.

References

"Replacement of Exchangeable Cations, Ammonium Acetate Method" Section 9-3.1 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

"Exchangeable Acidity, Potassium Chloride Method," Section 9-4.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

# APPENDIX D-19
## $NH_3$-N by Flow Injection Analysis: AP-0059

1.0 PURPOSE

This procedure provides a method for the determination of ammonia in drinking and surface waters.

2.0 SCOPE

2.1 This method covers the determination of ammonia in drinking and surface waters.

2.2 The method is based on reactions that are specific for the ammonium ion.

2.3 The applicable range is 0.1 to 20.0 mg N/L as NH3.

3.0 SUMMARY

This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample.

4.0 REFERENCES

4.1 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised March 1983, "Nitrogen, Ammonia, Method 350.1 (Colorimetric, Automated Phenate)."

4.2 U.S. Environmental Protection Agency, 40 CFR Part 36 Table 1B, footnote 6, 1994.

4.3 Lachat Instruments, *QuickChem Automated Ion Analyzer Methods Manual*, QuickChem Method 10-107-06-1-A, "Determination Of Ammonia By Flow Injection Analysis, Colorimetry."

4.4 Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual.*

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the Analysts to follow this procedure, evaluate data, and to report any abnormal results or unusual occurrences to the team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to ensure a representative sample and allow for quality control analysis (at least 100 mL).

6.1.2 Samples may be preserved by addition of a maximum of 2 mL of concentrated $H_2SO_4$ per liter (preferred - 1 mL of 1N $H_2SO_4$ per 100 mL) and stored at 4°C. Acid preserved samples have a holding time of 28 days.

6.2 Limitations and Actions

6.2.1 If the analyte concentration is above the analytical range of the calibration curve, the sample must be diluted to bring the analyte concentration within range.

6.2.2 Interferences

6.2.2.1 Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this problem.

6.2.2.2 Color, turbidity and certain organic species may interfere. Turbidity can be removed by filtration through a 0.45 um pore diameter membrane filter prior to analysis. Sample color may be corrected for by running the samples through the

manifold without color formation (omit Sodium Phenolate, reagent 1). The ammonium concentration is determined by subtracting the value obtained without color formation from the value obtained with color formation.

6.3 Apparatus/Equipment

6.3.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3.3 Flow injection analysis equipment (Lachat model 8000) designed to deliver and react samples and reagents in the required order and ratios.

6.3.3.1 Autosampler

6.3.3.2 Multichannel proportioning pump

6.3.3.3 Reaction unit or manifold

6.3.3.4 Colorimetric detector

6.3.3.5 Data system

6.3.4 Special Apparatus

6.3.4.1 Heating Unit

6.3.5 Syringe filters - Titan nylon 25-mm syringe filters - 0.45 micron. SRI Catalog number 44525-NN or equivalent.

6.3.6 Syringes - 10 cc syringe with Luer Lok, B-D Part 309604 or equivalent. (Smaller volumes are acceptable)

6.4 Reagents and Standards

6.4.1 Preparation of Reagents -

Use deionized water (10 megohm) for all solutions.

Degassing with helium: To prevent bubble formation, degas all solutions except the standards, Sodium Phenolate (Reagent 1) and Sodium Hypochlorite (Reagent 2) with helium. Bubble helium through a degassing tube (Lachat Part 50100) through the solution for at least one minute.

Refrigerate all solutions and standards.

6.4.1.1 **Reagent 1. Sodium Phenolate**

**CAUTION:** Wear gloves. Phenol causes severe burns and is rapidly absorbed in the body through the skin.

**By Volume:** In a **1 L** volumetric flask, dissolve **88 mL** of **88% liquefied phenol** or **83 g crystaline phenol** ($C_6H_5OH$) in approximately **600 mL water**. While stirring, slowly add **32 g sodium hydroxide** (NaOH). Cool, dilute to the mark, and mix. Do not degas this reagent.

**By weight:** To a tared **1 L** container, add **888 g water**. Add **94.2 g** of **88 liquefied phenol** or **83 g crystalline phenol** ($C_6H_5OH$). While stirring, slowly add **32 g sodium hydroxide** (NaOH). Cool and invert to mix. Do not degas this reagent.

6.4.1.2 **Reagent 2. Sodium Hypochlorite**

**By Volume:** In a **500 mL** volumetric flask, dilute **250 mL Regular Clorox bleach** [5.25% sodium hypochlorite (NaOCl), The Clorox Company, Oakland, CA] to mark with **water**. Invert to mix.

**By weight:** To a tared **500 mL** container, add **250 g Regular Clorox bleach** [5.25% sodium hypochlorite (NaOCl), The Clorox Company, Oakland, CA] and **250 g water**. Invert to mix.

6.4.1.3 **Reagent 3. Buffer**

**By Volume:** In a **1 L** volumetric flask, dissolve **50.0 g disodium ethylenediamine tetraacetate dihydrate** ($Na_2EDTA \cdot 2H_2O$) and **5.5 g sodium hydroxide** (NaOH) in about **900 mL water**. Dilute to the mark and invert or stir to mix.

**By weight:** To a tared **1 L** container, add **50.0 g disodium ethylenediamine tetraacetate dihydrate** ($Na_2EDTA \cdot 2H_2O$) and **5.5 g sodium hydroxide** (NaOH). Add **968 g water**. Invert or stir to mix.

6.4.1.4 **Reagent 4. Sodium Nitroprusside**

**By Volume:** In a **1 L** volumetric flask, dissolve **3.50 g sodium nitroprusside** (Sodium Nitroferrricyanide [$Na_2Fe(CN)5NO \cdot 2H2O$]) dilute to the mark with **water**. Stir or shake to mix.

**By weight:** To a tared **1 L** flask, dissolve **3.50 g sodium nitroprusside** (Sodium Nitroferrricyanide [$Na_2Fe(CN)_5NO \cdot 2H_2O$]) and **1000 g water**. Stir or shake to mix.

6.4.2 Preparation of Standards

**Note:** Following are standards preparations for running 3 channels simultaneously for $PO_4$-P, $NH_3$-N and $NO_2$-N + $NO_3$-N. Also included is the preparation of a $NO_2$-N standard which is used to assess the cadmium reduction column's efficiency.

6.4.2.1 **Standard 1. Stock Orthophosphate Standard - 1000 mg P/L as $PO_4$**

Dry **primary standard grade anhydrous potassium phosphate monobasic** ($KH_2PO_4$) for one hour at 105°C. In a **1 L** volumetric flask dissolve **4.396 g primary standard grade anhydrous potassium phosphate monobasic** ($KH_2PO_4$) in about **800 mL water**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.2 **Standard 2. Stock Ammonia Standard - 1000 mg N/L as $NH_3$**

Dry **ammonium chloride** ($NH_4Cl$) for two hours at 105°C. In a **1 L** volumetric flask dissolve **3.819 g ammonium chloride** ($NH_4Cl$) in about **800 mL water**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.3 **Standard 3. Stock Nitrate Standard - 1000 mg N/L as $NO_3^-$**

In a **1 L** volumetric flask dissolve **7.220 g potassium nitrate** ($KNO_3$) in about **600 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.4 **Standard 4. Stock Nitrite Standard - 1000 mg N/L as $NO_2^-$**

In a **1 L** volumetric flask dissolve **4.93 g sodium nitrate** ($NaNO_2$) in about **800 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.5 **Standard 5. Working Standard - 50 mg/L $PO_4$-P, $NH_3$-N and $NO_3$-N**

In a **1 L** volumetric flask add about **600 mL water**. Pipette **50 mL** from each of the **Stock Orthophosphate Standard** (standard 1), the **Stock Ammonia Standard** (standard 2), and the **Stock Nitrate Standard** (standard 3). Dilute to mark with **water** and mix.

6.4.2.6 **Standard 6. Working Nitrite Standard - 20 mg N/L as $NO_2^-$**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **20 mL Stock Nitrate Standard** (standard 4). Dilute to mark with **water** and mix.

6.4.2.7 **Standard 7. Working Quality Control Standard - 32.61 mg P/L as $PO_4^{3-}$, 31.06 mg N/L as $NH_4$, and 27.11 mg N/L as $NO_3^-$.**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the E M Science **1000 mg/L Phosphate Standard Solution** (326.1 mg P/L), **20 mL** of the E M Science **1000 mg/L Ammonia Standard Solution** (776.5 mg N/L), and **60 mL** of the E M Science **1000 mg/L Nitrate Standard Solution** (225.9 mg N/L). Dilute to mark with **water** and mix.

**Note:** 1000 mg/L standards by other reputable laboratory vendors may be substituted.

6.4.2.8 **Calibration Standards**

Standards are diluted to **500 mL** with **water**.

| | Calibration Standards Concentration mg/L | Prepared From | |
|---|---|---|---|
| | | Concentration mg/L | Aliquot mL |
| 1 | 20.00 | 50 | 200 |
| 2 | 10.00 | 50 | 100 |
| 3 | 4.00 | 50 | 40 |
| 4 | 2.50 | 50 | 25 |
| 5 | 1.00 | 10 | 50 |
| 6 | 0.10 | 1 | 50 |
| 7 | 0.02 | 0.10 | 100 |
| 8 | 0.00 | Water | 0 |

For standards for samples that have 1 mL of 1 N $H_2SO_4$ added per 100 mL, add **5 mL** of **1N $H_2SO_4$** to each standard after building to volume.

**Note:** If other acid concentrations are used to preserve samples, match for standards.

6.4.2.9 **Cadmium Reduction Column Efficiency Check Standard - 2.00 mg N/L as $NO_2^-$**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the **Working Nitrite Standard** (standard 6). Dilute to mark with **water,** add **5 mL** of **1N $H_2SO_4$** and mix.

6.4.2.10 **Laboratory Control Standard - 1.63 mg P/L as $PO_4$, 1.55 mg N/L as $NH_3$, and 1.36 mg N/L as $NO_3^-$.**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **50 mL** of the **Working Quality Control Standard** (standard 7). Dilute to mark with **water,** add **10 mL** of **1N $H_2SO_4$** and mix.

6.5 Quality Control Sample Requirements

Begin and end each run by measuring a laboratory control standard, a midpoint calibration standard run as a sample, and a reagent blank. When the run is long enough, every twentieth sample should be followed by the above three QC check samples. Recovery should be 90 to 110% of the expected value.

7.0 PROCEDURE

7.1 Procedure Instructions

7.1.1 The instrument is calibrated each day of use and may be calibrated with each sample tray.

7.1.2 Prepare reagents and standards as described in section 6.4.

7.1.3 Set up manifold as shown in section 9.2.

7.1.4 Enter data system parameters as in section 9.1.

7.1.5 Pump deionized water through all reagent lines and check for leaks and smooth flow. Allow 15 minutes for heating unit to warm up to 60°C. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

7.1.6 Pour samples and standards into vials. If samples have particulate matter, filter them into the sample vial with a syringe and nylon syringe filter. Load standard and sample trays.

7.1.7 Place samples and standards in the autosampler. Enter the information required by the data system, such as standard concentration, and sample identification.

7.1.8 Calibrate the instrument by injecting the standards. The data system will then associate the concentration with the instrument responses for each standard.

7.1.9 If samples require color correction, inject the samples with color development, then inject the samples with water replacing the color reagent (reagent 1).

7.1.10 At end of run, remove all transmission lines from reagents and place them in water. Pump for about five minutes.

7.1.11 To prevent baseline drifts, peaks that are too wide, or other problems with NH3-N precision, clean the $NH_3$-N manifold by placing the manifold reagent lines in 1M hydrochloric acid (1 volume concentrated HCl added to 11 volumes of water). Pump for about 5 minutes.

7.1.12 Remove all reagent lines from the hydrochloric acid and place them in water. Pump until the HCl is thoroughly washed out (about 5 minutes).

7.1.13 Remove the transmission lines from the water and pump all lines dry.

7.2 Calculations and Recording Data

7.2.1 Calibration is done by injecting standards. The data system will then automatically prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation provided by the software.

7.2.2 Create a custom report. (Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual*, page 43, "Task 11 - Creating a Custom Report")

7.2.3 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

7.2.4 Samples that require color correction: From the value obtained with color developer added, subtract the value obtained without color developer. When a large number of samples are analyzed, use a spreadsheet to calculate the color correction.

7.2.5 Report results in mg $NH_3$-N/L.

8.0 SAFETY

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use routine laboratory protective clothing (lab coat, gloves, and eye protection) when handling these reagents. Thoroughly wash any skin that comes into contact with any of these chemicals. Avoid creating or inhaling dust or fumes from solid chemicals.

9.0 NOTES

9.1 Data System Parameters

| | |
|---|---|
| Method Filename: | PANHANOW.MET |
| Method Description: | Ortho P (a) = 4.0 to 0.02 mg P/L |
| | $NH_3$-N (a) = 20.0 to 0.1 mg N/L |
| | $NO_2$-N/$NO_3$-N (a) = 20.0 to 0.2 mg N/L |

Analyte Data:

| | |
|---|---|
| Analyte Name: | Ammonia ($NH_3$)-N |
| Concentration Units: | mg $NH_3$-N/L |
| Chemistry: | Direct |
| Inject to Peak Start (s): | 28.0 |
| Peak Base Width (s): | 21.000 |
| % Width Tolerance: | 100.000 |
| Threshold: | 8000.000 |
| Autodilution Trigger: | Off |
| QuickChem Method: | 10-107-06-1-A |

Calibration Data:

| | | | |
|---|---|---|---|
| Levels: (mg $NH_3$-N/L) | 1: 20.000 | 2: 10.000 | 3: 4.000 |
| | 5: 1.000 | 6: 0.100 | 8: 0.000 |

| | |
|---|---|
| Calibration Rep Handling: | Average |
| Calibration Fit Type: | 1st Order Poly |
| Force through Zero: | No |
| Weighing Method: | None |
| Concentration Scaling: | None |

Sampler Timing:

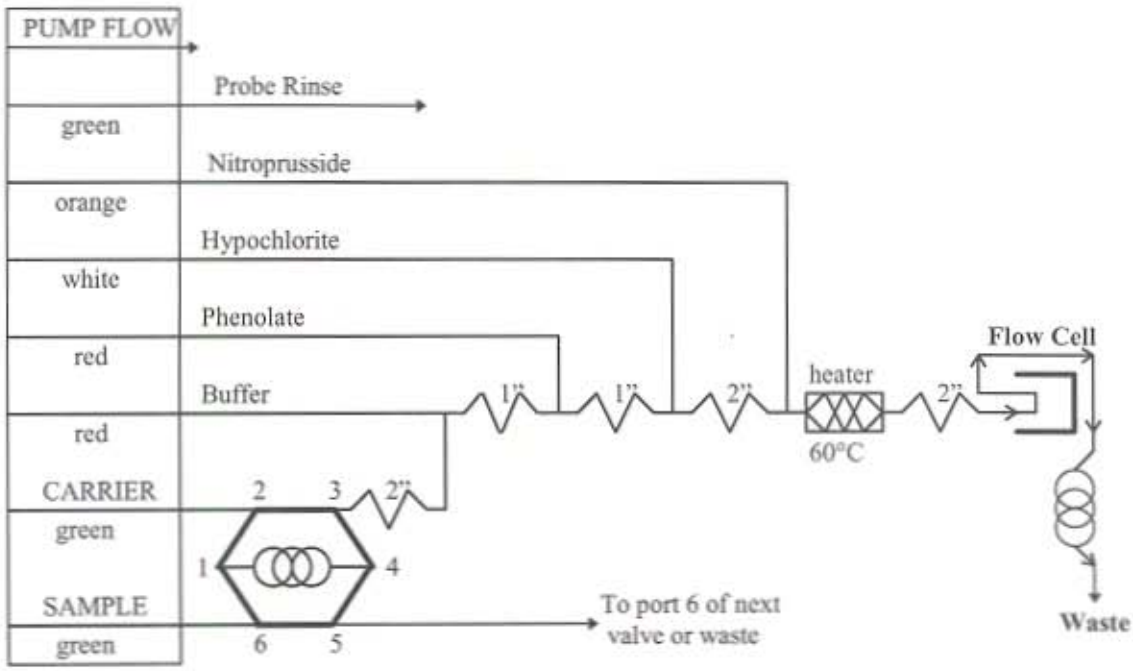
| | |
|---|---|
| Method Cycle Period: | 70.0 |
| Min. Probe in Wash Period: | 9.0 |
| Probe in Sample Period: | 30.0 |

Valve Timing:

| | |
|---|---|
| Method Cycle Period: | 70.0 |
| Sample Reaches 1st Valve: | 18.0 |
| Valve: | On |
| Load Time: | 0.0 |
| Load period | 25.0 |
| Inject Period: | 45.0 |

Sample Loop: 13 cm x 0.5 mm i.d.

9.2 Ammonia Manifold Diagram




Sample Loop = 13 cm x 0.5 mm i.d.

Interference Filter = 630 nm

Carrier is DI Water

All manifold tubing is **0.8 mm (0.32 in) i.d.** Lachat Part No. 50028. This is **5.2 uL/cm**. The sample loop uses **0.5 mm (0.022") i.d.** tubing.

**1** is **70 cm** of tubing on a **4.5 cm** coil support.

Apparatus: The includes 650 cm of tubing wrapped around the heater block at the specified temperature.

60°C

10.0 ATTACHMENTS AND APPENDICES

**None**

**End of Procedure**

# APPENDIX E
# Statistical Data

**Table E-1**
**Analysis of Variability of Grid Rows and Columns for Site C and Site 129-3.**
**Values Used for Analysis are Lead Concentrations for the 0- to 12-Inch Soil Depth**
**(Average of Lead Concentrations at the 0- to 6-Inch**
**and 6- to 12-Inch Soil Depth in Table 5-1)**

| Source | Degrees of Freedom | Mean Square | F Value | Probability>F |
|---|---|---|---|---|
| Site C | | | | |
| Rows | 5 | 1,776,090 | 1.85 | 0.1394 |
| Columns | 5 | 1,409,532 | 1.47 | 0.2354 |
| Error | 25 | 959,838 | | |
| | | | | |
| Site 129-3 | | | | |
| Rows | 5 | 81,678 | 1.57 | 0.2040 |
| Columns | 5 | 80,198 | 1.54 | 0.2121 |
| Error | 25 | 51,918 | | |

**Table E-2**
**Analysis of Variability of Grid Rows and Columns for Site C for Lead Concentrations in Corn After Soil Amendment Addition in Table 5-12.**

| Source | Degrees of Freedom | Mean Square | F Value | Probability>F |
|---|---|---|---|---|
| Rows | 5 | 3,353,991 | 1.20 | 0.3385 |
| Columns | 5 | 6,014,864 | 2.15 | 0.0925 |
| Error | 25 | 2,798,519 | | |

**Table E-2A**
**Least Significant Difference t-Test for Grid Columns for Lead Concentration in Corn at Site C**

| T grouping[1,2] | Mean | Number of Grids | Column |
|---|---|---|---|
| A | 7,800 | 6 | 4 |
| A B | 7,573 | 6 | 2 |
| A B C | 6,437 | 6 | 1 |
| B C | 5,777 | 6 | 6 |
| B C | 5,710 | 6 | 5 |
| C | 5,487 | 6 | 3 |

(1) Least Significant Difference = 1,989
(2) Alpha = 0.05

**Table E-3**
**Analysis of Variability of Grids Rows and Columns for Site 129-3 for Lead Concentrations in Corn After Soil Amendment Addition in Table 5-13.**

| Source | Degrees of Freedom | Mean Square | F Value | Probability>F |
|---|---|---|---|---|
| Rows | 5 | 1,994,593 | 2.99 | 0.0298 |
| Columns | 5 | 3,113,861 | 4.67 | 0.0038 |
| Error | 25 | 666,317 | | |

**Table E-3A**
**Least Significant Difference t-Test for Grid Rows for Lead Concentration in Corn at Site 129-3**

| T grouping[1,2] | Mean | Number of Grids | Row |
|---|---|---|---|
| A | 2,265 | 6 | 5 |
| A B | 1,622 | 6 | 4 |
| B | 1,264 | 6 | 1 |
| B | 1,145 | 6 | 6 |
| B | 830 | 6 | 3 |
| B | 683 | 6 | 2 |

(1) Least Significant Difference = 971
(2) Alpha = 0.05

**Table E-3B**
**Least Significant Difference t-Test for Grid Columns for Lead Concentration in Corn at Site 129-3**

| T grouping[1,2] | Mean | Number of Grids | Columns |
|---|---|---|---|
| A | 2,069 | 6 | 2 |
| A B | 1,896 | 6 | 3 |
| A B C | 1,758 | 6 | 1 |
| B C D | 970 | 6 | 4 |
| C D | 894 | 6 | 5 |
| D | 222 | 6 | 6 |

(1) Least Significant Difference = 970
(2) Alpha = 0.05

**Table E-4**
**Regression Analysis of Soil and Crop Parameters for First Soil Amendment Addition and Harvest With Corn**

| Regression | Probability > T | R-square |
|---|---|---|
| Site C | | |
| corn on initial lead 0”-12”[1] | 0.0001 | 0.4012 |
| corn on total lead 0”-12” | 0.3271 | 0.0291 |
| corn on total lead 12”-24” | 0.5906 | 0.0091 |
| corn on total lead 0”-24”[2] | 0.2719 | 0.0376 |
| | | |
| corn on water-soluble Pb 0”-12” | 0.2461 | 0.0405 |
| corn on water-soluble Pb 12”-24” | 0.3041 | 0.0320 |
| corn on water-soluble Pb 0”-24”[2] | 0.2189 | 0.0454 |
| | | |
| water-soluble Pb on initial Pb 0”-12”[1] | 0.5816 | 0.0093 |
| water-soluble Pb on total Pb 0”-12” | 0.6666 | 0.0057 |
| water-soluble Pb on total Pb 12”-24” | 0.8811 | 0.0007 |
| water-soluble Pb on total Pb 0”-24”[2] | 0.6858 | 0.0052 |
| | | |
| Site 129-3 | | |
| corn on initial lead 0”-12”[1] | 0.0375 | 0.1211 |
| corn on total lead 0”-12” | 0.0154 | 0.1607 |
| corn on total lead 12”-24” | 0.0001 | 0.4024 |
| corn on total lead 0”-24”[2] | 0.0010 | 0.2745 |
| | | |
| corn on water-soluble Pb 0”-12” | 0.0001 | 0.3709 |
| corn on water-soluble Pb 12”-24” | 0.0001 | 0.4086 |
| corn on water-soluble Pb 0”-24”[2] | 0.0001 | 0.4090 |
| | | |
| water-soluble Pb on initial Pb 0”-12”[1] | 0.0011 | 0.2735 |
| water-soluble Pb on total Pb 0”-12” | 0.0002 | 0.3449 |
| water-soluble Pb on total Pb 12”-24” | 0.0001 | 0.8079 |
| water-soluble Pb on total Pb 0”-24”[2] | 0.0001 | 0.4892 |

(1) Initial lead 0-12 inches is the average of lead concentrations at the 0- to 6-inch and 6- to 12-inch soil depth for the initial soil characterization in Table 5-1 (Site C) and Table 5-2 (Site 129-3).
(2) Average of lead concentrations at the 0- to 12-inch and 12- to 24-inch depths.

# APPENDIX F
# Revised Procedures for 1999 Corn

# Revised Procedures for 1999 Corn

This document details the procedural modifications that will be made for the 1999 demonstration season. These modifications will be implemented based on experiences and lessons learned in the 1998 demonstration year. These modifications address hindrances due to the locale, growing conditions, choice of crops, and the basis and methods of soil amendments application.

**1999 Corn**

1. A high vegetative biomass silage variety of corn (Novartis Mycogen 345 hybrid) rather than a grain corn will be used. This variety was developed for growth on sandy soils in the region and exhibits a rapid early growth, which is desirable for a strong rooting system. Expected maximum yields for this variety under optimal agronomic conditions are six tons per acre. However, actual yields may be lower than this due to less than ideal growing conditions at TCAAP.

2. Planting will be done with a mechanical, tractor-mounted seed planter (Covington Model TP-46) to conserve labor and costs, and to achieve more uniform planting.

3. Planting density will be increased (i.e., 15-inch row spacing *vs* 30-inch spacing) to increase biomass production.

4. Fertilizer amounts of nitrogen (N) and potassium (K) will be increased over recommended agronomic rates to maximize biomass production under the conditions at TCAAP. Fertilizer will be applied as a two-way split application, with one-half the designated amount being soil-applied at planting and the rest applied approximately four weeks later. The total amount of N and K fertilizer to be added to each site will be 200 pounds per acre of N as ammonium nitrate and 150 pounds per acre of K as potassium sulfate.

5. The amount of phosphate applied to the soil at planting will be increased to reduce the chances for a reoccurrence of the P deficiency that was manifested in early corn in 1998. Site C will receive 44 pounds per acre of P as triple super phosphate (TSP) and Site 129-3 will receive 31 pounds per acre of P as TSP. The fertilizer will be applied as a band 2-1/2 inches to the side, and 2 inches below the seed row.

6. Chelate application rates will be based on the frequency of lead concentration across the plot area rather than on the mean lead concentration of the entire plot. The frequency of occurrence of lead concentration should be 20% to 30% less than the mean concentration. This will reduce the total amount of EDTA added to the plots, which will reduce the potential for carry-over damage to a subsequent crop. The total amount of EDTA to be applied at Site C may be from 4,725 pounds to 5,400 pounds per plot. The amount of EDTA at Site 129-3 may range from 595 pounds to 680 pounds per plot. This is in contrast to the 6,750 pounds of EDTA per plot at Site C for corn (3,375 pounds for white mustard) and 850 pounds at Site 129-3. The amount of acetic acid applied (4,018 pounds per plot) will stay the same. The EDTA will be applied in 5,000 gallons of solution at each site.

7. Soil amendments (acetic acid and EDTA) will be applied via a drip delivery system consisting of 90-ft lengths of drip tubing connected every ten inches to a two-inch header (108 tubes). The tubing network will extend across the entire field parallel with the corn rows. This will allow adequate saturation of the soil with the amendment solutions in a short period of time (approximately 2 hours). This system contrasts with the previous system in that the number of tubes (108) will be triple that used with the white mustard in 1998.

8. Deep tilling will be performed and artificial irrigation will be reduced after the corn harvest to maintain lead within the rooting zone for the following cool season crop.

# APPENDIX G

## Final Report

### Screening Study to Determine Lead Uptake Capacity of Selected Cultivars of Brown Mustard (*Brassica juncea*), Oriental Mustard (*Brassica juncea*), White Mustard (*Brassica hirta*), and Safflower (*Carthamus tinctorius*)

David Behel, Paul Pier, and Patrick Jansen

September, 1999

**Introduction**

ER&S personnel were funded by the US Army Environmental Center during 1996 and 1997 to conduct greenhouse treatability and optimization studies for phytoremediation of lead-contaminated soil. This is an *in situ* method which uses plants, in conjunction with certain soil amendments, to extract lead from contaminated soils. In this approach, the soil amendments (acetic acid and the chelate EDTA) solubilize soil lead into a form that is available to the plant. Acidifying the soil causes dissolution of lead from the solid phases in the soil into the liquid phase (i.e., the soil solution). EDTA then complexes with the soluble lead and prevents it from re-precipitating in the soil into a form that is unavailable to plants. Although soil acidification alone or the use of EDTA without soil acidification will convert some of the soil lead into a plant-available form, the synergistic relationship between the two amendments usually produces the best results. The solubilized lead is taken up into the plant biomass which is harvested and removed from the contaminated area.

The plant species tested in the 1996 - 1997 treatability greenhouse studies were alfalfa, corn, sorghum-sudangrass, sunflower, Indian mustard, and white mustard. These studies showed corn to be an efficient warm season species for lead accumulation when a soil acidifier and a chelate were used to solubilize soil lead. White mustard appeared to be the most efficient cool season plant since it accumulated high concentrations of lead without the need for soil acidification, a step required for the other species tested. The results from these studies led to funding by the Environmental Security Technology Certification Program (ESTCP) of a two-year field demonstration in 1998, "Phytoremediation of Lead-Contaminated Soil at the Twin Cities Army Ammunition Plant (TCAAP)."

The 1998 field results at TCAAP (as measured by lead uptake in the crop) using corn as the warm season remediation species were entirely satisfactory. However, adverse environmental and field conditions later in the year resulted in marginal performance by the cool season white mustard crop, and lead uptake from the soil was below target levels. Excessive rainfall during the growing season resulted in a limited and shallow root system, and other contaminants in the soil, e.g., thallium and beryllium, may also have hampered root growth. This led to a search for a more extensively- and deeper-rooted variety of cool season crop that could perform well in TCAAP soil for use in the 1999 demonstration.

Discussions with commercial plant breeders, growers, and seed producers indicated that other crops in the same family as white mustard, such as the brown and oriental mustards, develop a more extensive rooting system. These also produce a larger biomass than white mustard, which would be desirable for a phytoremediation crop. A larger biomass generally equates to more water uptake, and thus the capacity for uptake of larger quantities of water-soluble metals. Although safflower is typically grown as a warm-season seed crop, it may also be grown as a cool-season forage crop by delaying planting until midsummer. This plant species develops a deep rooting system, has a high transpiration rate conducive to extraction of water-soluble lead, and can produce a large forage biomass when grown as a cool season crop.

**Objective**

The objective of this study was to conduct a short-term plant screening study to determine the potential of brown mustard, oriental mustard, and safflower as alternative cool season phytoextraction crops to white mustard for lead removal in TCAAP soil. Specific objectives were to determine: (1) the lead uptake capacity of the plants; (2) the growth habit; (3) the need for soil acidification to optimize lead uptake; and (4) tolerance to adverse conditions in a soil such as that at TCAAP.

**Materials and Methods**

The plants were grown in soil from the Site C demonstration area at TCAAP which had been amended with acetic acid and EDTA as part of the 1998 field study (Table 1). This soil had a total lead content of 3,400 mg lead/kg soil. The amount of lead that would normally be considered as immediately plant-available, i.e., the water-soluble fraction, was negligible at a concentration of 12 mg/kg. Brown mustard (*Brassica juncea)*, oriental mustard (*Brassica juncea*), white mustard (*Brassica hirta)*, and two cultivars of safflower (*Carthamus tinctorius)* were grown from seed in 6-inch diameter, 7-inch deep plastic pots containing 1.65 kg of soil. Three replicates per treatment of soil-applied EDTA alone or EDTA plus acetic acid (HOAc) were used for each of the 5 species for a total 30 pots. No untreated controls were utilized, since previous greenhouse tests showed that lead uptake from such soil would be minimal compared to treated soils.

During the planting process, each crop received one-half of the optimum amount of nitrogen (N) fertilizer needed to satisfy the plant requirements for N, and all of the required potassium (K) fertilizer. Urea was used as the N source for the mustards at a rate of 260 pounds of N per acre, and ammonium nitrate was used for safflower at a rate of 115 pounds of N per acre. Phosphorus was supplied as concentrated super phosphate (CSP) at a rate of 100 pounds of P per acre for mustard and at 35 pounds of P per acre for safflower. Potassium sulfate was the K source at a rate of 130 pounds of K per acre for mustard and 100 pounds of K per acre for safflower. The second half of the N fertilizer was applied at 4 weeks growth for mustard and at 5 weeks for safflower.

Cool season crop environmental conditions were simulated in an air-conditioned TVA laboratory with artificial lighting (Environmental Growth Chamber Co.(EGC) high-pressure sodium, metal halide mix) under a 12-hour day length and an ambient temperature of 21$^{o}$C. The moisture content of the soil was maintained at field capacity (12%) throughout the growing period. However, safflower exhibited depressed early growth which may have been due to the cooler conditions in the laboratory, and at the end of the third week the plants were placed in the TVA

Muscle Shoals Research Greenhouse to in an attempt overcome any growth limitations imposed by the cool season conditions.

The soil acidifier (acetic acid) and the EDTA chelate were added to the mustard plants after the fifth week of growth, and to safflower after 7 weeks of growth. This was done by allowing the soil in the pots to dry to approximately two-thirds field capacity, then adding acetic acid to designated pots to reduce the soil pH to 5.5. The amount of acetic acid added was based on buffer curves previously determined on the TCAAP soil. The acidifier was followed by EDTA at a concentration equal to the molar concentration of lead in the soil. The amendments were added in a volume sufficient to return the soil to field capacity. This amount of solution ensured that the soil was wetted throughout the pot for maximum exposure of the plant roots to solubilized lead.

The mustard plants were harvested 48 hours after the amendment application; this time period had been shown in previous experiments to be adequate for maximum lead uptake to occur while preventing excessive drying and shattering of the plant tissue. Safflower was harvested 72 hours after the application when the plants were dessicated, but not so brittle as to shatter when handled.

The plant tissue was further dried in an oven at 65$^{o}$C, then ground in a Wiley mill equipped with stainless steel knives and screen. Following digestion, the tissue was then analyzed for total lead concentration by Inductively Coupled Argon Plasma (ICP) spectrometry. The data were analyzed statistically using ANOVA (analysis of variance) to separate treatment effects within species and among varieties. ANOVA is part of a software package from Statistical Analysis Systems (SAS) Institute, Cary, NC, for statistical analysis of variance in data.

**Results and Discussion**

The TCAAP soil used in this experiment is considered agronomically poor having a low nutrient content, a low cation exchange capacity, low organic matter content, low water-holding capacity, and high pH (Table 1). A low level of plant-available phosphorus (P) in the soil is the primary limiting factor for good plant growth. Normally, low P levels can be corrected with additional phosphate fertilizer. However, with phytoextraction schemes, this must be done with caution since supplemental P can complex soil Pb into insoluble forms and complicate Pb removal by the plant. Although the amount of P added at planting of mustard was fairly high, due to the short-term nature of this study this amount of P would not likely react with soil lead to significantly reduce lead availability to the crop. In a longer-term field situation, P applications would have to be judiciously applied to balance crop needs against the potential for excess lead complexation by P. Since this soil did not produce optimum growth of field crops during the 1998 demonstration season, N and K were over-supplied by 10% to encourage adequate growth of the crops.

Regardless of the increased initial amount of N-P-K fertilizer, or the additional N added during the growing period, all the plants exhibited a general lack of vigor and growth throughout the experiment. Stunting reduced expected growth rates of all plants by about one-third to one-half, depending on the species. Bolting of the mustard began at 4 weeks growth, instead of at the 6 to 8 week stage of growth that is typically observed. Safflower began flowering at 6 weeks, which is also atypical for this plant. The reduced growth and early bolting and flowering was most likely due to a combination of the overall poor quality of the soil and perhaps another contaminant in the soil, such as thallium (see Lehn and Schoer, 1987, Section 5.2.2.1) which was toxic to the plants. This pattern of reduced growth also occurred in the field for the white mustard crop at TCAAP in

fall, 1998. Analysis of soil samples taken during the early growth of that crop appeared to rule out carry-over EDTA, soluble lead, or other metals as causative factors, but thallium was found at concentrations sufficiently high to be considered toxic. Safflower planted in an uncontaminated Lakeland sand for comparison under a similar fertility regime soil grew normally. However, untreated TCAAP soil was not used in this study.

In a separate study, the variety of brown mustard used herein exhibited very good growth on lead-contaminated soil obtained from the Volunteer Army Ammunition Plant (VAAP). The TCAAP soil and the VAAP soil were similar in texture and pH, and the two experiments have been conducted under almost identical fertility regimes. Several other metal contaminants which could potentially be toxic to plants, e.g., manganese, selenium, and zinc, were common to both soils. However, thallium was not a contaminant in the VAAP soil, and this could account for the difference in plant growth between the two soils.

The lead uptake capacity was essentially the same among the three mustard varieties if the soil was amended with EDTA without acidifying the soil (Table 2). However, lead concentrations in brown and oriental mustard plants doubled when EDTA was used in conjunction with acetic acid; this effect was not seen in white mustard. A similar pattern for lead uptake in white mustard was observed in previous greenhouse experiments conducted by ER&S researchers at Muscle Shoals in 1996-1997 ("Results of a Greenhouse Study Investigating the Phytoextraction of Lead from contaminated Soils Obtained from the Sunflower Army Ammunition Plant, Desoto, Kansas").

Lead concentrations in all mustard varieties were five- to tenfold lower than had been expected compared to results from the SFAAP experiments. Although the soils in the two studies were of similar pH and lead content, the SFAAP soil was very fertile, and plant growth was considerably better on that soil. The poor growth and early maturity caused by the adverse growing environment in the TCAAP soil most likely resulted in the reduced plant lead concentrations seen in this study.

Lead in the SFAAP soil was in a form that was amenable to complexation by the chelate and subsequent uptake by the plant. The chemical form of lead in soil (e.g., water-soluble, exchangeable, carbonate-bound, oxide-bound, organically-bound, and crystalline) controls the amount of lead complexation by EDTA. The water-soluble, carbonate- and oxide-bound forms, in that order, are more easily complexed by EDTA and potentially are the more plant-available forms. Due to the alkaline pH, a significant portion (>30%) of lead in the SFAAP soil was associated with the carbonate fraction. This form would be subject to ready dissolution by acetic acid and EDTA, which would make the lead available to the plant. However, in the highly buffered Sunflower soil, sequential extraction procedures showed that the overall equilibrium of lead among the various fractions remained relatively unchanged after an addition of acetic acid and EDTA, even though some lead was removed from the carbonate pool by the plant.

The various fractions of lead in the TCAAP soil have not yet been determined, but given the alkaline pH of the TCAAP soil, it would be logical to expect a significant portion of the soil lead to initially be present in the carbonate fraction. However, amendment additions and plant uptake of carbonate-bound lead in 1998 may have reduced the carbonate pool somewhat. Work is now in progress to determine the primary chemical forms of lead in the TCAAP soil.

In soil amended with EDTA alone, lead concentrations in safflower plants were about 50% lower than in mustard (Table 2). Acidifying the soil before adding EDTA resulted in lead concentrations in safflower statistically equivalent to the concentrations achieved in mustard without soil acidification. As with mustard, the overall poor growth of the plants, and the early flowering and termination of vegetative growth likely reduced the amount of lead taken into the plant. No information was available from the literature to indicate the levels of lead that might be expected in safflower. Therefore, the lead concentrations attained may be the limit for this species, and regardless of its other desirable qualities, safflower may not be suitable as a phytoextraction species for lead. However, safflower may have potential for use as an extraction crop for other metals.

**Conclusions**

Based solely on the lead concentrations found in the test plants, none of the five species would appear suitable for use as a phytoextraction crop for TCAAP soils. Of the plant species tested, the brown mustard, used in conjunction with soil acidification and EDTA, was the most effective at removing lead from the contaminated soil. Actual lead concentrations in the brown mustard under this treatment regime were about 7% greater than in Oriental mustard, although this difference was not statistically significant. A more definitive conclusion might be attained by growing the brown mustard under less adverse conditions, such as in another lead-contaminated soil of high fertility but which lacks plant-toxic constituents. Although safflower did not appear suitable for remediation of lead, the deep rooting system, high transpiration rate, and large biomass characteristics of the plant suggest that it may have potential for use with other metals.

**Table 1**
**Partial Characterization of Pb-Contaminated Soil from Site C at TCAAP**

| **Texture** | **Sandy Loam** |
|---|---|
| pH | 8.2 |
| Cation exchange capacity, cmol/kg | 4.9 |
| Field capacity, % | 12 |
| Organic carbon, % | 0.6 |
| Total nitrogen, % | 0.008 |
| Exchangeable Ca, mg/kg | 1,447 |
| " Mg " | 88 |
| Extractable P, mg/kg | 16 |
| " K " | 51 |
| " Fe " | 21 |
| Total Pb, mg/kg | 3,400 |
| Plant available Pb, mg/kg | 12 |

**Table 2**
**Effect of Soil Amendments (EDTA Alone or EDTA Plus Acetic Acid - HOAc) on Lead Concentrations in Mustard and Safflower Plants**

| Plant | Treatment | Pb conc. in plant, mg/kg | |
|---|---|---|---|
| | | Mean | s[1] |
| *B. juncea* - Brown mustard | EDTA | 2,070 | 456 |
| | EDTA + HOAc | 4,257 | 653 |
| | | | |
| *B. juncea* - Oriental mustard | EDTA | 1,740 | 687 |
| | EDTA + HOAc | 3,990 | 567 |
| | | | |
| *B. hirta* - White mustard | EDTA | 2,327 | 133 |
| | EDTA + HOAc | 2,427 | 428 |
| | | | |
| *C. tinctorius* - Safflower *cv* 1 | EDTA | 902 | 305 |
| | EDTA + HOAc | 2,497 | 442 |
| | | | |
| *C. tinctorius* - Safflower *cv* 2 | EDTA | 1,125 | 663 |
| | EDTA + HOAc | 2,657 | 250 |
| | | | |
| LSD (0.05) [2] | | 834 | |

[1] s - Standard deviation of the mean for 3 replicates of each treatment.

[2] Least Significant Difference at the 5% level of significance. ANOVA based on differences in Pb concentration in plants due to species and amendment effects.

# APPENDIX H

## Geostatistical Analyses

**TENNESSEE VALLEY AUTHORITY**
Energy Research & Technology Applications
Environmental and Engineering Services
Special Projects

# Mapping of Soil Lead at the Twin Cities Phytoremediation Site

WR99-2-520-207

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October 1999

# Mapping of Soil Lead at the Twin Cities Phytoremediation Site

## 1.0 Introduction

During phytoremediation studies at Sites C and 129-3, soil samples were manually collected from shallow soil horizons and analyzed for total lead. The spatial locations of all samples are based on 90- x 90-ft sampling grids subdivided into 36 cells with dimensions of 15 x 15 feet. Generally, soil samples were obtained at two depths, both before and after remedial crop amendments, at a respective site (as follows).

| Sampling Event | Sample Intervals (inches) |
|---|---|
| Initial | 0 to 6 and 6 to 12 |
| Pre-Corn Amendment | 0 to 12 and 12 to 24 |
| Post-Corn Amendment | 0 to 12 and 12 to 24 |
| Pre-Mustard Amendment | 0 to 12 and 12 to 24 |
| Post-Mustard Amendment | 0 to 12 and 12 to 24 |

In order to examine the spatial characteristics of soil lead sampling results at the site, comparative mapping of two sampling events has been conducted using exact and smoothing interpolation techniques. For the purposes of this analysis, only initial and post-mustard amendment sampling results are considered. As the names imply, the initial sampling event was conducted prior to any remedial work at the site; whereas, post-mustard soil samples were collected subsequent to the last site remedial amendment.

## 2.0 Methods

For this analysis, the commercial software package, Surfer (Golden Software, Inc., 1999), was used in developing two-dimensional plots of interpolated soil lead data. The exact interpolation technique used for generating soil lead maps is triangulation with linear interpolation based on optimal Delaunay triangulation. Lee and Schachter (1980) present a complete discussion of (Delaunay) triangulation, including the details of two algorithms and the underlying mathematical proofs. Lawson (1977) is equally informative. The algorithm presented in Guibas and Stolfi (1985) form the basis for this implementation. Triangulation with linear interpolation works best when data are evenly distributed over the grid area. Data sets that contain sparse areas result in distinct triangular facets on the resultant map. Exact interpolators honor data points exactly when the point coincides with the grid node being interpolated. In other words,

a coincident point carries a weight of essentially 1.0 and all other data points carry a weight of essentially zero.

The smoothing interpolation technique used in developing corresponding soil lead maps is point kriging based on a two-dimensional algorithm contained in Abramowitz and Stegun (1972). Kriging is a geostatistical gridding method that has proven useful and popular in many fields. This method produces visually appealing maps from irregularly spaced data. Kriging attempts to express spatial trends suggested in data, so that, for example, high values might be interconnected rather than isolated by “bull's-eye” type contours. For a detailed derivation and discussion of kriging, see Journel and Huijbregts (1978) or Cressie (1991). In this analysis, the krigged grid is custom-fit to a given data set by specifying an appropriate variogram model (a measure of how quickly things change on the average). The underlying principle is that, on the average, two observations closer together are more similar than two observations farther apart. Because the underlying processes of the data often have preferred orientations, values may change more quickly in one direction than another. As such, the variogram is a function of direction. The variogram model mathematically specifies the spatial variability of the data set and the resulting grid file. The interpolation weights, which are applied to data points during the grid node calculations, are direct functions of the variogram model.

## 3.0 Data Analysis

Table 1 presents summary statistics or total lead in soil at Site C from initial and post-mustard sampling events. As shown, although samples were obtained from every cell (36 each) before remediation began at the site, only 22 samples could be collected following the mustard crop amendment. The standard deviations and variance values associated with each sampling event are very high.

**Table 1**
**Summary Statistics of Total Lead in Soil (mg/kg) at Site C**
**From Initial and Post-Mustard Sampling Events**

| Sampling Event | Sample Interval (inches) | Number of Samples | Minimum | Median | Maximum | Average | Standard Deviation | Variance |
|---|---|---|---|---|---|---|---|---|
| Initial | 0 to 6 | 36 | 1240 | 2360 | 8170 | 2615 | 1318 | 1.74E+06 |
| Initial | 6 to 12 | 36 | 1050 | 2570 | 7150 | 2851 | 1319 | 1.74E+06 |
| Post-Mustard | 0 to 12 | 22 | 659 | 1610 | 10300 | 2317 | 2236 | 5.00E+06 |
| Post-Mustard | 12 to 24 | 22 | 428 | 3190 | 10300 | 3862 | 2889 | 8.34E+06 |

Figure 1 shows variograms developed for Site C soil sampling results. Variograms for the initial lead sampling event (by depth interval) were fit using similar Gaussian models. The nugget effect of both initial lead variograms (Figure 1a) is high (1,740,000 $[mg/kg]^2$). In the case of all variograms generated for this study, the nugget effect represents error variance, a measure of the direct repeatability of the data measurements. The specified nugget effect causes kriging to become more of a smoothing interpolator, implying less confidence in individual data points versus the overall trend of the data (i.e., the higher the nugget effect, the smoother the resulting grid). Variogram models (Figure 1b) for post-mustard sampling intervals are Gaussian and linear curves for the shallow (0 to 12 inches) and deeper (12 to 24 inches) soil horizons, respectively. As in the case of the initial lead variograms, post-mustard variograms exhibit large nugget effects (3,000,000 $[mg/kg]^2$).

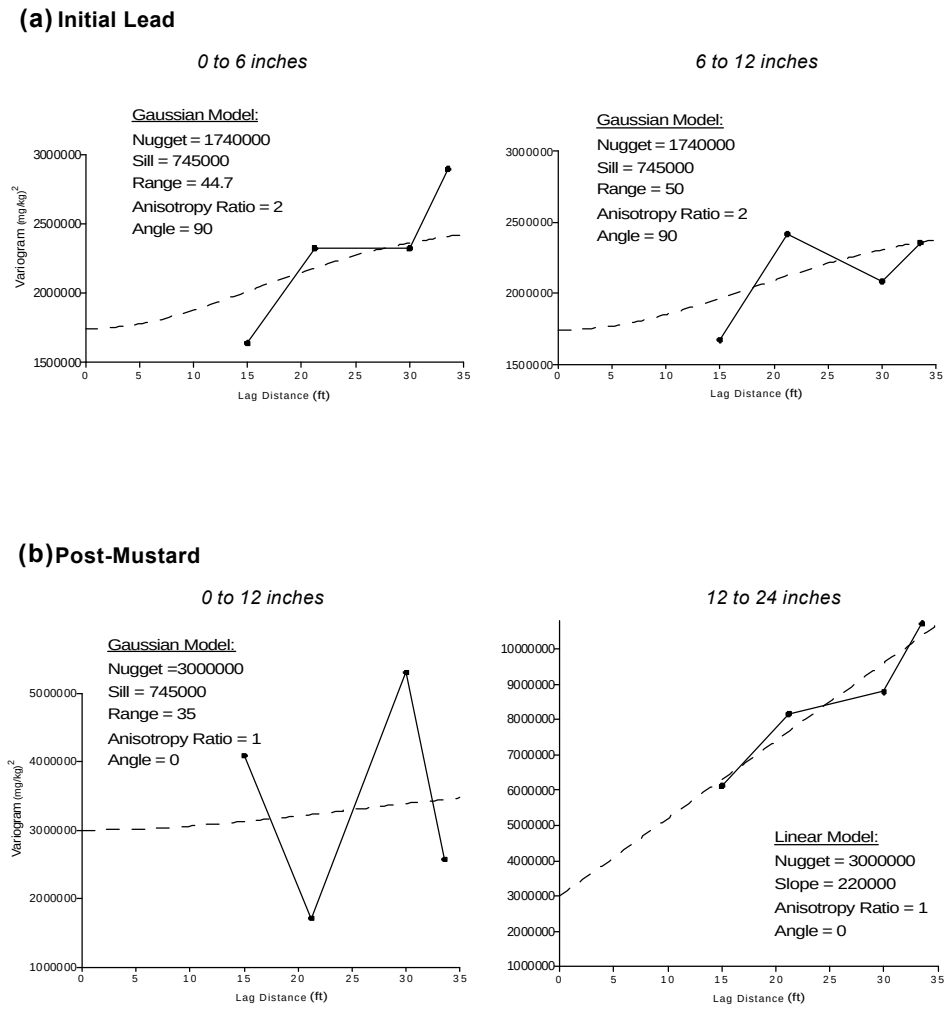


**Figure 1**
**Variograms of Site C Analytical Data from**
**(a) Initial Soil Lead Sampling and (b) Post-Mustard Amendment Soil Lead Sampling**

Table 2 presents summary statistics of total lead in soil at Site 129-3 from initial and post-mustard sampling events. As shown, samples were obtained from every cell (36 each) at the site for all sampling events. As at Site C, the standard deviations and variance values associated with each sampling event at Site 129-3 are very high.

**Table 2**
**Summary Statistics of Total Lead in Soil (mg/kg) at Site 129-3**
**From Initial and Post-Mustard Sampling Events**

| Sampling Event | Sample Interval (Inches) | Number of Samples | Minimum | Median | Maximum | Average | Standard Deviation | Variance |
|---|---|---|---|---|---|---|---|---|
| Initial | 0 to 6 | 36 | 6 | 188 | 1730 | 329 | 353 | 1.25E+05 |
| Initial | 6 to 12 | 36 | 3 | 218 | 918 | 259 | 237 | 5.61E+04 |
| Post-Mustard | 0 to 12 | 36 | 10 | 62 | 1382 | 200 | 317 | 1.00E+05 |
| Post-Mustard | 12 to 24 | 36 | 3 | 40 | 669 | 114 | 150 | 2.25E+04 |

Figure 2 shows variograms developed for Site 129-3 soil sampling results. Variograms for the initial lead sampling event (by depth interval) were fit to a linear model. The nugget effects of both initial lead (Figure 2a) and post-mustard (Figure 2b) variograms are high as found with Site C.

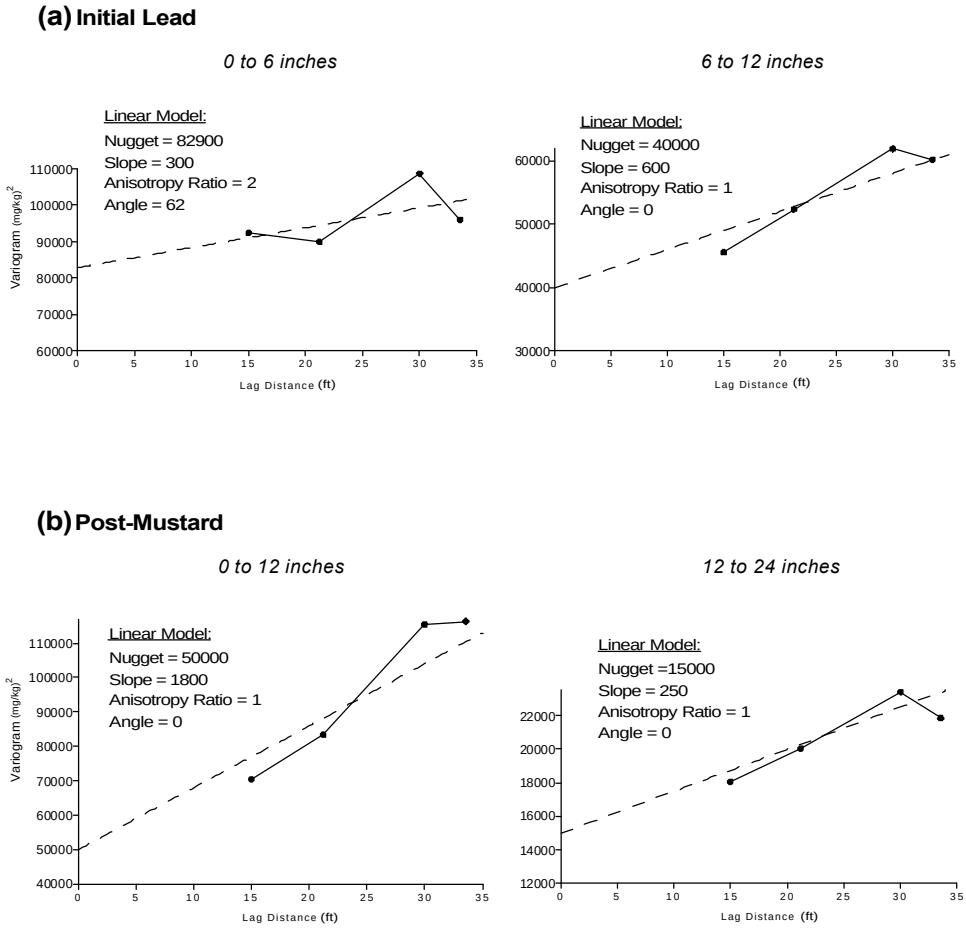


**Figure 2**
**Variograms of Site 129-3 Analytical Data from**
**(a) Initial Soil Lead Sampling and (b) Post-Mustard Amendment Soil Lead Sampling**

## 4.0 Results and Conclusions

The mapped results of exact and smoothing interpolations of the Site C initial soil lead data are shown in Figures 3a and 3b, respectively, based on depth interval. As shown in Figure 3b, there are no obvious spatial trends in the data. Observations are similar in Figure 4, which displays maps of post-mustard sampling results. There appear to be no obvious trends in the data that can be delineated using geostatistical methods and there is no clear advantage for its application in this particular case. There were high variance values exhibited at both depth intervals.

Other than possible higher soil lead concentrations on the southern side of Site 129-3, no obvious spatial trends are observed in mapped results of soil lead data (Figures 5 and 6). As at Site C, soil sampling results at Site 129-3 exhibit a high degree of variance, regardless of depth.

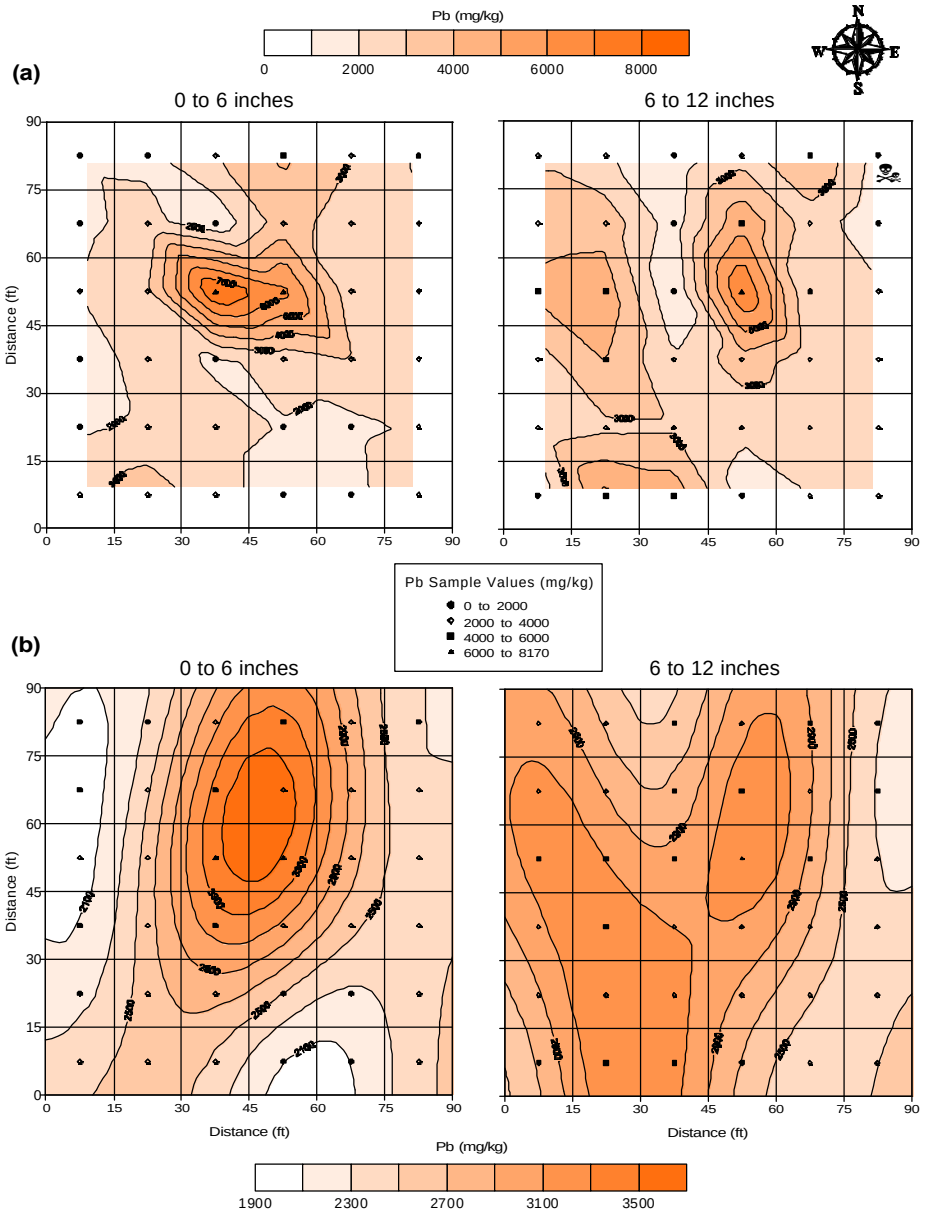


**Figure 3**
**Maps of Site C Initial Soil Lead Based on**
**(a) Triangulation with Linear Interpolation and (b) Kriging Interpolation**

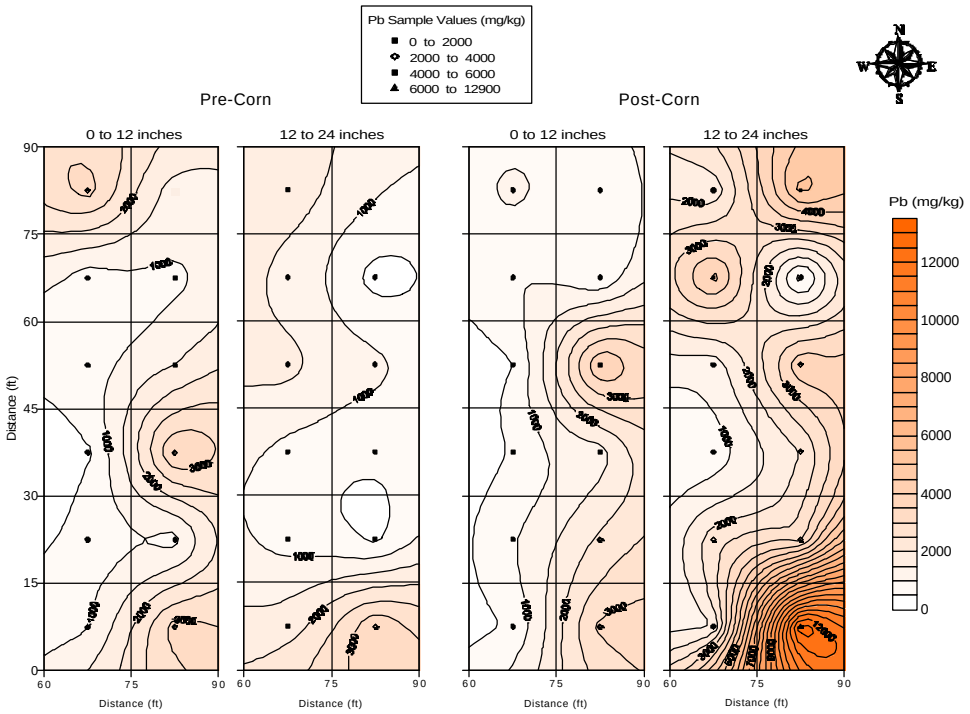


**Figure 4**
**Maps of Site C Pre- and Post-Corn Soil Lead Based on**
**(a) Triangulation with Linear Interpolation and (b) Kriging Interpolation**

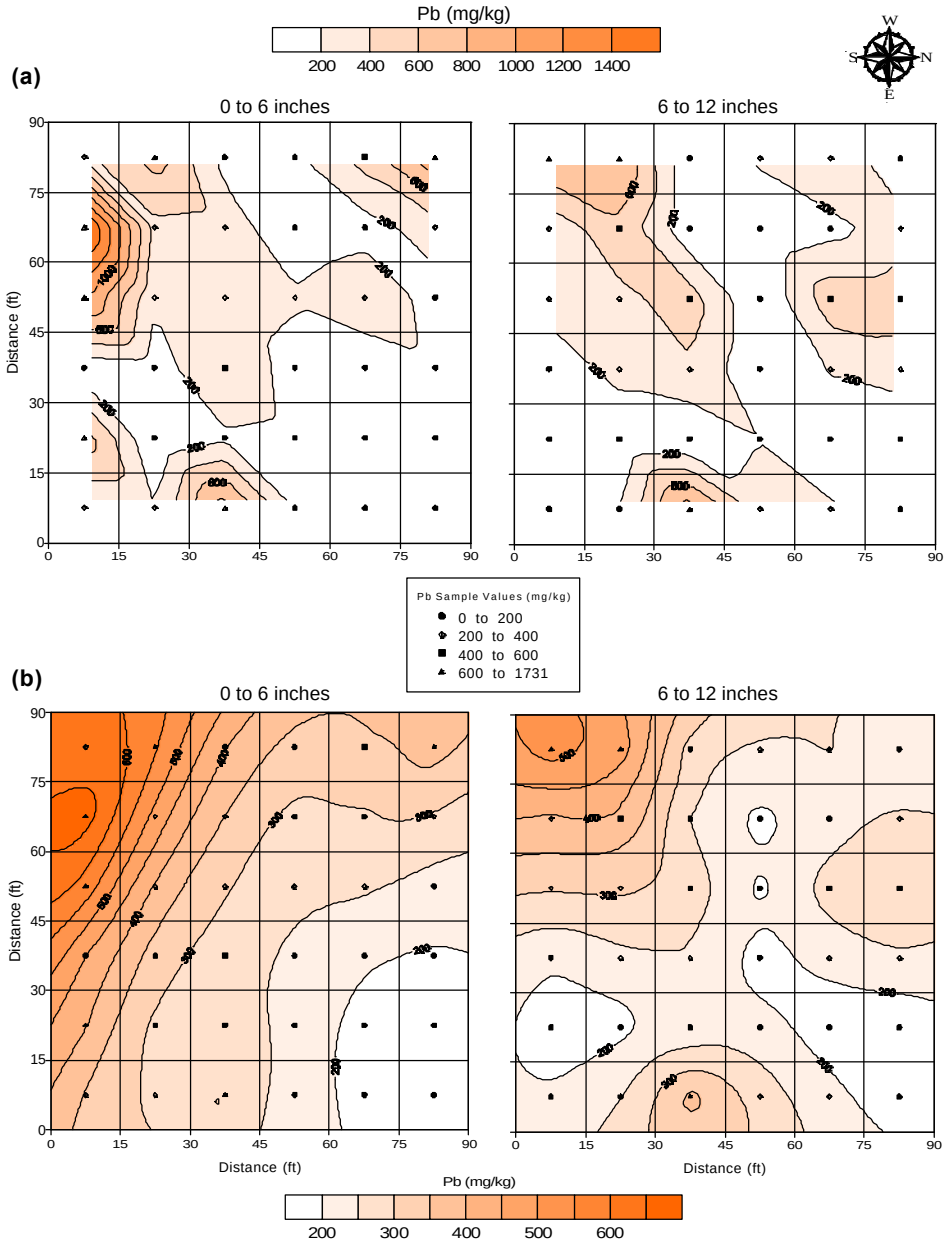


**Figure 5**
**Maps of Site 129-3 Initial Soil Lead Based on**
**(a) Triangulation with Linear Interpolation and (b) Kriging Interpolation**

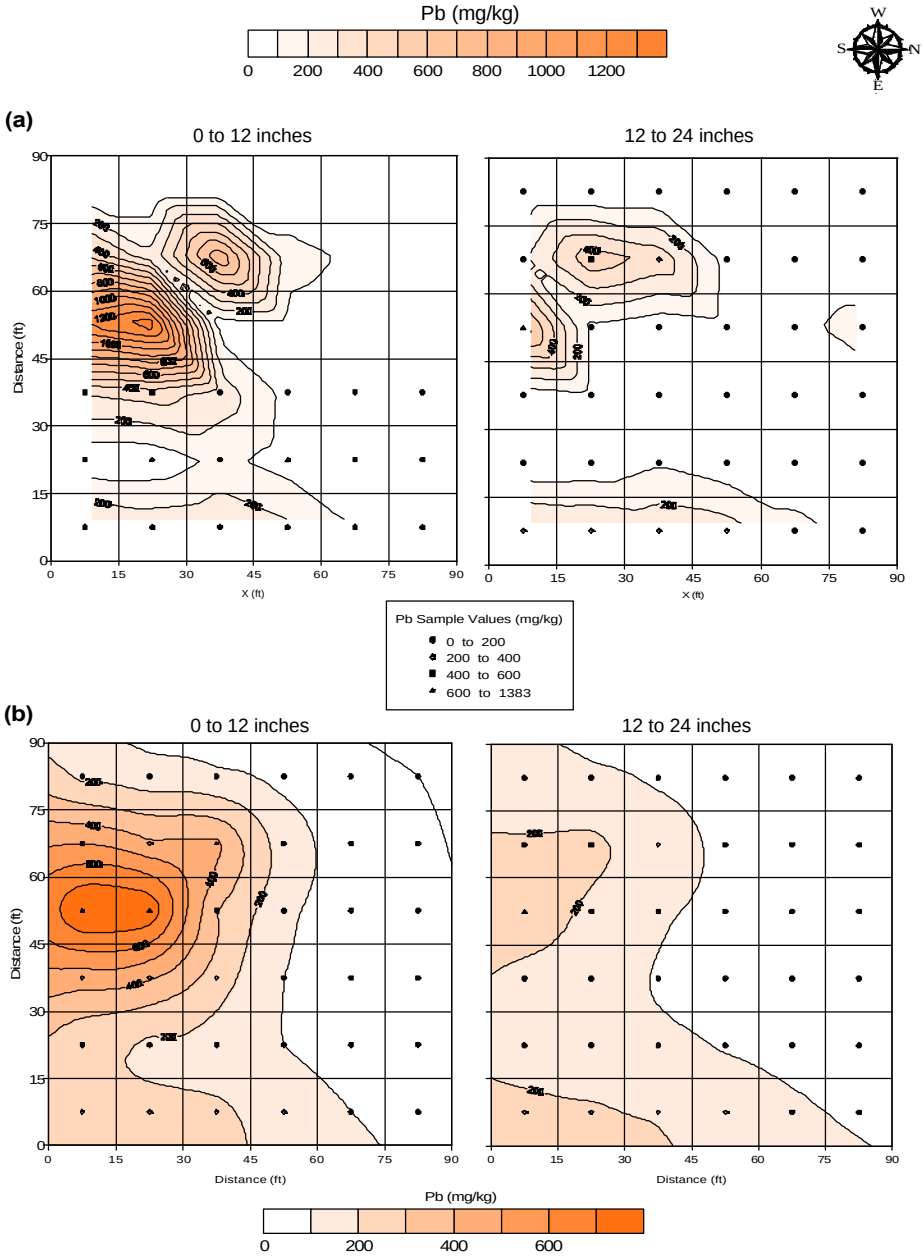


**Figure 6**
**Maps of Site 129-3 Post-Mustard Soil Lead Based on**
**(a) Triangulation with Linear Interpolation and (b) Kriging Interpolation**

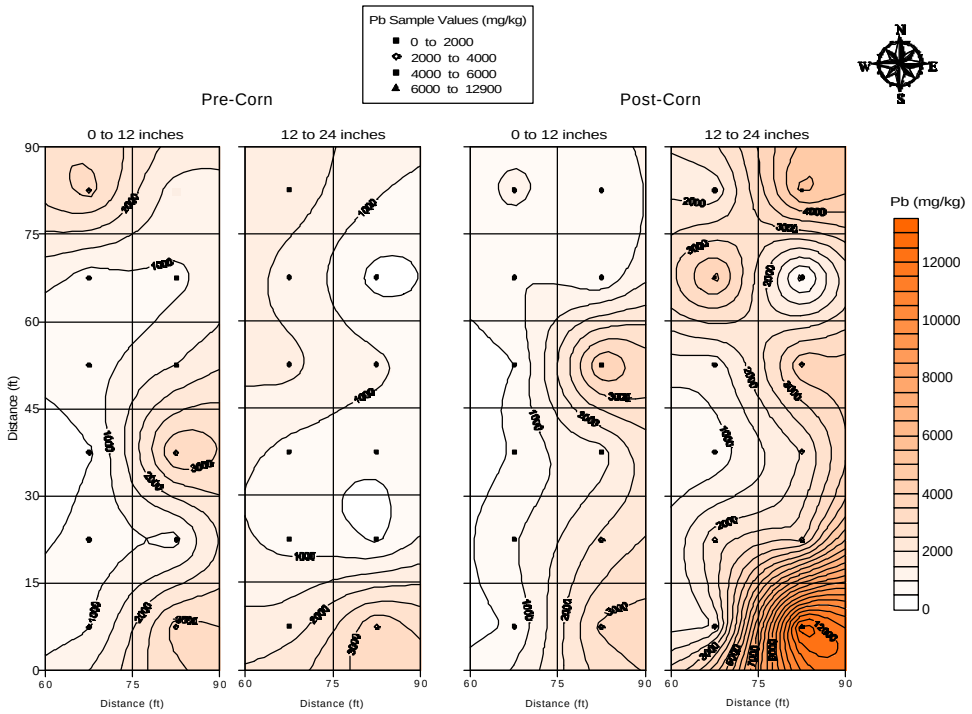


**Figure7**
**Maps (Kriging Interpolation) of Site C, Pre- and Post-Corn, from 1999 Results for Total Lead in Soil**

The above plots are for the 1999 total lead in soil at Site C specified by time interval and sampling depth. The sampling event for 1999 Site C was limited to the eastern 1/3 of the site due to poor crop growth. The very high value of 12,900 mg/kg observed at the southeastern corner of the site is an anomaly most likely due to particulate lead in the soil.

## References:


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Appendix I

ADDENDUM TO HEALTH AND SAFETY PLAN (HASP) FOR TWIN CITIES ARMY AMMUNITION PLANT (TCAAP) PHYTOREMEDIATION PROJECT

Please use this memorandum as an addendum to the HASP to address concerns caused by the presence of asbestos containing material (ACM) at the TCAAP Site C. I spoke with Tanya Drake, ERM, Incorporated, one of the people who found the ACM and she provided some additional information. The ACM found at Site C is presumed to be transite construction material. The material has not been analyzed for asbestos content, but transite was widely used on military installations and it is widely assumed in the asbestos abatement industry to be an ACM. I concur with this assumption.

Transite is a Category II, non-friable ACM, and it is not hazardous unless it is vigorously disturbed. Grinding, sawing, drilling, crushing, or other such activities on transite can release hazardous, airborne asbestos fibers.

Future work on this project can continue with a little modification to our operations. The following list of precautions should prevent exposure to airborne asbestos fibers.

1. Prior to plowing or tilling the test plots, police the area to be disturbed and pick up visible pieces of the transite. The pieces need to be bagged in asbestos waste bags for disposal at a licensed asbestos landfill. Those workers who pick up the transite need to complete the 2 hour asbestos awareness training required by OSHA standard 29 CFR 1926.1101. Other activities at the test plot should not significantly disturb the transite in the soil. The personal protective equipment (PPE) and decontamination procedure specified in the HASP to protect against airborne lead exposure will be adequate to protect against airborne asbestos during plowing and tilling or any of these other activities.

2. Keep samples wet if possible. Handle soil samples in a laboratory hood if there is a chance of releasing asbestos fibers into the air. Good laboratory practices that prevent lead exposure from these samples will also prevent asbestos exposure.

3. Assess future work and plan activities to prevent generating airborne asbestos exposure. This can be done by removing as much of the visible transite as feasible, conducting as much of the work as possible with the ground wet, using the PPE and decontamination procedures already in the HASP, and communicating with other people who have site or laboratory responsibilities.

# APPENDIX J

## Sequential Extraction Procedure

## 1.0 PURPOSE

This procedure describes an analytical process for partitioning of soil bound particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe and Mn) into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual. A separate extraction for water-soluble lead is also performed.

## 2.0 SCOPE

This procedure applies to soil samples from studies of phytoremediation of lead contaminated soils.

## 3.0 SUMMARY

A two gram sample of soil or sediment is subjected to extraction by five different chemical reagents each progressively more reactive to the sample (magnesium chloride, then sodium acetate, then hydroxylamine hydrochloride in acetic acid, then nitric acid and hydrogen peroxide and finally hydrofluoric and perchloric acids). Complementary measurements are then performed on the individual leachates and on the residual solids following each extraction to evaluate the selectivity of the various metals (Cd, Co, Cu, Ni, Pb, Zn, Fe and Mn) toward specific geochemical phases.

A separate extraction with water provides an estimate of bio-available or water-soluble lead.

## 4.0 REFERENCES


4.1 "Sequential Extraction for the Speciation of Particulate Trace Metals", Tessier, A., P.G.C. Campbell and M. Bisson. 1979. Anal. Chem. 51:844-850.

4.2 Method 6010B, "Inductively Coupled Plasma - Atomic Emission Spectroscopy", Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods, SW-846, 3rd Edition, December 1996.

4.3 "Standard Specification for Reagent Water", ASTM D1193-91, 1996 Annual Book of ASTM Standards, Volume 11.01, Water and Environmental Technology, p.116-118

4.4 "Selective Extraction," Section 21-5 in Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

5.0 RESPONSIBILITIES

5.1 The laboratory supervisor, or his designee, shall ensure that this procedure is followed during the sequential extraction for the speciation of particulate trace metals.

5.2 The laboratory group leader, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure and is responsible for the training of new personnel on this procedure. Data shall be reviewed by the laboratory group leader or his designee.

5.3 The analyst shall follow this procedure and report any abnormal results or nonconformance to the laboratory group leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 All sample containers must be prewashed with detergents, acids and ASTM Type II water. Plastic and glass containers are both suitable.

6.1.2 Samples shall be refrigerated upon receipt and analyzed as soon as possible.

6.1.3 All samples shall be air dried at room temperature to a constant weight and ground to pass through a #10 sieve.

6.2 Limitations and Actions

For this procedure, a batch is defined as a group of no more than 20 samples extracted at the same time with the same set of reagents.

6.3 Requirements

6.3.1 Apparatus/Equipment

6.3.1.1 Analytical balance: capable of weighing to 0.1 mg

6.3.1.2 Centrifuge: capable of centrifuging at 10,000 rpm

6.3.1.3 Centrifuge tubes: polypropylene, 50 ml

6.3.1.4 pH meter with appropriate electrode

6.3.1.5 Platinum crucibles

6.3.1.6 Magnetic stirrer and stirring bars

6.3.1.7 Laboratory oven

6.3.1.8 Normal laboratory glassware

6.3.2 Reagents and Standards

6.3.2.1 ASTM Type II water (ASTM D1193): Water shall be monitored for impurities by conductivity (conductivity of less than 1.0 µmho/cm at 25$^{o}$C).

6.3.2.2 Magnesium chloride: reagent grade

6.3.2.3 Magnesium chloride, 1M: weigh 95.23 g of reagent grade magnesium chloride into a 1 liter volumetric flask and dilute to volume with ASTM Type II water

6.3.2.4 Glacial acetic acid: reagent grade

6.3.2.5 Sodium acetate: reagent grade

6.3.2.6 Sodium acetate, 1M: weigh 82.04 g of reagent grade sodium acetate into a 1 liter volumetric flask and dilute to volume with ASTM Type II water

6.3.2.7 Carbonate extracting solution: 1 M sodium acetate adjusted to pH 5.0 with glacial acetic acid

6.3.2.8 Hydroxylamine hydrochloride: reagent grade

6.3.2.9 Hydroxylamine hydrochloride, 0.04 M in 24% acetic acid: Weigh 2.780 g of hydroxylamine hydrochloride into a 1 liter flask and dissolve in 500 ml ASTM Type II water. Add 250 ml glacial acetic acid and make to volume with ASTM Type II water.

6.3.2.10 Nitric acid: concentrated, reagent grade

6.3.2.11 Nitric acid, 0.02 M: add 1.27 ml of concentrated, reagent grade nitric acid to 500 ml of ASTM Type II water in a 1 liter flask, swirl to mix and make to volume with ASTM Type II water

6.3.2.12 Hydrogen peroxide, 30%: reagent grade

6.3.2.13 Hydrogen peroxide, 30% adjusted to pH 2: Add concentrated reagent grade nitric acid to 30% reagent grade hydrogen peroxide until the pH drops to 2.0

6.3.2.14 Ammonium acetate: reagent grade

6.3.2.15 Ammonium acetate, 3.2 M in 20% nitric acid: Add 246.66 g of reagent grade ammonium acetate to 500 ml ASTM Type II water in a 1 liter volumetric flask and swirl to dissolve. Add 200 ml concentrated reagent grade nitric acid, swirl and make to volume with ASTM Type II water.

6.3.2.15 Hydrofluoric acid: reagent grade

6.3.2.16 Perchloric acid: concentrated, reagent grade

6.3.2.17 Hydrochloric acid: concentrated, reagent grade

7.0 PROCEDURE

7.1 Procedure Instructions

7.1.1 Weigh a 2 gram sample of dried (room temperature) soil or sediment into a 50 ml polypropylene centrifuge tube.

7.1.2 Add 16 ml of magnesium chloride solution and stir on a magnetic stirrer for 1 hour.

7.1.3 Centrifuge at 10,000 rpm for 30 minutes.

7.1.4 Remove supernatant with a pipette and submit this solution for analysis of trace metals by ICP. This is the exchangeable fraction.

7.1.5 Add 16 ml of ASTM Type II water to the centrifuge tube, suspend the solids by stirring and centrifuge at 10,000 rpm for 30 minutes.

7.1.6 Remove this wash solution with a pipette and discard it.

7.1.7 Add 16 ml of 1 M sodium acetate adjusted to pH 5.0 with acetic acid.

7.1.8 Stir continuously for 5 hours.

7.1.9 Centrifuge at 10,000 rpm for 30 minutes.

7.1.10 Remove the supernatant with a pipette and submit this solution for analysis of trace metals by ICP . This is the fraction bound to carbonates.

7.1.11 Add 16 ml of ASTM Type II water and suspend the solids by stirring.

7.1.12 Centrifuge at 10,000 rpm for 30 minutes.

7.1.13 Remove this wash solution with a pipette and discard it.

7.1.14 Add 40 ml of 0.04 M hydroxylamine hydrochloride in 25% acetic acid and stir to suspend solids.

7.1.15 Place in a laboratory oven set at $96^{o}C$ and heat with occasional agitation for 6 hours.

7.1.16 Cool and centrifuge at 10,000 rpm for 30 minutes.

7.1.17 Remove the supernatant with a pipette and submit this sample for analysis of trace metals by ICP. This fraction is defined as the fraction bound to Fe-Mn oxides.

7.1.18 Add 16 ml of ASTM Type II water and stir to suspend solids.

7.1.19 Centrifuge at 10,000 rpm for 30 minutes.

7.1.20 Remove the wash solution with a pipette and discard it.

7.1.21 Add 6 ml of 0.02 M $HNO_3$ and 10 ml of $H_2O_2$ adjusted to pH 2 with $HNO_3$ and heat in a laboratory oven at $85^0C$ for 2 hours with occasional agitation.

7.1.22 Add a second aliquot of 10 ml of 30% $H_2O_2$ (pH 2 with $HNO_3$) and heat an additional 3 hours in a laboratory oven at $85^0C$ with intermittent agitation.

7.1.23 Cool and add 10 ml of 3.2 M ammonium acetate in 20% $HNO_3$ and dilute to 40 ml.

7.1.24 Stir continuously for 30 minutes.

7.1.25 Centrifuge at 10.000 rpm for 30 minutes.

7.1.26 Remove the supernatant with a pipette and submit for analysis of trace metals by ICP. This is the fraction bound to organic matter.

7.1.27 Add 16 ml of ASTM Type II water and stir to suspend solids.

7.1.28 Remove wash solution with a pipette and discard it.

7.1.29 Transfer the residue to a platinum crucible.

NOTE: The steps 7.1.30, through 7.1.33 must be performed in a perchloric acid hood.

7.1.30 Add 1 ml $HClO_4$ and 15 ml HF and evaporate to near dryness without boiling.

7.1.31 Add a second aliquot of 1 ml $HClO_4$ and 15 ml HF and again evaporate to near dryness without
boiling.

7.1.32 Add 1 ml $HClO_4$ and heat until the appearance of white fumes.

7.1.33 Cool and add 7 ml ASTM Type II water and 4 ml concentrated reagent grade HCl.

7.1.34 Warm to dissolve solids, transfer to a 50 ml volumetric flask and make to volume with ASTM Type II water.

7.1.35 Submit this solution for analysis of trace metals by ICP. This is the residual fraction.

7.2 Quality Control Sample Requirements

7.2.1 One duplicate sample will be analyzed for every batch.

7.2.2 One method blank will be analyzed for every batch.

7.2.3 A matrix spike will be analyzed for each batch for each of the five sequential extractions. To 10 ml of each extract solution, 1 ml of a 100 mg/L standard will be added. (The spike concentration will then be 9.09 mg/L.)

Note: Smaller quantities may be used in the same ratio if sample size does not permit using 10 ml.

7.3 Bio-Available or Water-Soluble Lead

7.3.1 Extract 5.0 grams (dry weight) soil with 50 ml water for three hours on a reciprocating shaker at 180 cycles per minute. Centrifuge the sample as needed and then filter the supernatant through a 1-micron syringe filter. Acidify a 10-ml portion of the filtered sample with 10 ml nitric acid and dilute to 50 ml.

7.3.2 Submit for lead analysis by inductively coupled plasma (ICP). Report sample weight, percent moisture, extraction volume and dilution factor to the metals workgroup so that analytical values may be calculated.

8.0 SAFETY

8.1 Concentrated perchloric acid can react explosively with organic material such as paper or plant tissue. Caution is advised. Work with perchloric acid in a perchloric acid hood which has been specifically designed for operations with that chemical.

8.1 General laboratory safety rules shall be observed.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

None

END OF PROCEDURE