Results of the 1998 Field Demonstration and Preliminary Implementation Guidance for Phytoremediation of Lead-Contaminated Soil at the Twin Cities Army Ammunition Plant Arden Hills, Minnesota

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This report describes the first-year (1998) 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 preliminary implementation guidance for implementing this technology based on the 1998 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 phytoextraction methods using corn performed near expectations; however, methods using white mustard did not meet the expected level of performance. Alternative crops to white mustard for cool season use are being considered and tested. A preliminary economic analysis indicates the technique will be economically viable.

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Executive Summary

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. A number of DoD installations have soils which will require remediation for heavy-metal contamination. Of the heavy metals, the DoD is currently emphasizing lead (Pb) removal due to the inherent toxicity of lead and the quantity discharged. The contamination consists of both particulate and ionic lead. The metallic particulates (bullet fragments, etc.) were often deposited as the result of firing range use. The ionic metals were commonly deposited when metal-bearing propellants, ammunitions, and powders were burned at explosive disposal sites or when metallic particulates in the soil were dissolved and converted into the ionic forms. One of the methods proposed to remediate DoD sites contaminated with ionic forms of lead is phytoextraction. Phytoextraction is an *in situ* remediation method in which plants are used to remove ionic metals from contaminated soils. The project goal was to demonstrate the effectiveness of phytoextraction techniques for removing ionic lead from contaminated soils. The two-year field demonstration (1998 and 1999) was funded in fiscal 1998 and is currently being conducted at the Twin Cities Army Ammunition Plant (TCAAP). This report describes the demonstration results for the first year of operation. The project does not address particulate metals, but instead focuses specifically on the removal of ionic forms of lead.

Phytoextraction is generally considered a category of phytoremediation, which is a broad term describing a variety of methods which use plants to remediate contaminated soils, surface waters, and ground waters. During the phytoextraction process, water-soluble lead is taken up by plant species selected for the ability to take up large quantities of lead. The metals are stored in the plant aerial shoots which are harvested and are either smelted for potential metal recycling/recovery or are disposed of as a hazardous waste.

The primary objective of this project is to determine if phytoextraction is a technically and economically feasible means of reducing lead contamination. One method for improving the phytoextraction process is to increase the water solubility of lead adsorbed in soil by the addition of soil amendments. Lead solubility can be increased both by adjusting the soil pH and by adding chelating agents to the soil. However, if a particular plant species can uptake significant qualities of heavy metals without soil pH adjustment, this step can be eliminated.

This project was executed under a partnering agreement among the:

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

The U.S. Army's Industrial Operations Command (IOC) also provided assistance to the USAEC by providing sites with lead-contaminated soil at TCAAP.

The USAEC was the lead agency and provided overall project management for the team. TVA provided environmental expertise in research and technology demonstration, and technical expertise in plant lead uptake, application of soil amendments, and the chemical analysis of soil and plant samples taken from the sites. ATK, the operating contractor at TCAAP, conducted day-to-day operations at the field demonstration site.

Based on a review of various Army installations, two demonstration sites at TCAAP were selected: Sites C and 129-3. These sites were selected based on geologic, soil, and climatic considerations including:

- TCAAP had sites with both moderate and low levels of ionic lead contamination. Site C had an average of 2,610 ppm of lead in the first six inches of soil and Site 129-3 had an average of 358 ppm of lead.

- Metallic debris (i.e., bullet jackets and copper scrap) were present in the soil at Site C, therefore, a demonstration at that site would provide a perspective on the impact of metallic particulate on remediation efforts.

- The soils at TCAAP contained more sand than those used during a previous study.[ref. 1] This provided an opportunity to observe the potential for leaching problems.

- 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 is two to six feet below the surface, whereas at Site 129-3, the water table is estimated to be 140 to 200 feet below the surface.

- TCAAP, located in 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 less than ideal climate for growing crops.

To conduct the demonstration, two 0.2-acre sites were cleared, fenced, and plowed to create farm plots, with one plot at Site C and one at Site 129-3. Irrigation systems were also installed at each site. During the demonstration, two crops were grown, the soil was treated with soil amendments to induce lead solubilization, and the crops were harvested and smelted. The first crop was corn and the second was white mustard. These crops had been selected based on previous optimization studies conducted by the USAEC and TVA.[ref.1] The soil amendments included acetic acid, which temporarily increases soil acidity and, thereby solubilizes lead in soil of the solid phase and into the solution phase, and ethylenedinitrilo-tetraacetic acid (EDTA), a chelate which complexes with lead and enhances the water solubility and subsequent plant availability of lead.

The first-year demonstration results with corn produced yields of 2.1 to 3.6 tons of corn stover per acre. Corn stover is corn prior to grain production. The yields produced were low compared to the expected yield of 6.0 tons of corn stover per acre. The low yield at TCAAP has been attributed to the agronomically poor soils at TCAAP and the presence of other soil contaminants that may have been toxic to the plants.

Lead concentrations in the harvested corn averaged 0.65% and 0.13% dry weight for Sites C and 129-3, respectively, and were lower than the 0.85% obtained during a previous greenhouse study.[ref. 1] The higher lead levels obtained during the greenhouse study are attributed to the fact that the corn used in that study was grown under controlled conditions in pots containing highly fertile soil, factors which enabled optimum lead uptake.

The first-year demonstration results with white mustard produced yields of 1.9 to 2.1 tons of white mustard per acre of land in those areas of the plot where there was a viable crop. However, on a per plot basis, the total yields for Site C were half this value, because the white mustard grew in only about 50% of the plot area. In the areas where plants grew, the yields produced were comparable to the maximum expected yield of 2 tons/acre.

Lead concentrations in the harvested white mustard were very low, with average lead concentrations of 0.083% and 0.034% dry weight for Sites C and 129-3, respectively. This compares with an average lead concentration of 1.5% obtained during greenhouse studies conducted with soil from the Sunflower Army Ammunition Plant.[ref.1] The lower lead levels obtained during the TCAAP demonstration are attributed to several factors:

- The rooting system of the white mustard on the demonstration plots was shallow and limited. The limited rooting pattern of the white mustard may have been partially due to some EDTA remaining in the soil after the corn amendment application.

- 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. Most of the original soil lead was still present in the top 24 inches of soil, but was generally below the shallow rooting zone of the white mustard.

- 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. Since the soil was not quickly saturated, an aqueous medium did not exist for the constant movement of water-soluble lead to the plant roots during the period when the plants were continuously exposed to EDTA. EDTA is toxic to plants at these concentrations. Consequently, prolonged exposure to EDTA may have killed the white mustard plants before they could take up significant amounts of lead.

Normally, white mustard plants do not have shallow rooting systems. In the field, the root systems are usually 2 to 3 feet deep with a 1-foot lateral spread and an extended tap root. The tap root starts as bulky and thick at the surface, but tapers rapidly and is very fine at two feet. The shallow rooting systems produced during the first-year demonstration at TCAAP suggest:

- Over-watering either in total amount or frequency, quite possibly due to excessive rainfall.
- Root damage due to other contaminants in the soil. Contaminants present which may have affected the plants include EDTA, lead, beryllium, and thallium.

Solutions to the problems with white mustard are currently being investigated. An Addendum to this document (Appendix G) details the results of a greenhouse study conducted to evaluate the performance of alternative cool season crops. Other changes may be made to improve the performance of the cool season crop during the 1999 demonstration year. These include:

- Use of alternate mustard varieties or alternate crops which may produce greater biomass and may be less sensitive to other contaminates in the soil.

- Use of higher fertilizer rates to encourage greater biomass. (This is not normally practiced since vegetative growth is enhanced at the expense of seed yields.)

- Varying the irrigation scheme if possible to encourage mustard rooting and growth.

- Investigating alternative amendment delivery systems or methods, i.e., subterranean drip systems or higher delivery rate drip systems.

- Deep tilling, where practical, to bring lead which may have moved downward in the soil profile back closer to the surface and in closer proximity to the roots.

- Using methods other than tillage/irrigation cycling to degrade EDTA.

These alternatives will be considered prior to the 1999 demonstration.

A preliminary estimate of the cost of a typical phytoextraction remediation project was developed as part of this project. For cost estimating purposes, it was assumed that a phytoremediation project would be conducted in a relatively unattractive growing environment with moderate levels of lead contamination such as the conditions encountered at Site C. Under these circumstances, it was assumed that:

- The growing season would be shortened due to the northern U.S. location of the site
- Two crops could be grown per year (one corn crop and one white mustard crop)
- Soil conditions would not be optimal for plant growth
- The level of lead in the soil would be about 2,500 ppm
- Five years of remediation would be required to meet the regulatory standard

Based on these assumptions, TVA estimated that a typical remediation project would cost about $30.61 per cubic yard of soil per year or about $153 per cubic yard of soil over the entire life of the project. Literature data indicates that phytoremediation generally costs between $25 and $127 per cubic yard. Comparison of these figures with TVA's preliminary estimate of $30.61 per cubic yard of soil per year suggests that the preliminary estimate is reasonable given that:

- Growing conditions at TCAAP were unfavorable.
- Phytoremediation projects are speculated to last one to five years, based on the initial lead content of the soil, with five years being assumed as a reasonable ceiling.

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ABBREVIATIONS

2,4-D	-2,4-Dichlorophenoxy Acetic Acid
AA	-Atomic Absorption
AAP	-Army Ammunition Plant
AEC	-U.S. Army Environmental Center (officially USAEC)
AETRA	-Army Environmental Requirements and Technology Assessments
Al	-Aluminum
ARARs	-Applicable or Relevant and Appropriate Requirements
As	-Arsenic
ATK	-Alliant Techsystems
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
COC	-Contaminants of Concern
CRZ	-Contamination Reduction Zone
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
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
HAP	-Hazardous Air Pollutant
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

ABBREVIATIONS (continued)

IEUBK	-Integrated Exposure Uptake Biokinetic
IOC	-Industrial Operations Command
IRP	-Installation Restoration Program
K	-Potassium
kg	-Kilogram
L	-Liter
lb	-Pound
m^3	-Cubic Meter
MCES	-Metropolitan Council Environmental Services
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 Health and Safety
OSHA	-Occupational Safety and Health Administration
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
PTO	-Power Takeoff
PVC	-Polyvinyl Chloride
QA	-Quality Assurance
QC	-Quality Control
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
Sb	-Antimony
SDWA	-Safer Drinking Water Act

ABBREVIATIONS (continued)

SZ	-Support Zone
TCAAP	-Twin Cities Army Ammunition Plant
TCE	-Trichloroethylene
TCLP	-Toxicity Characteristic Leaching Procedure
TDP	-Technology Demonstration Plan
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
VOA	-Volatile Organic Analyte
VOC	-Volatile Organic Compounds
WZ	-Work Zone
Zn	-Zinc

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 dissolve. 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.

The phytoremediation technique being 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 die, due to excessive lead uptake, the shoots are harvested and the plants smelted using a standard smelting technique.

The expected benefit of the technology is 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) is funding 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, provide a clean site and normally avoid future liability and restrictions to site use. As discussed in Section 6.0, phytoremediation is believed to be among the lowest cost options.

1.2 Official DoD Requirement Statement

The DoD requirement statements being addressed, as stipulated in the Army Environmental Requirements and Technology Assessments (AERTA) documents, 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

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. 2] Four pillars are described for managing environmental problems. The cleanup pillar which this project addresses has three objectives:

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

This project is aimed at the second objective. 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: Inorganic and heavy metal contamination occurs 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 treatment of metal-contaminated soils. This program will develop such technologies.

This project is directly aimed at providing a cost-effective method for treating lead contamination in soil. It provides a means of removing lead from the soil, not just isolating the contamination. 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 is 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 is being conducted in two 0.2-acre (90-ft by 90-ft) plots. The two plots have different concentrations of lead contamination in the soil representing use of phytoremediation in two different stages of site cleanup.

The demonstration is taking place at the Twin Cities Army Ammunition Plant (TCAAP) in Arden Hills, Minnesota. The project is being 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 Industrial Operations Command (IOC) is assisting the USAEC by providing sites containing lead-contaminated soil at TCAAP. TVA provides environmental and scientific expertise, research, and technology demonstration. In particular for this project, TVA is providing 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, conducts day-to-day field demonstration site operations.

The project is being executed in six 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.

- Demonstration Plan Development (Phase 2) - During this phase, the Technology Demonstration Plan was developed, written, reviewed, and approved.

- 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. This interim results report with preliminary implementation guidance has been issued at the end of this phase to document results and provide planning for future implementation.

- 1999 Field Demonstration (Phase 5) - This phase will consist of a second demonstration of the use of two crops in a growing season.

- Final Report Writing (Phase 6) - During this phase, the final results document will be written using the preliminary implementation guidance document developed in Phase 4 and the Final Report will be reviewed, approved, and published. The final implementation guidance document will be included in the document.

This project began on October 7, 1997, when TVA began to implement site selection procedures (Phase 1). During Phase 1, lead-contaminated soil samples were collected from two sites located within TCAAP. 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 a demonstration plan could be devised. Development of the Demonstration Plan was initiated on December 15, 1997, (Phase 2).

Upon approval of the 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. The soil at Site C contained lead concentrations in the range of 1,300-8,000 parts per million (ppm). The demonstration conducted within Site C is 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, is 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 is considered to be important because the effectiveness of a phytoextraction technique can vary with soil lead concentration. Consequently, it is 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 are being conducted over a two-year period. These periods are referred to as the 1998 Demonstration (Phase 4) and the 1999 Demonstration (Phase 5). Two crops are being planted within each demonstration year: a warm season crop and a cool season crop. All crops will be harvested. This interim results document with preliminary implementation guidance is being issued as part of the 1998 Demonstration (Phase 4). The final results document, including the final implementation guidance, will be written and issued in a separate phase (Phase 6).

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 provides 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 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

Currently, phytoremediation techniques are being investigated for potential use at DoD sites. In the mid-1990s, the USAEC became interested in phytoremediation methods after private-sector laboratory studies and field trials suggested that the technique could become a cost-efficient means of remediating metals-contaminated soils (see Tables 1-1 and 1-2).

In 1997, 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 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. 1]

Specific findings of the greenhouse study[ref. 1] are:

- Amending the soil with chelates, or chelates in conjunction with soil acidification, to a pH of 5.5 increased lead concentrations in corn and white mustard 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.

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 is being 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 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% Zinc (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 is being 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]

- 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 that ethylenedinitrilo-tetraacetic acid (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.

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 3,000-4,000 ppm range. Lead concentrations are reduced by 200 to 700 mg lead/kg soil per year. Treatment at higher concentrations is technically feasible; however, the time required to achieve complete remediation may be excessive.

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 other remediation methods, phytoextraction techniques allow for the extraction and recovery of metals *in situ*; mechanical removal of the soil is not 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 ethylenedinitrilo-tetraacetic acid (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 adapted to 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

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

Sites with soil lead concentrations less than 3,000 to 4,000 mg ionic lead/kg soil are the most suitable for phytoextraction, since this type of site could be remediated within several years. Phytoextraction may be used to remediate soil containing lead concentrations greater than 3,000

to 4,000 mg lead/kg soil without interfering with plant growth. However, the expected reduction in soil lead ranges from 200 to 700 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 to leach lead 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).

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. 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.

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 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.

Relative to other remediation technologies, phytoextraction methods have a number of advantages. These 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.

2.3 Factors Influencing Cost and Performance

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

- Soil 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 Characteristics
  - Contaminants
  - Ambient Temperatures
  - Geology and hydrogeology
  - Cleanup levels

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. Additionally, applied chelate and inorganic contaminants solubilized by the chelate may be subject to leaching. Leaching may move contaminant of interest beyond root interception zone of remediation crop and uptake by crop may be reduced. 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. 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. 2. Fast in sand. May result in too rapid downward movement of amendments and reduced contact time with roots--reduced treatment effectiveness. 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. 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 leaching rates. May limit usefulness of suction lysimeters as monitoring tool for solubilized metals in leachates. 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. 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. 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 3,500 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 200 to 700 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 leaching 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 leaching 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.

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 sandier than those used during the Sunflower greenhouse study and, therefore, more prone to potential leaching.
- 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 was two to six feet below the surface, whereas 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 demonstrations 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 and tended to thoroughly review project plans, as well as provide constructive input.

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 Industrial Operations Command (IOC). The IOC was formed on October 1, 1995, and has its headquarters at the Rock Island Arsenal, Rock Island, Illinois. IOC is a major subordinate command of the U.S. Army Materiel Command. TCAAP is in modified caretaker status.

From 1941 to 1976, the mission of Twin Cities 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, Twin Cities today is in modified caretaker status. This means that there is no active Army production activities

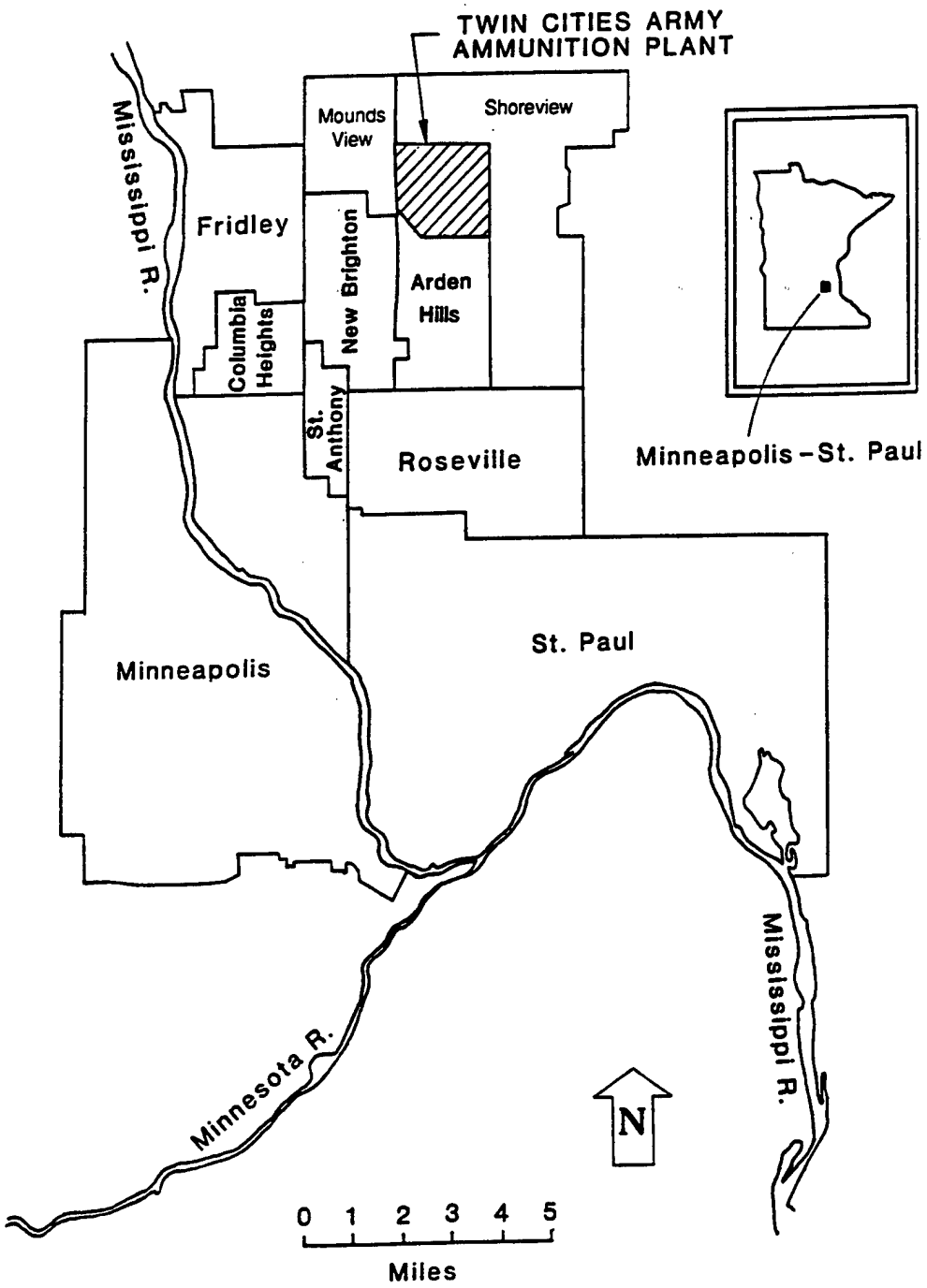


Figure 3-1

Location of TCAAP in the State of Minnesota

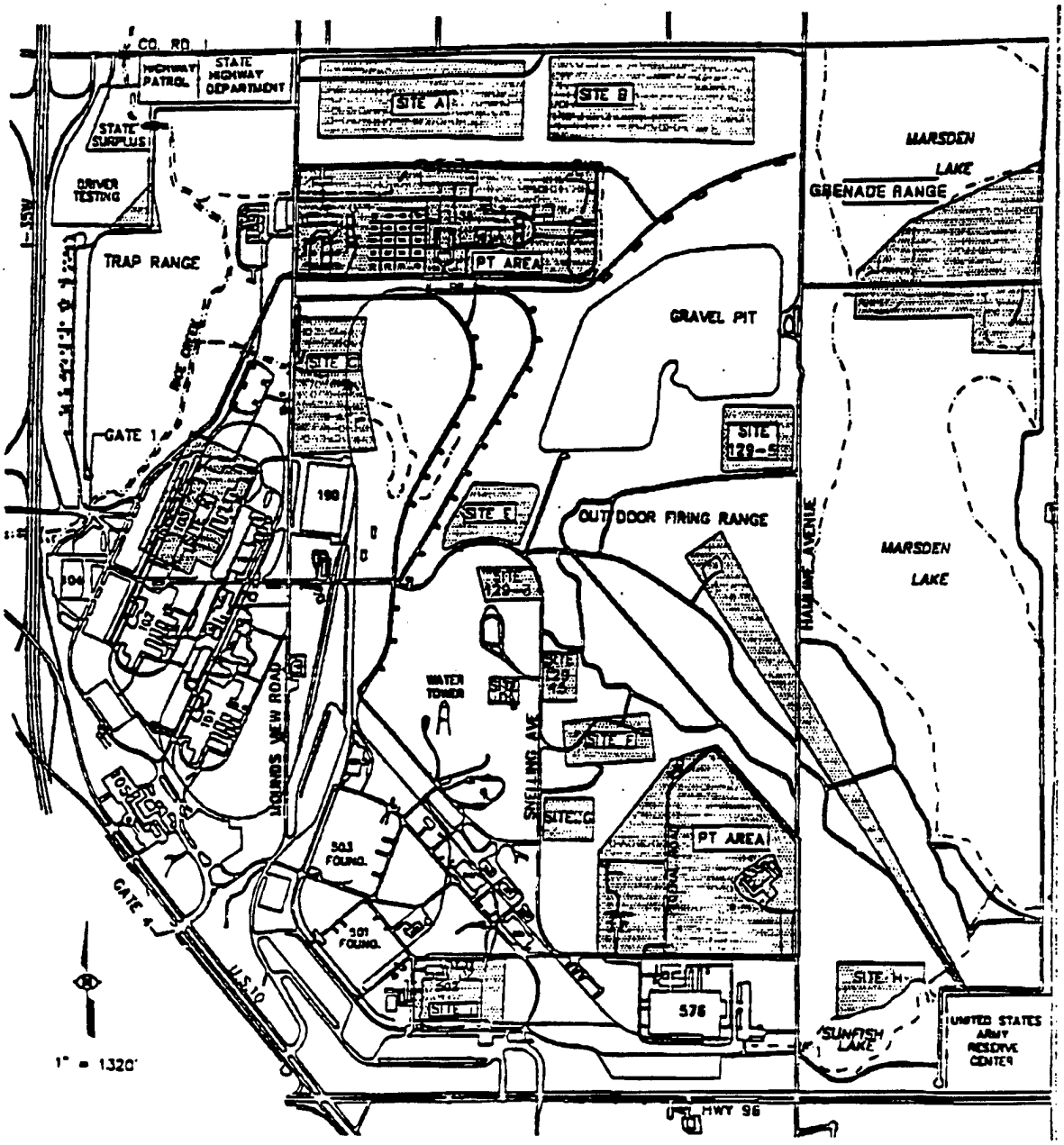


Figure 3-2

TCAAP Boundaries and Potential Contaminant Sources

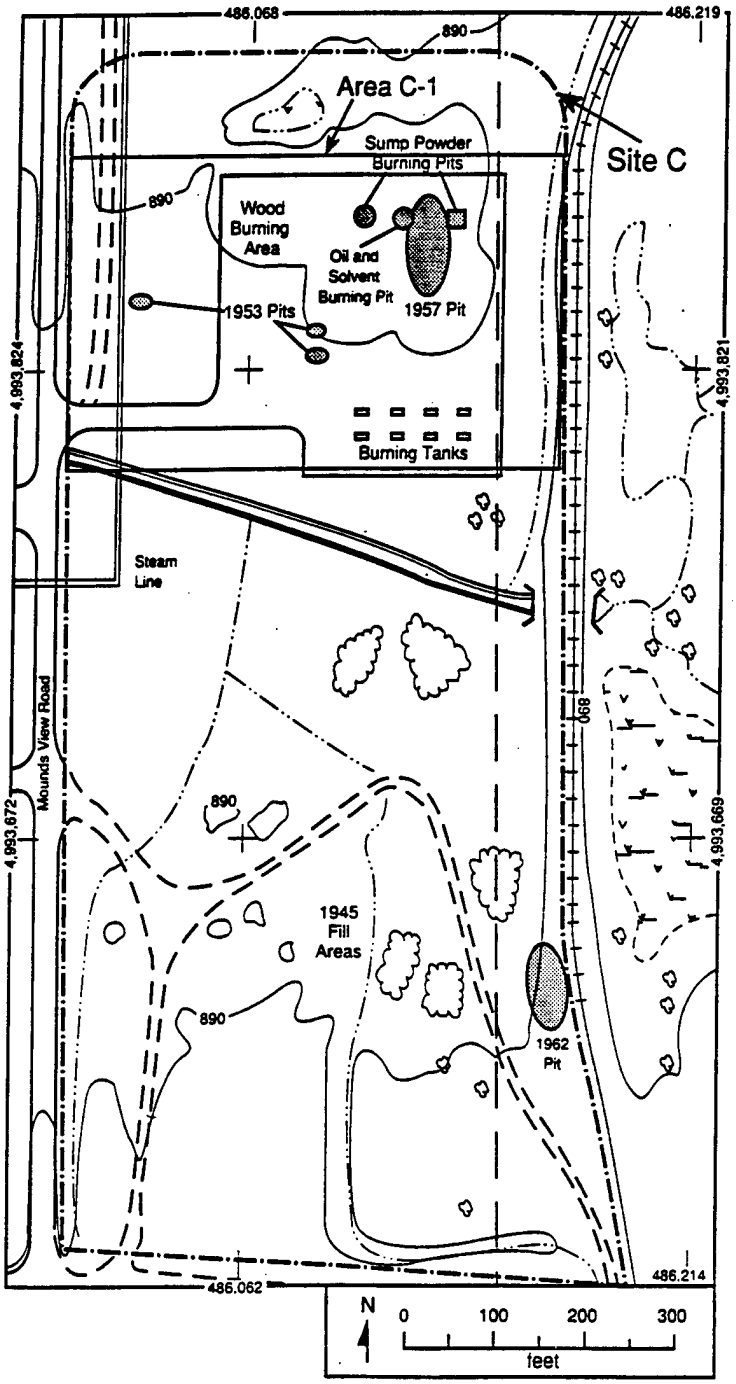


Figure 3-3

Layout of Site C

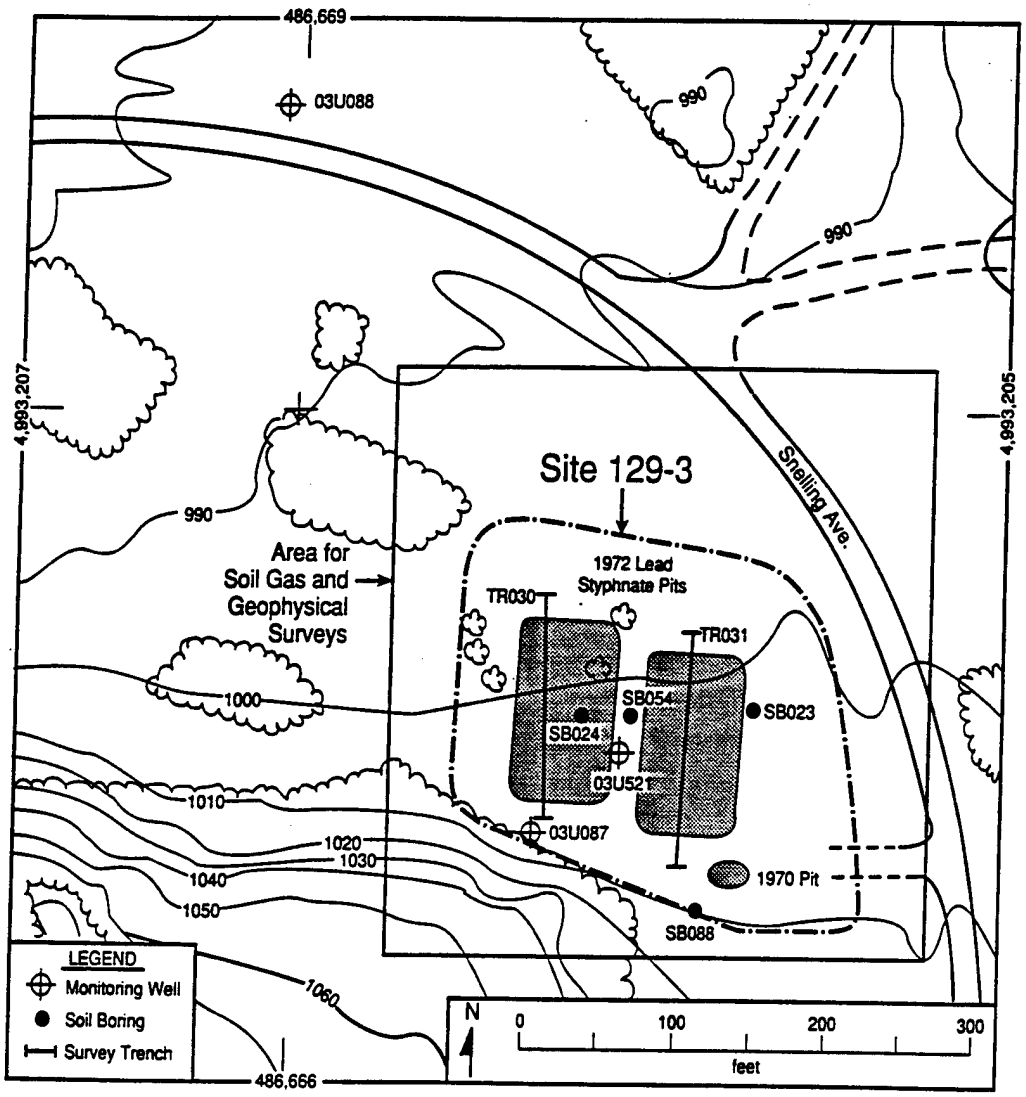


Figure 3-4

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. Department of Defense (DoD) contractor Alliant Techsystems Inc. (Alliant) is such a tenant that also currently serves as the Installation Support Services contractor. In addition, Twin Cities serves as host to the U.S. Army Reserves and the Minnesota National Guard. Twin Cities has focused its attention on the mission of environmental cleanup and is implementing its comprehensive environmental cleanup program under the Comprehensive Environmental Response, Compensation, and Liability Act (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 IOC.

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 is the facility installation support services contractor. ATK also operates production facilities on TCAAP property for DoD production contracts. The property was declared excess by IOC 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 Pit 1962, 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 Pit 1962.

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 Pit 1970 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°F. Monthly highs average 83°F in July with the highest recorded temperature being 105°F. The area experiences an average of 15 +90°F days per year. Monthly lows average 2°F in December with the lowest recorded temperature being -34°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 to the northwest.

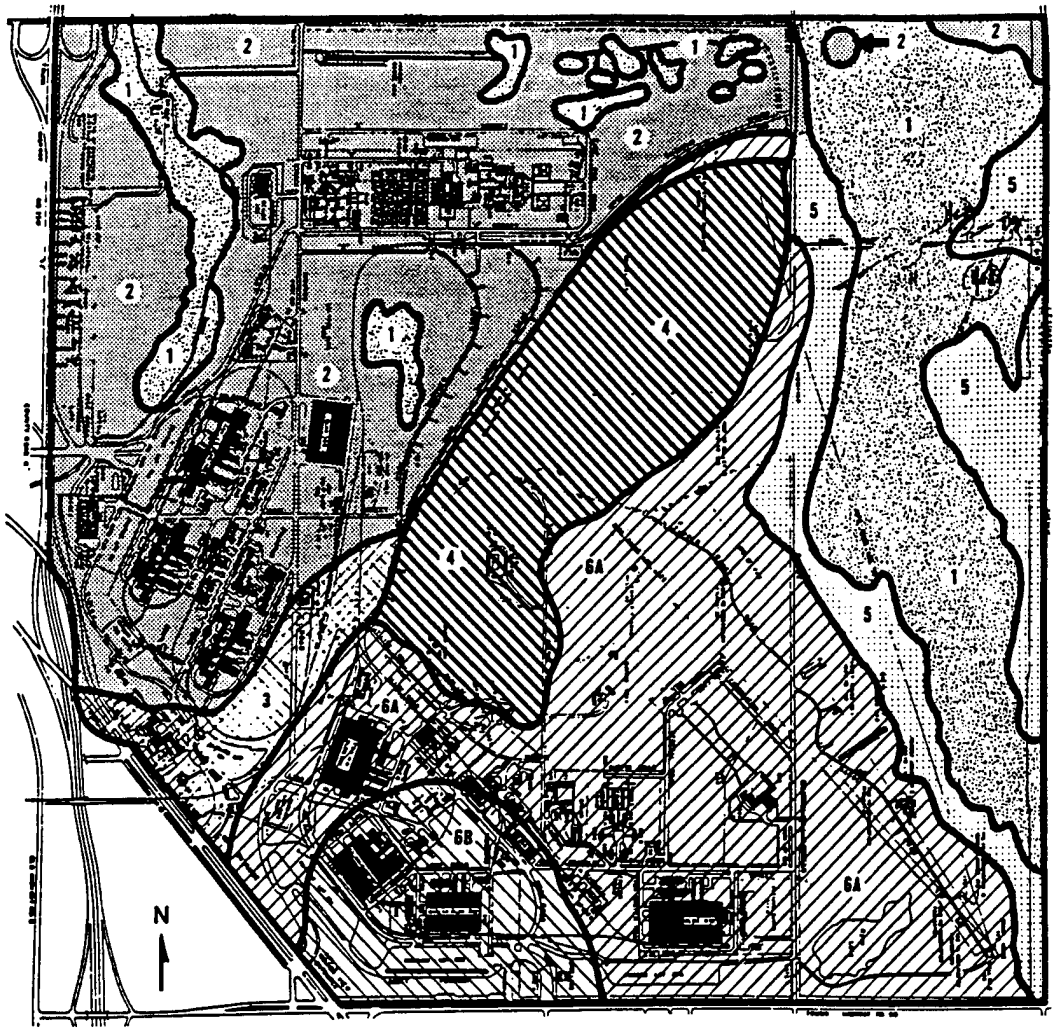
3.2.2 Regional and Local Geology

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-foot-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.

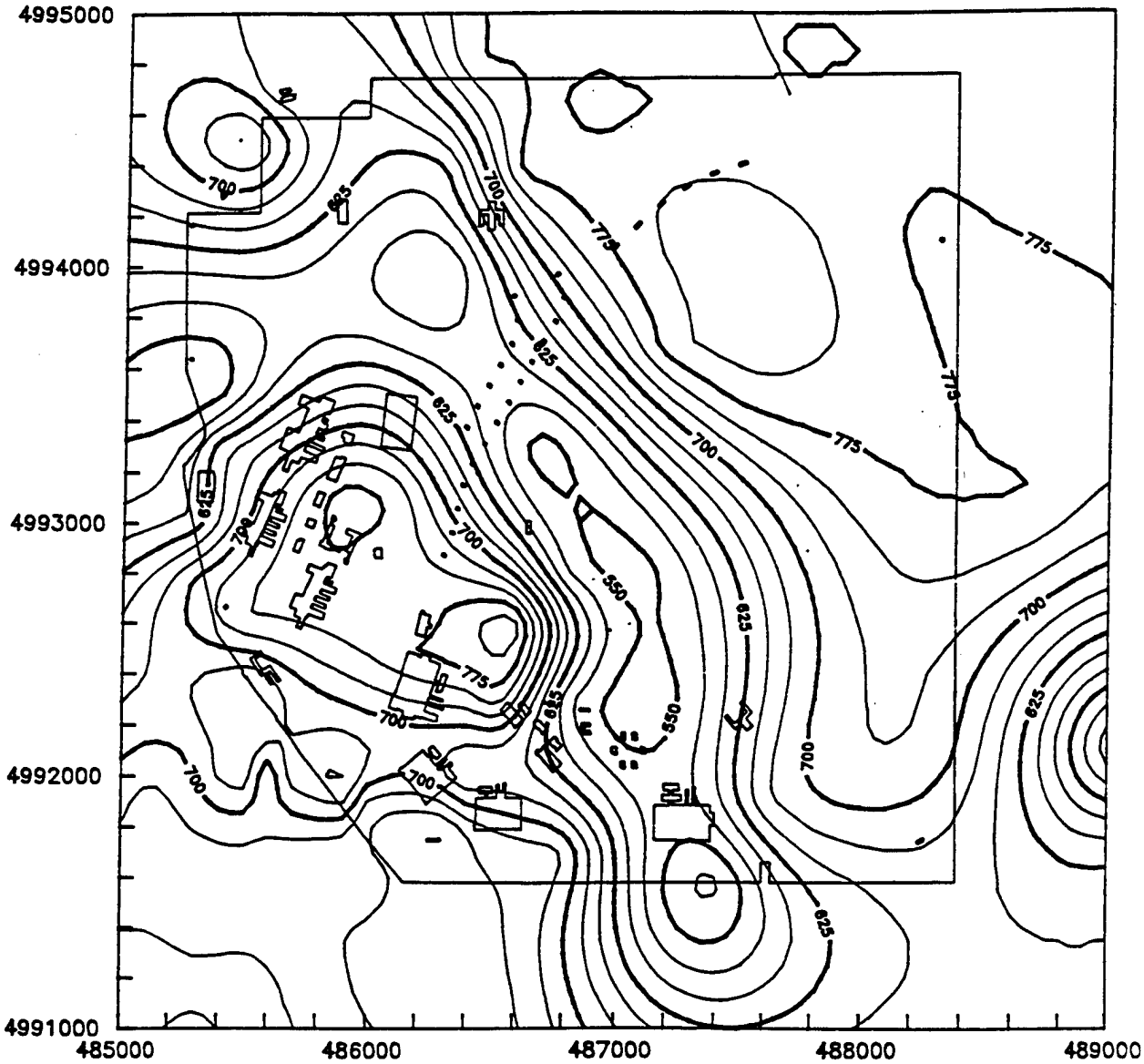


Figure 3-6

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 ranges from two to six 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 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 current 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 Pit 1962, 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 OlUO85, which is located within the burning area. No sign of contamination was detected in wells OlUO45 and OlUO46, 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 03UO25 and 03UD83) indicates that contamination may originate from other up-gradient 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

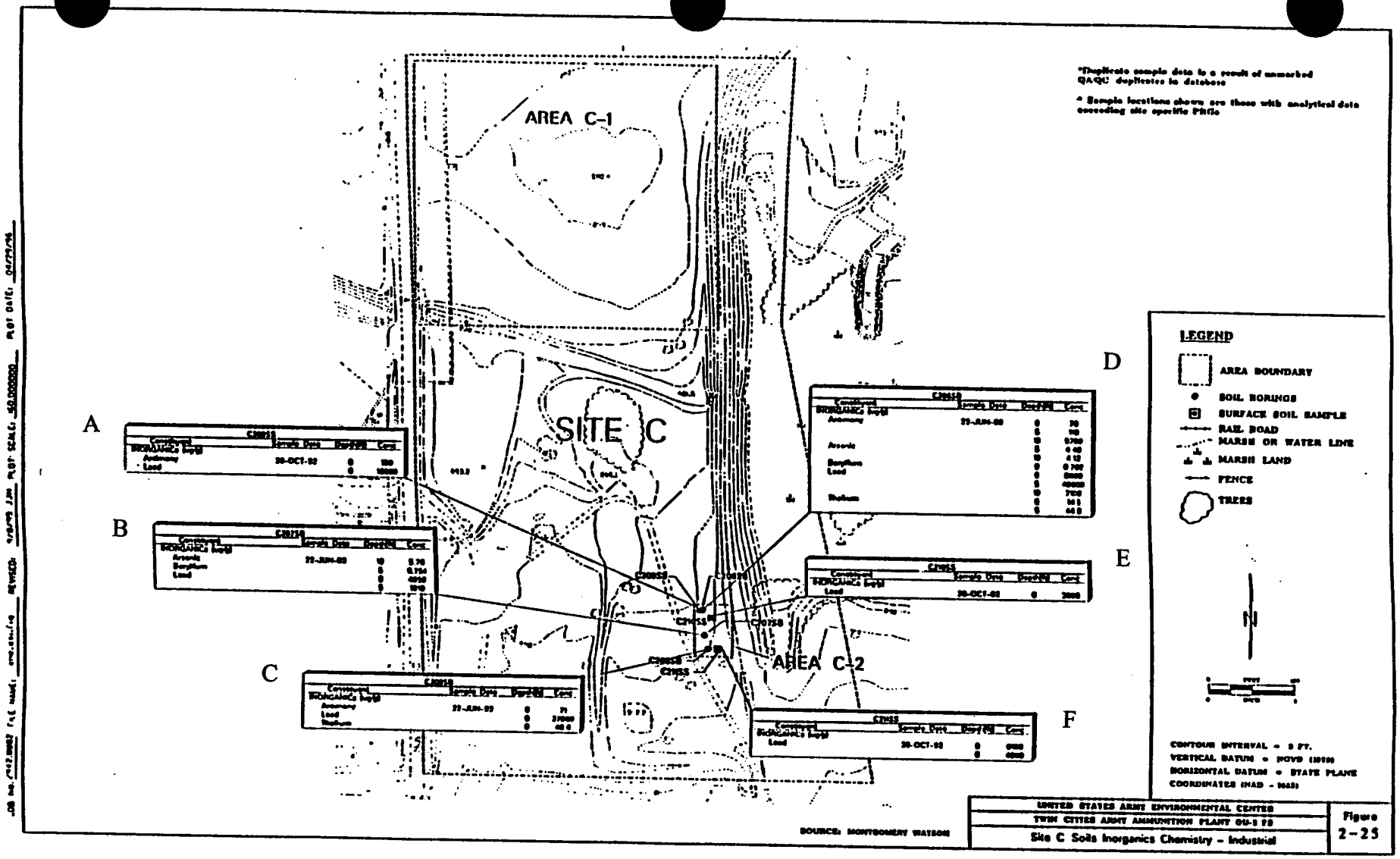


Figure 3-7

Inorganic Contamination at Site C

Table 3-1

Inorganic Contaminates 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.

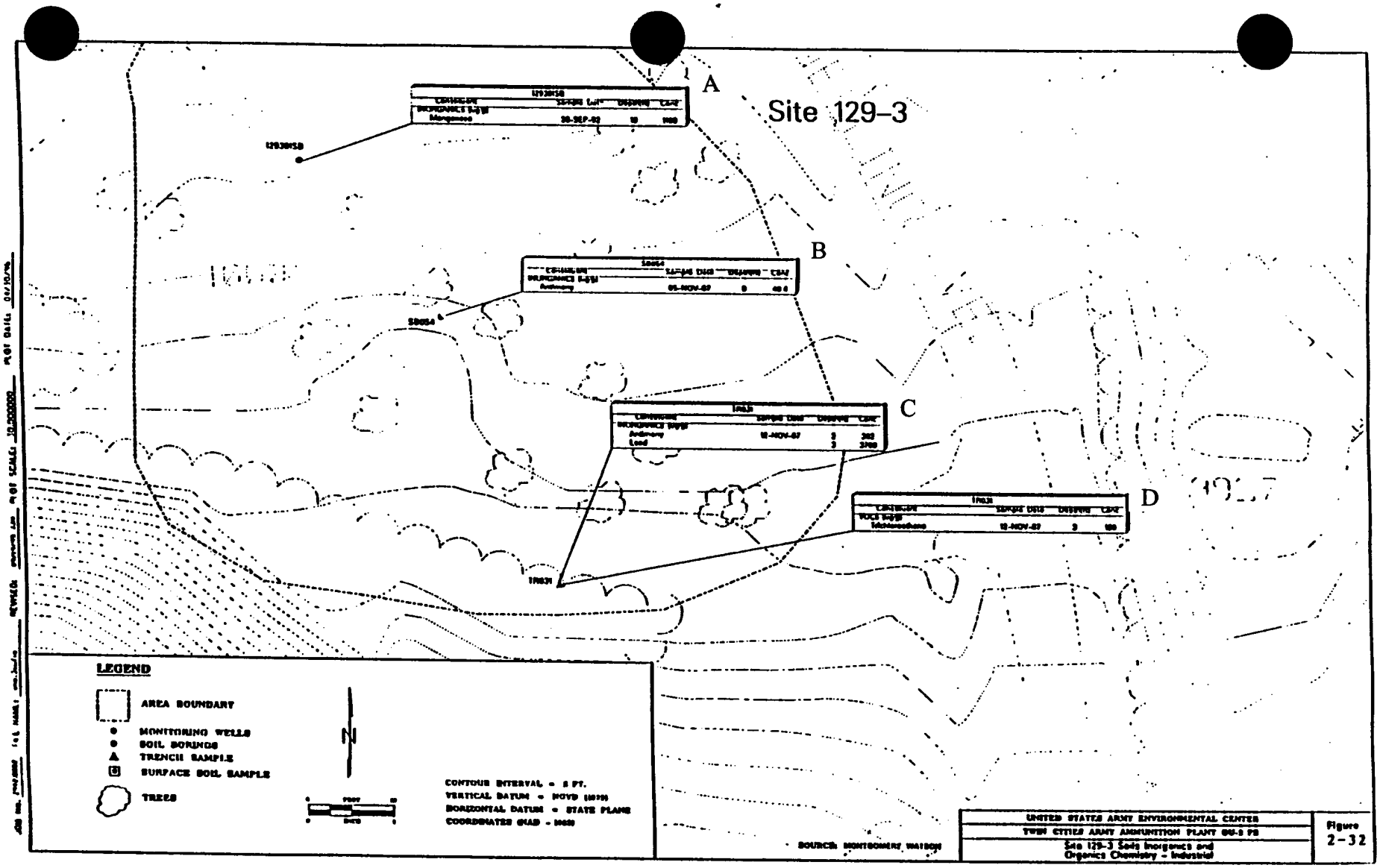


Figure 3-8

Inorganic Contamination at Site 129-3

Table 3-2

Inorganic Contaminates 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.

moisture, pH, and conductivity; it is difficult to predict the mobility of metals in the unsaturated soil layer.

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.

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Section 4.0
Demonstration Approach

4.1 Performance Objectives

The objective of this project was to evaluate the technical and economic feasibility of a particular phytoremediation technique. 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. However, the regulatory goal may not actually be met over the duration of the demonstration. 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.

- Crop total uptake of lead as calculated on the basis of aboveground total biomass production. A desired biomass production target was 6 tons per acre of corn stover prior to grain production and 2 tons per acre for white mustard. The 6 tons of corn stover per acre figure is approximately equivalent to 18 tons per acre of mature corn, including grain. These targets may not be achievable in soils of low productivity.

- 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. TCAAP Site C is to be remediated to the industrial use standard. Lead concentrations at Site 129-3 are already below the industrial use standard. The demonstration at Site 129-3 is intended to illustrate remediation at lower lead levels. (If the residential use targets were being implemented, the regulatory target would be 400 mg Pb/kg soil).

- The concentration of lead in soil solutions beneath the plant's rooting zone. A soil solution target concentration was not set. (At Site C, this may be difficult to differentiate due to elevated lead concentrations, up to 49,000 ppm, at lower (≥3 foot) soil depths.)

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

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 two-year demonstration: a corn (*Zea mays*) crop in the spring and a white mustard crop (*Sinapis alba*) in the late summer.

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]

Modified Level D protective equipment and clothing included:

1. Disposable coveralls - required for all field operations where soil, herbicide, insecticide, or other chemical contamination is possible.
2. Hard hat - when overhead or bump hazards exist.
3. Safety glasses - required at all times.
4. Protective toe and shank boots - required at all times.
5. Disposable glove liners - required for all collection and handling of water and soil samples and other work.
6. Outer nitrile gloves - required for all collection and handling of water and soil samples and other work.
7. Disposable outer boots or covers - required in areas of contaminated surface soil or water.

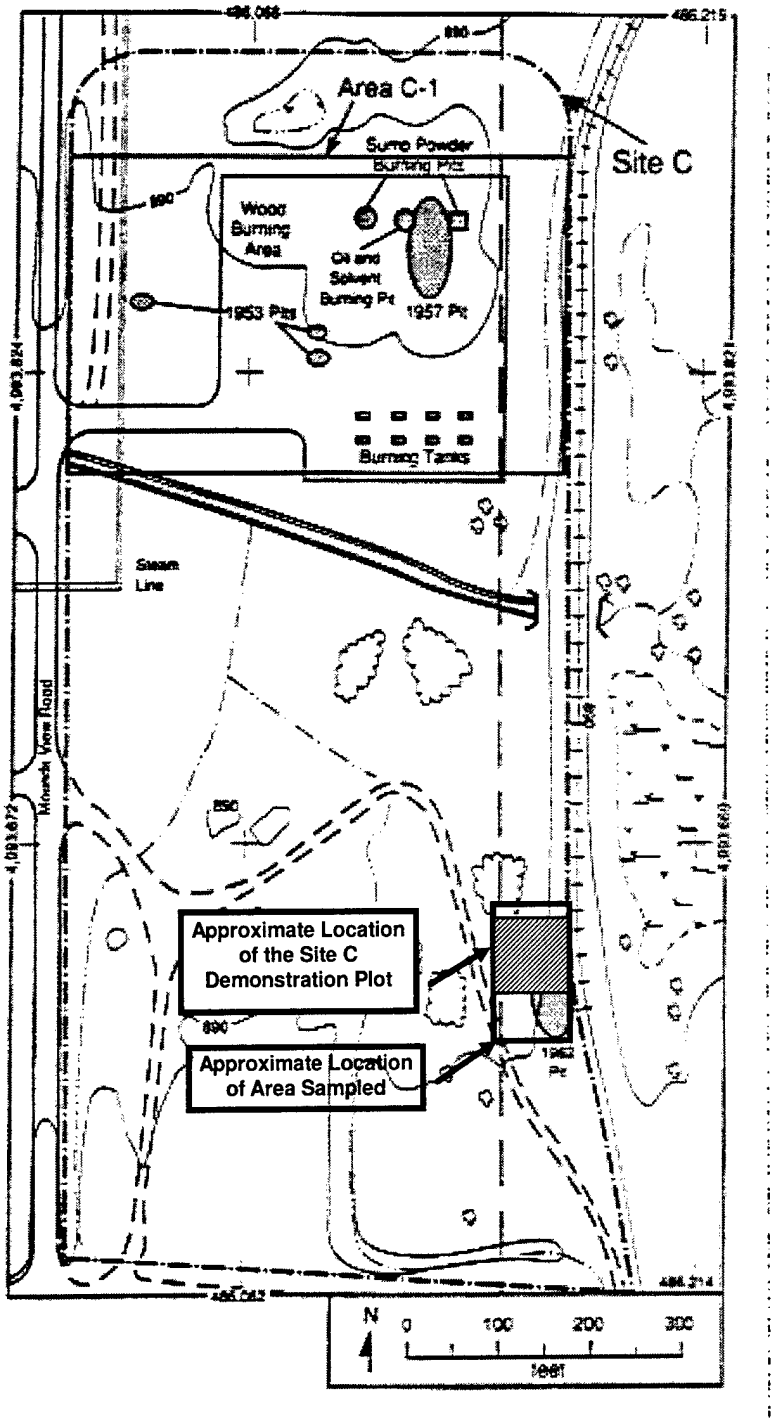
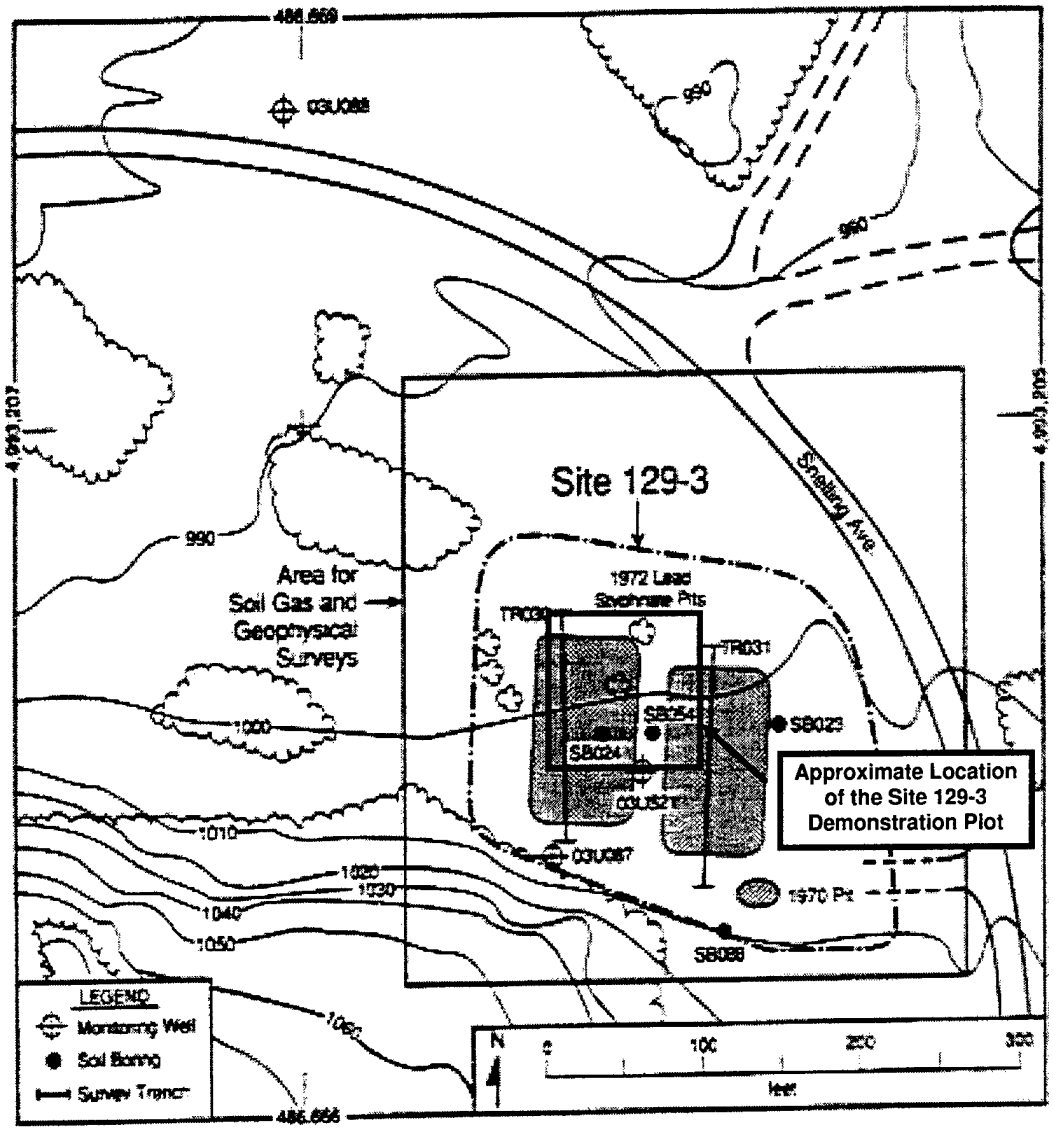


Figure 4-1

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

Level C protective equipment and clothing included:

1. Disposable coveralls - required for all field operations where soil, herbicide, insecticide, or other chemical contamination is possible. Coveralls are coated with Saranex™ for splash protection.
2. Half mask face air purifying respirator - National Institute for Occupational Health and Safety (NIOSH)-approved respirator fitted with appropriate cartridges, usually a combination of cartridge acid gas/organic vapor/high efficiency particulate (HEPA) will be used. This cartridge is good for lead-contaminated soil dust, pesticide mist and vapor, and acetic acid mist and vapor.
3. Hard hat - when overhead or bump hazards exist.
4. Safety glasses - required at all times.
5. Protective toe and shank boots - required at all times.
6. Disposable glove liners - required for all collection and handling of water and soil samples and other work.
7. Outer nitrile gloves - required for all collection and handling of water and soil samples and other work.
8. Disposable outer boots or covers - required in areas of contaminated surface soil or water.

4.2.2 Site Characterization

Prior to beginning the demonstration, TVA and ATK 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 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 only (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 (Table 4-2). The analytical methods used are listed in Table 4-10 (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.

Table 4-1

Chemical Analyses for the Initial Soil Characterization Work

Sample Type	Minimum Sample Size[1]	Parameter Measured
Soil	12 grams	pH 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.

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. 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 4-10 (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 4-10 (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 during this period included:

- 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)

ATK personnel conducted these tasks.

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.

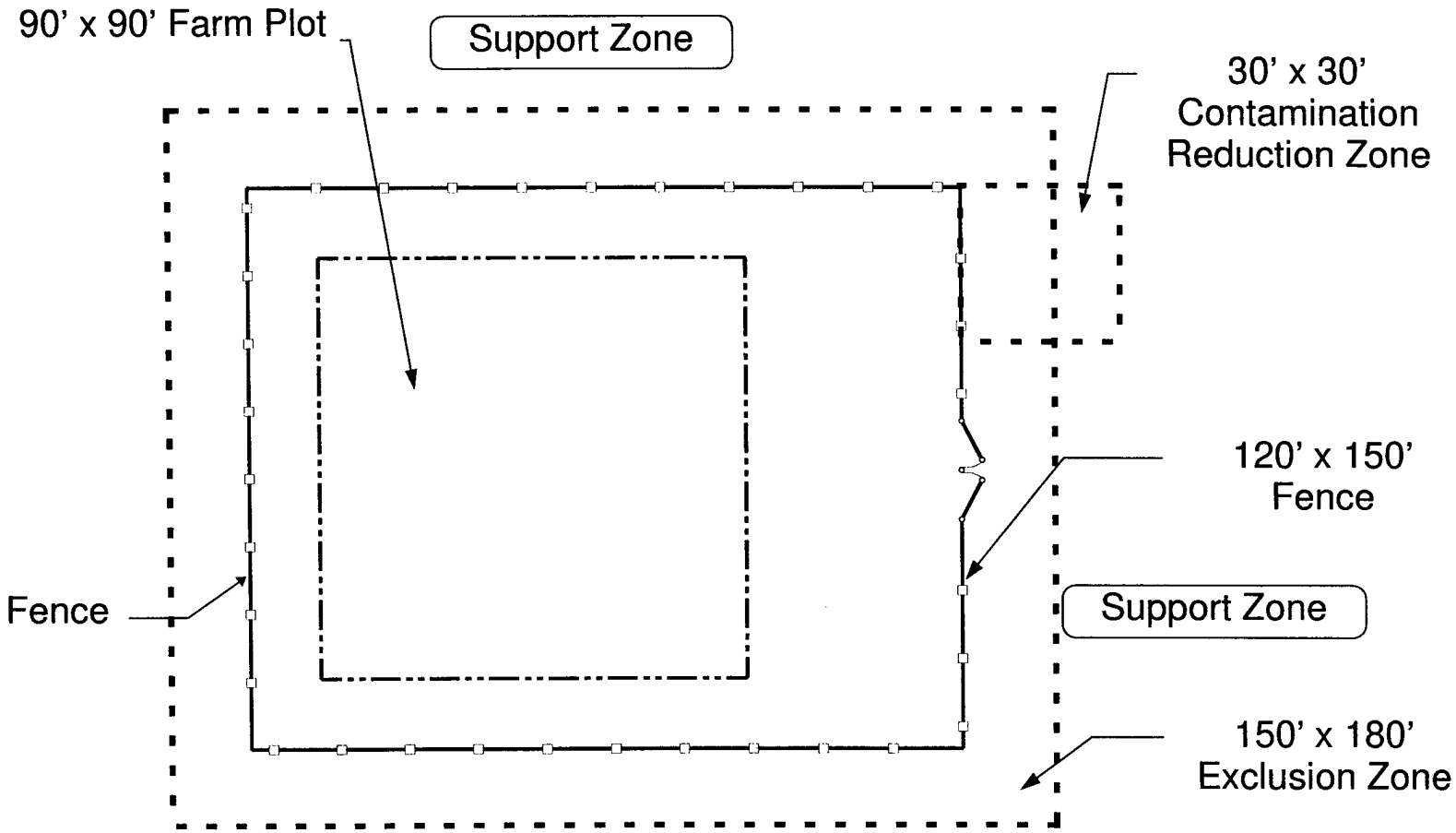


Figure 4-3

Layout for the Initial Site-Controlled Access Zones

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. Locks were provided to secure the demonstration sites. 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.

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.

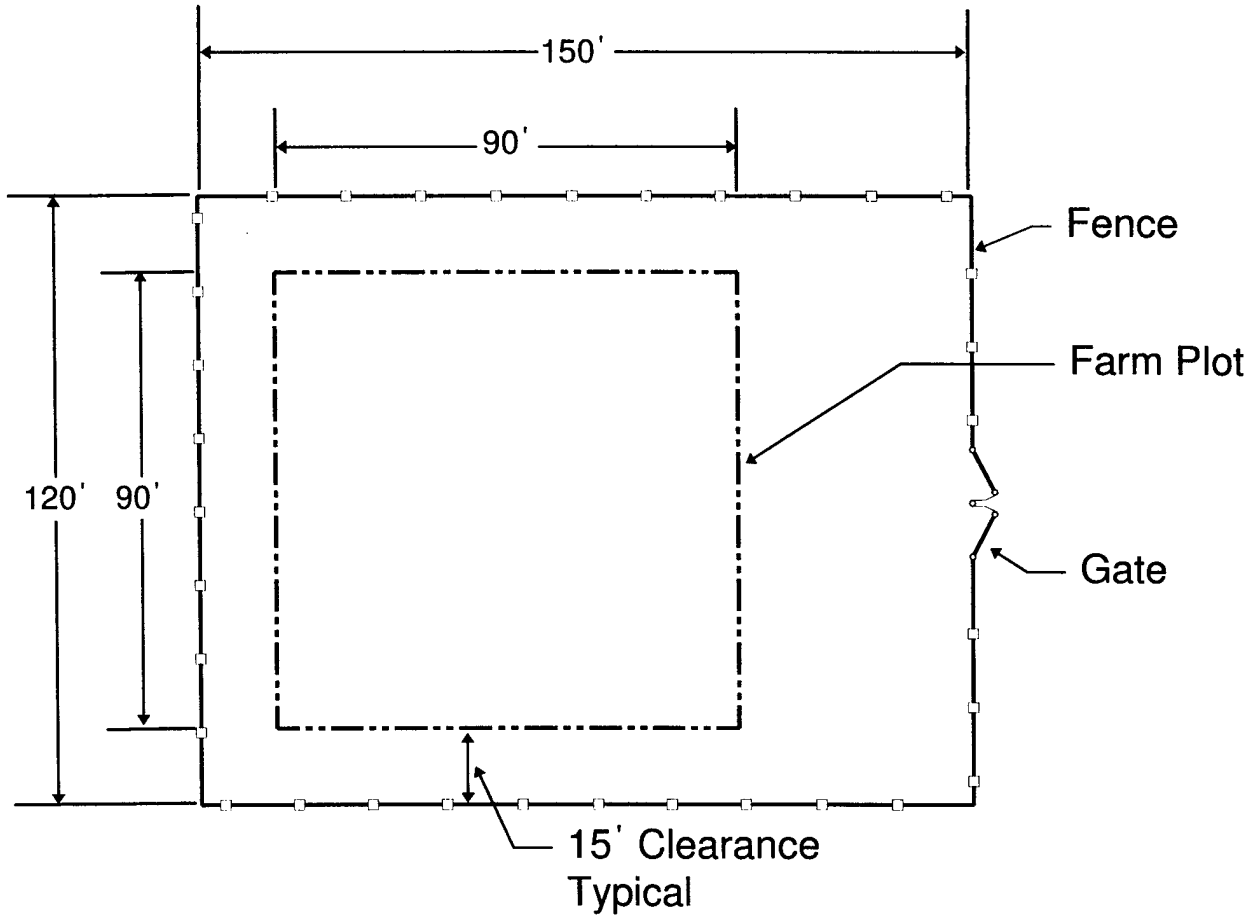


Figure 4-4

Layout of Demonstration Sites

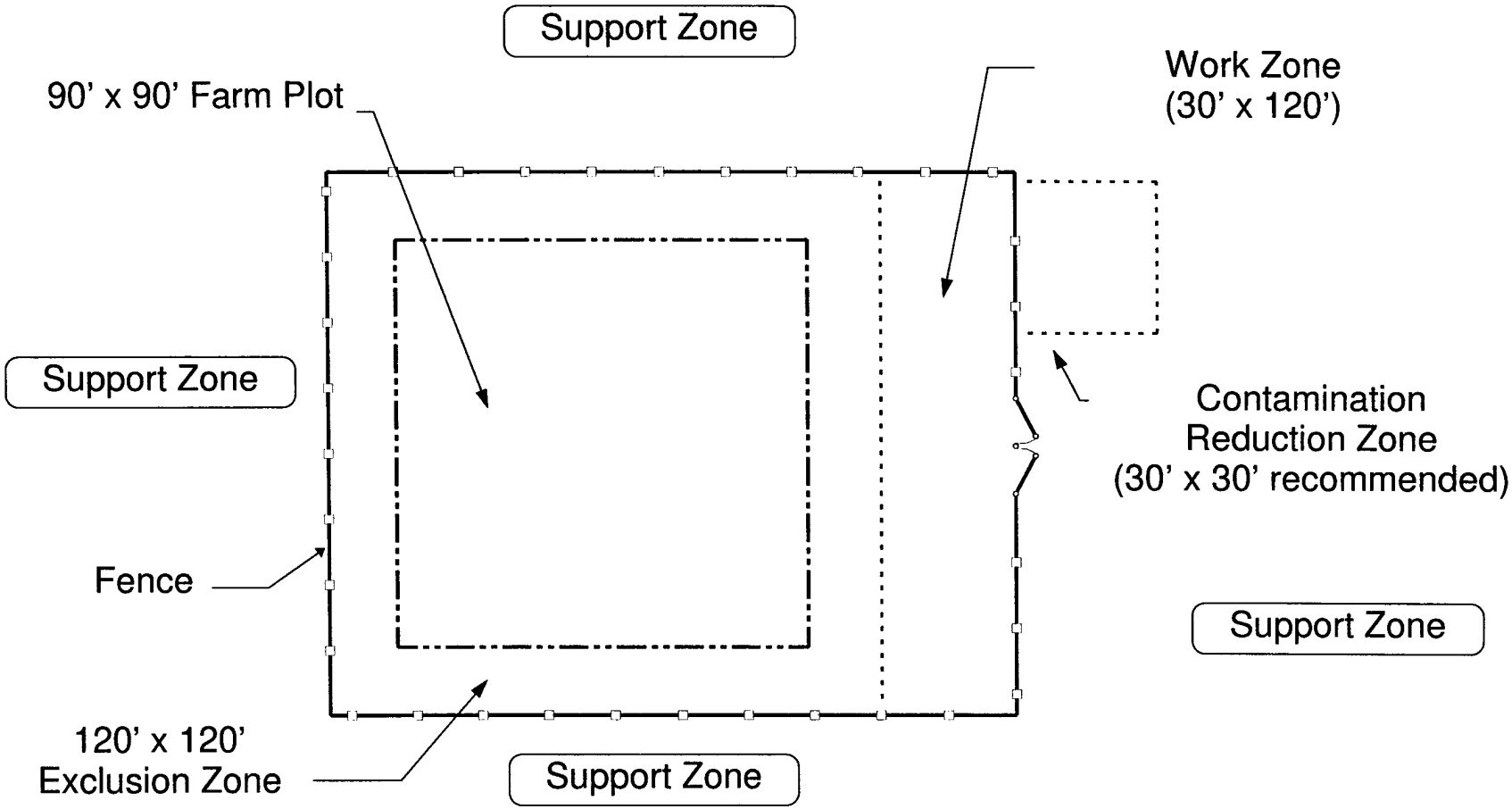


Figure 4-5

Layout for the Final Site-Controlled Access Zones

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 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 necessary to meet 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 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

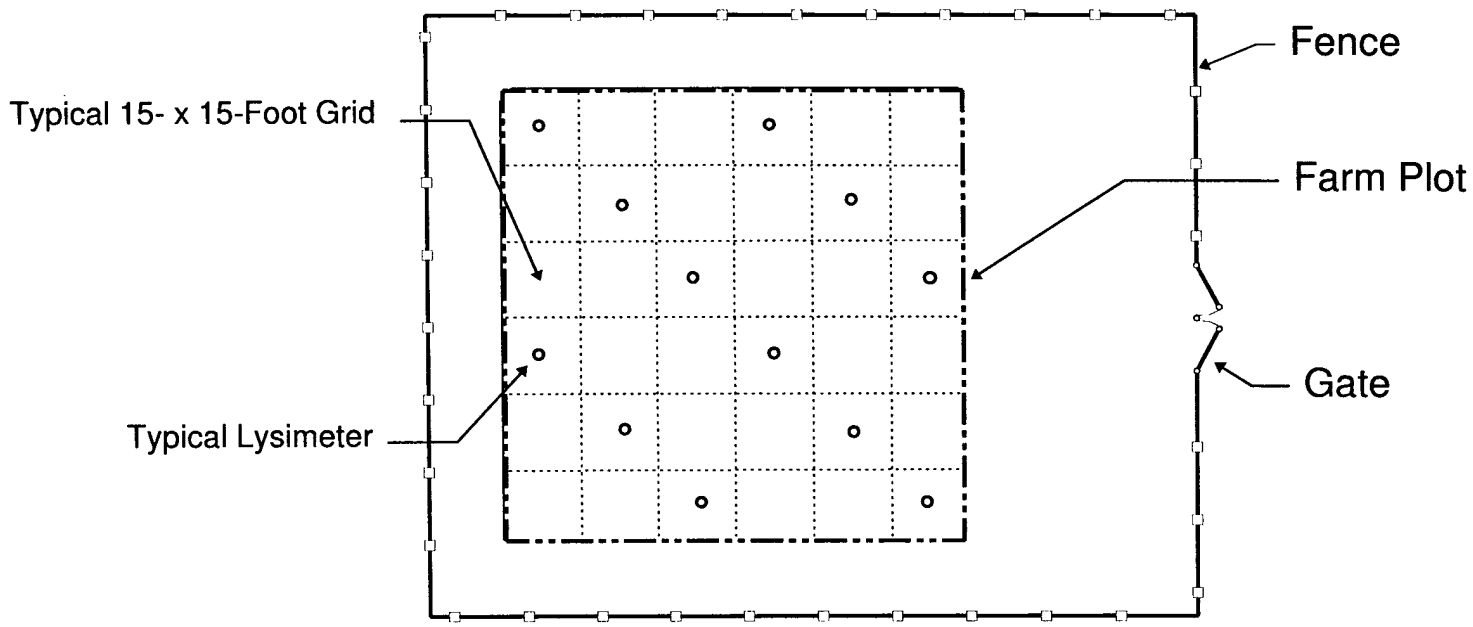


Figure 4-6

Position of Lysimeters in a Soil Solution Monitoring System

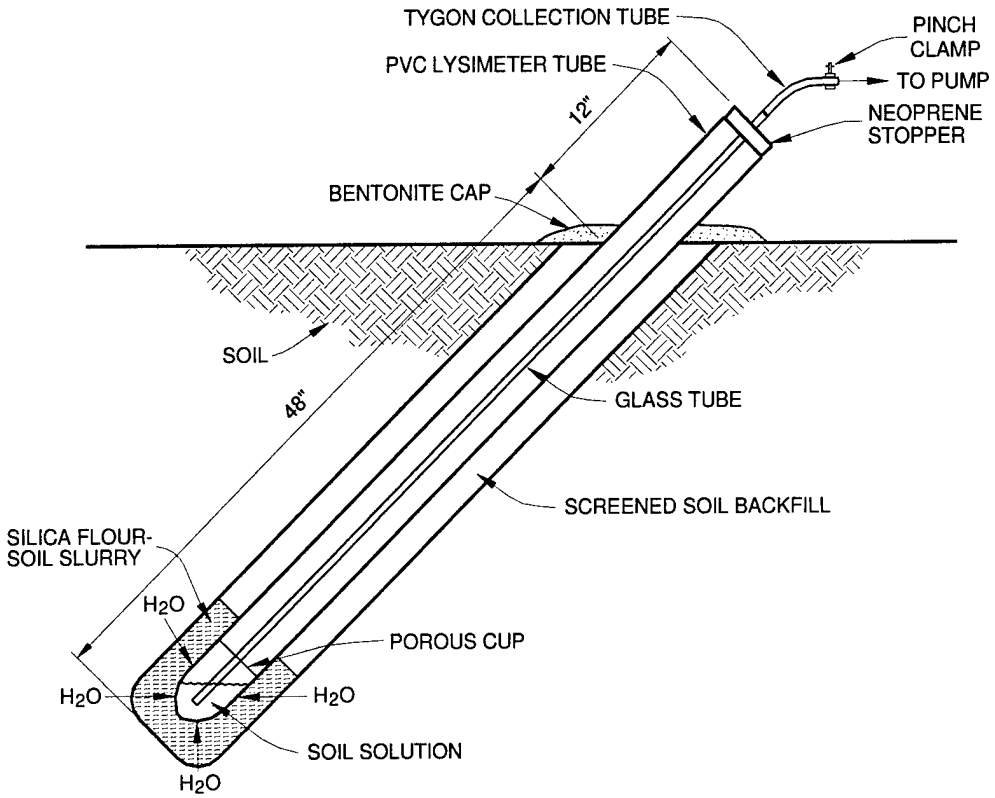


Figure 4-7

Diagram of a Lysimeter

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.

During the warm and cool growing seasons, soil solution was collected when possible from the soil solution monitoring systems under Sites C and 129-3. A description of the water-sampling procedure is provided in Section 4.3.2.2. Soil solution sampling began three weeks before the chelate was added to each crop. For four weeks after this point, the lysimeters were sampled after the first significant rainfall of each week. A significant rainfall was defined to mean any 24-hour rainfall event exceeding 0.25 inch of rain. If soil solution was present, samples from the sites were analyzed for heavy metals and chelate. Repeated attempts were made to collect enough sample from the designated lysimeter to analyze for trichloroethylene; however, these attempts failed. A previous soil analysis taken from the area where trichloroethylene was reported was reported in the remedial investigation showed trichloroethylene was not present.

The lysimeters were installed using Level C PPE until air monitoring showed that Level D PPE was appropriate. The air monitoring samples 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 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 that purpose. 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 setting up the decontamination equipment and disposing of the residuals produced. 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 subset of the TCAAP installation-wide Health and Safety Plan.[ref. 22]

4.2.4.2 Crop Planting

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

Tasks accomplished during the planting periods included:

- Tilling the 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 leaching of unused fertilizer. 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 are 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.

4.2.4.3 Crop Tending

Tasks accomplished during the crop-tending periods included:

- Inspecting the crops
- Cultivating soil and weeding (corn crop only)
- Applying pesticides, fungicides, or 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 would have consulted with TVA on the need to apply pesticides, fungicides, or herbicides if inspection of the corn and white mustard crops indicated the presence of predatory insects, fungi, plant diseases, or persistent weeds. None of these were required during the growing season. Had pesticides, fungicides, herbicides, etc., been needed, these would have been manually applied using a hand sprayer and would have been applied on a post-emergent basis (i.e., after plant germination and stand establishment). For broadleaf weed control in corn, 2,4-D (dichlorophenoxyacetic acid) was specified at a rate of 0.25 pound per acre (0.46 pound per plot). For grass control in corn, Accent (nicosulfuron) was specified at a rate of 0.67 ounce per acre (0.12 ounce per plot). No weed control measures were specified for white mustard. For general spectrum insect control, Malathion or Dursban insecticides were chosen. Microthiol (micronized wettable sulfur), at an application rate of 5 pounds per acre (0.92 pound per plot), was the fungicide of choice for white mustard. A fungicide was not specified for corn. Level C PPE was specified for all pesticide, herbicide, and fungicide applications. ATK personnel would have been responsible for applying these chemicals. Upon completion of these

activities, all tools and equipment would have been decontaminated in accordance with TCAAP's installation-wide Health and Safety Plan.[ref. 22]

The second half of the split fertilizer application for corn was conducted four weeks after planting the corn crop. The fertilizer was applied in a manner identical to that described above for fertilization during planting (Section 4.2.4.2). 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.

4.2.4.4 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.

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. 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. 1] 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. At Site C, the EDTA application rate was 6,750 pounds for corn and 3,375 pounds for white mustard. 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 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. The soil amendments were applied by TVA and ATK personnel.

4.2.4.5 Crop Harvesting and Processing

After senescence, the corn and white mustard crops were sampled for analysis of lead and other contaminants of concern (see Section 4.3.2.1), then the entire crop was harvested for processing. In addition to lead, contaminants of concern at Site C included arsenic (As), beryllium (Be), manganese (Mn), antimony (Sb), and thallium (Tl). Contaminants of concern 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. The crop weight was expected to drop approximately 50% during the drying process. 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, 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.

4.2.4.6 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.

4.2.5 Demobilization and Site Restoration

Since the demonstration will be continued for a second year, no demobilization activities were conducted at this time.

4.2.6 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 of this project 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 heavy metals, trichloroethylene, or chelate leaching occurred at depths below the plant root structures during the demonstration period.

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 remaining two objectives are documented here since they are indicators of system performance. For the purpose of this document, the last 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. A listing of the characteristics to be monitored to meet these objectives is provided in Table 4-3.

To achieve the demonstration objectives, soil and plant samples were taken before and after soil amendment additions. Soil solution samples were taken from the lysimeters throughout the demonstration period and analyzed for heavy metals and chelate. A sufficient amount of sample could not be collected from the lysimeter designated for trichloroethylene analysis. The sampling and analytical tasks required to meet these objectives were conducted by TVA and ATK.

4.3.2 Experimental Design for Demonstration Phases

4.3.2.1 Experimental Design for Soil and Plant Sampling

During the 1998 demonstration, a crop of corn (*Zea mays*), followed by a crop of white mustard (*Sinapis alba*), were grown and harvested. Two 90- x 90-foot farm 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,

Table 4-3

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 two years
	Heavy metals concentration in plants before and after soil amendment additions	Total Metals (As, Be, Pb, Sb, Tl, Mn) in plant shoots		2 times/yr. for two years
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 two years
	Chelate concentrations in plants after soil amendment additions	Chelate in plants		
Document heavy metal, trichloroethylene, and chelate leaching	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

bio-available lead, other contaminants of concern (COC), moisture, and pH. The corn tissue was sampled and analyzed for lead and other COC's (Tables 4-4 and 4-5). 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 Tables 4-6 and 4-7.

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 COC's, 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 4-8.

Sampling and analysis for the 1999 growing season will be the same as executed in 1998, except soil samples will be analyzed for residual chelate prior to adding the soil amendments during the 1999 growing season for corn. An overview of the experimental design for soil and plant sampling is given in Tables 4-6 and 4-7 for the 1999 growing season. Details for the experimental design for sampling are given in Table 4-9. A listing of the methods used to conduct the chemical analyses for both years are provided in Table 4-10.

Analysis of the plant data was used to quantify the amount of lead taken up by the plants and will 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 leaching. 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 will be used to estimate the number of harvests needed to reduce the soil lead concentration to acceptable levels. The soil solution data was used to estimate potential environmental effects of the technology.

4.3.2.2 Experimental Design for Soil Solution Sampling

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 is defined here to mean 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

Table 4-4

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

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 1998 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 4-5

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

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 1998 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 4-6

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

First Growing Season (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

Second Growing Season (1999)

- 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

Grand Total: 792 samples

Table 4-7

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

First Growing Season (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

Second Growing Season (1999)

- 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

Grand Total: 396 samples

Table 4-8

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

Plot	Crop	Sampling Time	Soil pH	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 4-4	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	Natural	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 4-5	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	Natural	1:1 molar ratio of EDTA:Lead	36	2		72	36
							Total	198	99
							Grand Total	396	198

Table 4-9

Experimental Design Details for 2nd Growing Season (1999) for Soil and Plant Sampling

Plot	Crop	Sampling Time	Soil pH	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 4-4	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	Natural	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 4-5	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	Natural	1:1 molar ratio of EDTA:Lead	36	2		72	36
							Total	198	99
							Grand Total	396	198

Table 4-10

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 QuikKCEM 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.

for heavy metals and chelate. A single lysimeter at Site 129-3 was designated for collection of soil solution for trichloroethylene analysis. However, during the demonstration, the lysimeter did not produce enough soil solution to allow trichloroethylene analysis. The specific analytes for each site are listed in Tables 4-4 and 4-5. A listing of the methods for the chemical analyses is provided in Table 4-10. Details of the sampling procedures are given in Section 4.3.3.5 below.

4.3.2.3 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. Dr. Henao is a world-recognized biometrician with over 32 years experience in both parametric statistics and geostatistics. He received his Ph.D. in 1976 from Iowa State University, and spent 5 years with the Central American Program for Research and Development (CATIE) in Costa Rica, 12 years at Columbian Agricultural Institute (ICA) in Columbia, and 15 years at IFDC.

Statistical analysis of the data produced was based on the following assumptions:

1. There were two treatments (amendments). 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 determined 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.

The general model used to test the hypotheses was:

$$\mathbf{Y_{ijk} = u + p_i + \Upsilon_{ji} + \Phi_{ki} + \varepsilon_{ijk}} \quad \textbf{(Model 1)}$$

$\mathbf{Y_{ijk}}$: Lead concentration in plant (or total lead uptake)
$\mathbf{u}$: Concentration mean or uptake mean for the two sites
$\mathbf{p_i}$: Site effect
Υ_{ji}: Variability of rows within sites
Φ_{ki}: Variability of columns within sites
ε_{ijk}: Random variation assumed N (0, σ)

4.3.2.3.2 Model 2 - Changes in Soil Concentrations in Sampled Grids

Since not all grids were sampled before soil amendments were applied, Model 2 is 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 is used to determine whether the mean of the differences between soil lead concentrations before and after soil amendments is 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 Concentration 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.

$$\mathbf{Y_{ijk} = u + \psi_{ji} + \Upsilon_{ji} + \Phi_{ki} + \varepsilon_{ijkl}} \quad \textbf{(Model 3)}$$

ψ_{ji}: Variability of periods

The analysis of variance will test the variation due to sampling periods.

Orthogonal contrasts can be used to evaluate period trends or other changes in soil Pb concentration over the two-year remediation period.

The above-discussed parametric statistical analysis will provide a practical and realistic assessment of the 1998 data for the sites under the existing conditions. However, a detailed geostatistical analysis and evaluation will also be performed. This analysis will incorporate 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 will include 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). TVA will then make a comparison between the two methods of analysis to obtain the maximum benefit from the data. A detailed explanation of the theory, methodology, and results of the geostatistical analysis is presented in Appendix H.

4.3.3 Sampling Plan

4.3.3.1 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.

4.3.3.2 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.

4.3.3.3 Soil Sampling

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. 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 4-4 and 4-5). Those 15- x 15-foot grids were designated with a flag.

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 demonstration plan.

4. A field blank was collected by sampling a clean area outside the plot area in the same manner in which other samples were taken.

5. 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 4.3.4.

6. 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.

7. 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 4.3.4.

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

9. 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]

10. 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.

11. 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).

12. 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.

13. Upon drying, the soil samples were analyzed, as outlined in Tables 4-4 and 4-5. The specific analytical methods used are shown in Table 4-10. A total of 396 soil samples were taken during the 1998 demonstration year. Over the two-year duration of the project, a total of 792 soil samples will be taken (Table 4-6).

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

4.3.3.4 Plant Sampling

Plant sampling was performed primarily by TVA personnel with assistance from ATK personnel. The sampling procedure was, and will continue to be, 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 4.3.3.3).

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. 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 4-4 and 4-5). These 15- x 15-foot grids were designated with a flag.

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 4.3.4. 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 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 4-4 and 4-5. The specific analytical methods to be used are provided in Table 4-10. Over the two-year duration of the project, a total of 396 plant samples will be taken (Table 4-7).

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

4.3.3.5 Soil Solution Sampling

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

4.3.3.5.1 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 is designed so that soil solution in the porous ceramic cup at the bottom of the lysimeter will flow 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 is 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. 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 4.3.4). 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]

4.3.3.5.2 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. 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 4.3.4). 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.

4.3.4 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 (Table 4-11). 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 the plant sample was taken from (Table 4-12). 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) (Table 4-13). 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.

4.3.5 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).

4.3.6 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.

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.

Table 4-11

Sample Labeling for Soil Samples[1]

Sampling Time	Year (Date)	Site	Grids	Soil Depths
Corn - Before Soil Amendments	1998	C	1-36 (every 4th grid)	0-12" 12-24"
		129-3		
Corn - After Soil Amendments		C	1-36 (all grids)	
		129-3		
White Mustard - Before Soil Amendments		C	1-36 (every other grid)	
		129-3		
White Mustard - After Soil Amendments		C	1-36 (all grids)	
		129-3		
Corn - Before Soil Amendments	1999	C	1-36 (every 4th grid)	0-12" 12-24"
		129-3		
Corn - After Soil Amendments		C	1-36 (all grids)	
		129-3		
White Mustard - Before Soil Amendments		C	1-36 (every other grid)	
		129-3		
White Mustard - After Soil Amendments		C	1-36 (all grids)	
		129-3		

1) An example label for a soil sample taken in the first sampling period would be: 7-1-98, plot C, grid 16, 0-12 inches.

Table 4-12

Sample Labeling for Plant Samples[1]

Sampling Time	Year (Date)	Plant Species	Site	Grids
Corn - Before Soil Amendments	1998	Corn	C	1-36
			129-3	(every 4th grid)
Corn - After Soil Amendments			C	1-36
			129-3	(all grids)
White Mustard - Before Soil Amendments		White Mustard	C	1-36
			129-3	(every other grid)
White Mustard - After Soil Amendments			C	1-36
			129-3	(all grids)
Corn - Before Soil Amendments	1999	Corn	C	1-36
			129-3	(every 4th grid)
Corn - After Soil Amendments			C	1-36
			129-3	(all grids)
White Mustard - Before Soil Amendments		White Mustard	C	1-36
			129-3	(every other grid)
White Mustard - After Soil Amendments			C	1-36
			129-3	(all grids)

1) An example label for a plant sample taken in the first sampling period would be: 7-1-98, corn, Site C, grid 16.

Table 4-13

Sample Labeling for Soil Solution Samples[1]

Date	Demonstration Site	Type
day/month/yr.	Site C	Demonstration
day/month/yr.	Site C	Rinse Blank
day/month/yr.	Site C	Trip Blank
day/month/yr.	Site C	Field Duplicate
day/month/yr.	Site 129-3	Demonstration
day/month/yr.	Site 129-3	Rinse Blank
day/month/yr.	Site 129-3	Trip Blank
day/month/yr.	Site 129-3	Field Duplicate
day/month/yr.	Site C	Demonstration
day/month/yr.	Site C	Rinse Blank
day/month/yr.	Site C	Trip Blank
day/month/yr.	Site C	Field Duplicate
day/month/yr.	Site 129-3	Demonstration
day/month/yr.	Site 129-3	Rinse Blank
day/month/yr.	Site 129-3	Trip Blank
day/month/yr.	Site 129-3	Field Duplicate

1) An example label for a soil solution sample being taken from the 1998 crop for demonstration purposes would be: date, Site C, rinse blank.

4.4.2 Analytical Equipment

The equipment used for collecting laboratory data is outlined in Table 4-14. 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 spectrophotometry. 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, 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 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
Total Kjeldahl Nitrogen (TKN)	Lachat Quick Chem 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 Quick Chem 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)	NA[1]	ICP
Total Metals (As)	NA	AA
Trichloroethylene	NA	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.

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 0-6-inch depth and ranged between 1,240 mg/kg to 8,170 mg/kg. The average lead concentration at the 6-12-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. From a demonstration point of view, the soil contained lead concentrations which were just within the practical and economic limits of the technology.

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 0-6-inch depth and ranged from 6 mg/kg to 1,730 mg/kg; the average lead concentration at the 6-12-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 low-end concentrations was an important aspect of the phytoextraction demonstration, since removal of lead by plants can vary with soil concentration.[ref. 1]

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). Variability for rows and columns for both Site C and Site 129-3 were not significant, which would indicate that the lead concentrations across these two plots were homogeneous. However, this result could also occur if the variation of the grids within each row and column is large, which would give a large error

Figure 5-1

Map of Initial Lead Contamination (mg/kg) at Site C

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
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 5-2

Map of Initial Lead Contamination (mg/kg) at Site 129-3

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

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***

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, suggest 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 contaminants of concern (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 may indicate 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. This value also could be an artifact, as the presence of a considerable amount of iron scrap could have added to the iron oxide. 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 of significance. 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.

5.2.2 1998 Corn Crop - Soil Sampling

5.2.2.1 Pre-Amendment Soil Sampling - 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

Table 5-3

Characterization of Bulk Soil From Sites C and 129-3

	Site C	Site 129-3
Texture	sandy loam	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 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[2,3]	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 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.

the protons which are responsible for the decrease in pH. The reaction is as follows:

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

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 0-12-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 0-12-inch and 12-24-inch depths, respectively. In contrast, the average lead concentrations at the 0-12-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. In some cases, the higher lead concentrations in the 12-24-inch depth indicate a downward movement of lead may have occurred. Since U.S. Army records indicate that lead was surface deposited by dumping and open burning cases, the higher concentrations of lead in the 12-24-inch depth may indicate that downward movement of lead occurred naturally over time in these sandy soils, or the lead may have been moved from the surface to lower depths by tilling operations.

An average of 2 mg/kg arsenic (As) 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. 23] the concentrations reported may be of natural origin and not the result of disposal practices.

Although beryllium (Be) is listed as a Contaminant of Concern 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 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. 24] 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 (Mn) 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. 25]

Antimony (Sb) 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. 26] 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, leaching 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 leaching of antimony to the levels observed here.

Thallium (Tl) 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 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 12-24-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. 11] 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.11,29] 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. 30] 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 - 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.

By Monday, 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 effect of the application on pH, EDTA, and contaminants of concern.

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 Sunflower 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 downward to the full extent

Table 5-6

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

Grid No.	pH[1]		Water-soluble EDTA[1], mg/kg		Water-Soluble Pb, mg/kg		Pb[2,3], 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	
	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	0-12	12-24
1	NS[4]	NS[4]	NS[4]	NS[4]	268	90	15,000	8,950	6.2	3.2	1.2	1.2	249	275	<40[5]	<40[5]	92	74
2	8.3	8.0	251	130	150	97	2,870	2,210	3.2	2.6	1.2	1.2	281	210	<40	<40	99	74
3	NS	NS	NS	NS	293	114	4,550	11,800	2.3	2.9	1.2	1.2	288	204	63	<40	<50[5]	89
4	8.4	8.2	363	1,540	185	700	5,000	3,820	2.7	2.3	1.2	1.1	240	186	<40	<40	<50	<50[5]
5	NS	NS	NS	NS	780	429	2,780	3,360	5.1	3.7	1.3	1.4	324	357	<40	20	123	106
6	8.2	8.5	1,834	172	656	122	5,800	11,300	3.9	3.8	1.3	1.2	283	287	<40	<40	106	94
7	NS	NS	NS	NS	451	33	627	1,500	2.2	1.9	1.2	1.2	231	202	<40	<40	<50	64
8	8.3	8.5	655	61	295	74	4,870	8,240	2.8	3.2	1.2	1.2	225	216	<40	<40	<50	71
9	NS	NS	NS	NS	138	64	2,660	2,940	2.4	9.9	1.1	1.1	187	209	<40	<40	63	74
10	8.3	8.4	27	380	36	207	732	1,810	1.9	2.0	1.1	1.1	174	194	<40	<40	56	61
11	NS	NS	NS	NS	306	13	2,100	1,290	11.8	16.3	1.5	1.6	550	826	<40	<40	241	470
12	8.3	8.5	5,740	198	1,270	116	2,670	2,080	3.7	3.3	1.2	1.3	361	278	<40	<40	115	102
13	NS	NS	NS	NS	92	56	5,450	1,710	2.4	2.6	1.1	1.2	198	251	<40	<40	<50	71
14	8.3	8.1	543	469	256	209	3,060	2,240	2.8	2.7	1.2	1.2	218	445	<40	<40	96	66
15	NS	NS	NS	NS	449	208	5,090	6,550	2.6	2.7	<0.5[5]	<0.5[5]	211	299	<40	<40	64	62
16	8.2	8.4	743	1,020	359	506	4,680	4,880	2.5	2.9	<0.5	<0.5	214	170	<40	<40	66	80
17	NS	NS	NS	NS	811	137	2,370	5,470	9.4	9.6	<0.5	<0.5	517	528	<40	<40	188	196
18	8.2	8.5	2,380	551	761	100	2,340	1,100	4.6	3.8	<0.5	<0.5	267	307	<40	<40	107	107
19	NS	NS	NS	NS	54	51	3,490	4,860	2.4	2.5	<0.5	<0.5	179	379	<40	<40	<50	53
20	8.4	8.5	1,280	517	563	179	2,870	5,570	2.2	3.3	<0.5	<0.5	182	215	<40	<40	<50	64
21	NS	NS	NS	NS	496	58	3,390	3,620	2.6	4.1	<0.5	<0.5	210	319	<40	<40	58	64
22	8.3	8.3	235	19	129	44	3,980	3,130	3.5	2.5	<0.5	<0.5	421	241	<40	<40	71	60
23	NS	NS	NS	NS	1,280	196	3,320	3,730	3.3	3.0	<0.5	<0.5	252	276	<40	<40	67	83
24	8.1	8.4	1,180	42	448	25	2,370	1,480	3.2	3.1	<0.5	<0.5	209	212	<40	<40	62	75
25	NS	NS	NS	NS	371	538	6,270	2,550	1.9	2.4	<0.5	<0.5	181	208	<40	<40	57	71
26	8.3	8.3	1,660	37	652	64	9,180	6,460	3.0	2.9	<0.5	<0.5	230	189	107	<40	64	61
27	NS	NS	NS	NS	259	73	3,870	3,880	2.3	2.4	<0.5	<0.5	238	513	<40	<40	51	57
28	8.3	8.3	314	265	127	108	4,570	4,940	2.6	2.2	<0.5	<0.5	337	151	<40	<40	58	<50
29	NS	NS	NS	NS	1,900	92	3,710	3,860	3.7	3.2	<0.5	<0.5	264	311	139	<40	64	<50

(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 5-6 (Continued)

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

Grid No.	pH[1]		Water-soluble EDTA[1], mg/kg		Water-Soluble Pb, mg/kg		Pb[2,3], 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	
	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	0-12	12-24
30	8.0	8.5	867	296	400	127	1,740	2,870	1.9	2.0	<0.5[5]	<0.5[5]	242	164	<40[5]	<40[5]	<50[5]	<50[5]
31	NS[4]	NS[4]	NS[4]	NS[4]	670	44	4,660	6,380	2.4	3.0	<0.5	<0.5	192	179	<40	<40	<50	<50
32	8.4	8.5	1,170	602	477	199	5,970	7,700	2.3	2.3	<0.5	<0.5	205	172	3.2	<40	<50	<50
33	NS	NS	NS	NS	181	49	2,750	3,440	2.1	1.8	<0.5	<0.5	233	196	<40	<40	<50	<50
34	8.4	8.7	809	380	277	121	5,020	5,630	2.2	2.6	<0.5	<0.5	181	206	<40	19.6	<50	<50
35	NS	NS	NS	NS	416	35	2,870	1,750	7.3	3.2	<0.5	<0.5	640	339	<40	<40	159	92
36	8.1	8.7	305	24	136	41	2,100	1,650	1.9	2.0	<0.5	<0.5	191	192	<40	<40	<50	<50
Mean	***8.3***	***8.4***	***1,130***	***372***	***455***	***148***	***4,020***	***4,300***	***3.4***	***3.6***	***0.5***	***0.5***	***267***	***275***	***8.6***	***1.1***	***59***	***59***
Std. Dev.	***0.1***	***0.2***	***1,310***	***392***	***388***	***156***	***2,520***	***2,730***	***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, Water-Soluble EDTA, Water-Soluble Pb, and Contaminants of Concern at Site 129-3 After Soil Amendment Additions to Corn

Grid No.	pH[1]		Water-Soluble 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
1	NS[4]	NS	NS	NS	29	44	233	265	222	258	<40[5]	<40[5]
2	8.5	8.6	237	89	96	44	301	258	229	223	<40	<40
3	NS	NS	NS	NS	121	61	305	230	281	216	<40	<40
4	8.6	8.4	296	62	132	39	363	403	227	191	<40	<40
5	NS	NS	NS	NS	43	11	161	123	281	324	<40	<40
6	8.2	8.6	296	38	23	4	114	57	244	208	<40	<40
7	NS	NS	NS	NS	15	11	49	57	209	196	<40	<40
8	8.5	8.9	341	319	38	17	88	78	257	689	<40	<40
9	NS	NS	NS	NS	45	14	99	65	262	217	<40	<40
10	8.7	8.7	73	18	3	<1.0[5]	30	23	245	274	<40	<40
11	NS	NS	NS	NS	3	<1.0	32	26	276	241	<40	<40
12	8.4	8.6	69	36	2	<1.0	25	17	226	204	<40	<40
13	NS	NS	NS	NS	3	6	29	32	224	220	<40	<40
14	8.4	8.7	346	246	30	21	89	140	236	330	<40	<40
15	NS	NS	NS	NS	49	25	361	140	272	285	<40	<40
16	8.5	8.3	966	69	35	2	83	36	297	307	<40	<40
17	NS	NS	NS	NS	6	3	36	104	286	279	<40	<40
18	8.1	8.2	451	282	47	12	105	52	278	244	<40	<40
19	NS	NS	NS	NS	63	54	376	447	228	225	<40	<40
20	8.6	8.6	70	31	34	14	226	143	183	277	<40	<40
21	NS	NS	NS	NS	38	2	74	32	230	304	<40	<40
22	8.2	8.7	16	5	2	<1.0	37	42	255	322	<40	<40
23	NS	NS	NS	NS	11	9	45	42	238	244	<40	<40
24	8.4	8.6	321	130	15	11	54	46	229	268	<40	<40
25	NS	NS	NS	NS	210	116	795	600	317	265	<40	73
26	8.6	8.7	672	166	227	65	563	246	231	265	<40	<40
27	NS	NS	NS	NS	102	44	540	235	189	249	<40	<40
28	8.5	8.4	116	100	12	11	35	46	209	210	<40	<40
29	NS	NS	NS	NS	22	7	84	40	228	215	<40	<40
30	8.4	8.5	125	182	5	14	33	49	272	280	<40	<40
31	NS	NS	NS	NS	23	18	41	48	189	209	<40	<40
32	8.8	8.7	561	200	32	19	83	62	240	212	<40	<40
33	NS	NS	NS	NS	31	5	117	49	279	231	<40	<40
34	8.4	8.6	43	8	25	15	171	211	216	221	<40	<40
35	NS	NS	NS	NS	106	12	2,130	144	269	216	<40	<40
36	8.4	8.7	429	139	25	8	135	40	255	215	<40	<40
Mean	***8.5***	***8.6***	***302***	***118***	***47***	***20***	***223***	***128***	***245***	***259***	***<40***	***<40***
Std. Dev.	***0.2***	***0.2***	***250***	***97***	***54***	***24***	***372***	***134***	***32***	***83***	***NA[6]***	***NA***

(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.

predicted based on the amount of solution applied. 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) 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 Sunflower 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 very close to the soil surface, within 6 inches in some areas of the plot, 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 0-12-inch and 12-24-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 12-24-inch depth, which coincided with the lower EDTA concentrations. The corresponding average concentrations of water-soluble EDTA were 1,130 mg/kg and 372 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 water-soluble EDTA to water-soluble lead was approximately 1:1, which is similar to the ratio found for water-soluble EDTA and lead in soil after amendment additions during the Sunflower Army Ammunition Plant (AAP) greenhouse treatability study.[ref. 1] The soils from the Sunflower AAP (i.e., silty clay, silt loam) are very different from the soils at TCAAP (sand, sandy loam). However, since this ratio is fairly constant across these four soil types, this finding may prove useful as a tool to predict the impact of chelate and acidifier additions on dissimilar soils. It is also encouraging to confirm that results of greenhouse studies could be extrapolated into useful practices for the field demonstration. 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 0-12-inch depth (probability>T of 0.9320) and the 12-24-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 water-soluble EDTA concentrations were 302 and 118 mg/kg for the 0-12-inch and 12-24-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 a water-soluble form, as is observed here.

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

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 0-12-inch depth and the 12-24-inch depth. In only two instances were thallium not found at the 12-24-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 12-24-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 1998 Corn Crop - Plant Sampling

5.2.3.1 Plant Growth

The marginal levels of soil phosphorus (P) 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 (N) 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.

For the 1999 season, additional P will be band-applied along the seed row to prevent a recurrence of P deficiency in the corn. Not all of the 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.

5.2.3.2 Pre-Amendment Plant Sampling

Lead concentrations in corn plants grown on Site C averaged 30 mg/kg before soil amendment addition (Table 5-8). Of the other contaminants of concern, 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. 31] 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. 28]

Table 5-8

Contaminants of Concern in 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.

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 contaminants of concern 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.

5.2.3.3 Post-Amendment Plant Sampling

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 yields were lower than those reported in the literature. Apparently, the values in the literature were for reproductively mature plants, i.e., full-grown plants with mature ears.

The EDTA content of post-amendment corn samples at Site C (Table 5-10) averaged 5% (50,000 mg/kg) and ranged from 2.6% (26,000 mg/kg) up to 8.3% (83,000 mg/kg). Values attained with corn in the previous greenhouse study[ref. 1] 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 Sunflower AAP greenhouse pot study.[ref. 1] 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. This indicates that this technology is applicable across differing soil types. 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.

Table 5-9

Contaminants of Concern in 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 Corn From Site C After Soil Amendment Additions

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

(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.

Table 5-11

EDTA and Contaminants of Concern in Corn From Site 129-3 After Soil Amendment Additions

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

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.

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.

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 contaminants of concern that accumulated in significant concentrations in the corn at either site. Other contaminants of concern 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 regression of corn lead concentrations on water-soluble lead concentrations also were not significant. 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 (data not shown). The leaves of apparently unaffected trees 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 very 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. In addition, 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 - data not shown). 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 natural variation could have accounted for a significant amount of the increase in tissue lead.

5.2.4 1998 White Mustard Crop - Soil Sampling

5.2.4.1 Pre-Amendment Soil Sampling - White Mustard

Prior to planting the white mustard crop, 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). However, at Site 129-3, soil pH decreased slightly from 8.5 to 8.1 for the 0-12-inch depth and from 8.6 to 8.1 for the 12-24-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 decrease in soil pH. Less EDTA was added at Site 129-3 than at Site C.

At Site C, the average water-soluble EDTA concentration in the 0-12-inch depth decreased from 1,130 mg/kg after adding the soil amendments to corn (Table 5-6) to 414 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 of EDTA did occur since concentrations in the 12-24-inch depth increased from 372 mg/kg in the post-amendment soil samples for corn (Table 5-6) to 1,020 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 12-24-inch level (Table 5-12); whereas, with post-amendment soil samples for corn, the higher concentrations were observed in the 0-12-inch level (Table 5-6). This indicated that water-soluble lead moved downward in the soil, similar to the downward movement observed for EDTA. However, a decrease in water-soluble Pb, particularly in the 0-12-inch level, may also have been due to degradation of EDTA from the tillage/irrigation cycles. EDTA degradation would release complexed lead, which then would react with soil to revert to an insoluble form. 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.

Table 5-12

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

Grid No.	pH		Water-Soluble EDTA, mg/kg		Water-Soluble Pb mg/kg		Pb[1,2] 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	0-12	12-24
1	8.5	8.6	4	11	70	56	2,739	4,170	<5[3]	<5[3]	<0.4[3]	<0.4[3]	183	201	<40[3]	<40[3]	<50[3]	<50[3]
3	8.6	8.6	<0.3[3]	8	4	79	131	2,710	<5	<5	<0.4	<0.4	81	143	<40	<40	<50	<50
5	8.8	8.3	3	7	5	1	661	752	9	5	<0.4	<0.4	329	272	<40	<40	150	111
8	8.5	8.1	6	98	33	66	13,500	4,020	<5	<5	<0.4	<0.4	173	348	<40	<40	63	57
10	9.1	8.7	<0.3	53	12	23	346	222	<5	<5	<0.4	<0.4	91	120	<40	<40	86	70
12	8.4	8.0	<0.3	20	3	6	381	348	<5	<5	<0.4	<0.4	169	134	<40	<40	<50	<50
13	7.9	8.2	297	1,660	137	693	2,460	1,380	<5	<5	<0.4	<0.4	223	352	<40	<40	<50	<50
15	NS[4]	NS	NS	NS	13	860	263	4,463	<5	<5	<0.4	<0.4	88	169	<40	<40	92	<50
17	8.1	7.9	2,090	3,440	592	305	4,696	2,340	8	12	<0.4	<0.4	976	649	<40	<40	163	263
20	9.0	8.8	21	165	102	28	50,900	6,040	<5	<5	<0.4	<0.4	166	200	<40	<40	103	62
22	NS	NS	NS	NS	80	939	4,590	2,080	<5	<5	<0.4	<0.4	147	178	<40	<40	60	<50
24	9.1	7.9	43	1,540	33	691	8,930	3,280	<5	<5	<0.4	<0.4	161	246	<40	<40	77	60
25	8.6	8.2	397	2,880	110	1,100	3,860	1,360	<5	<5	<0.4	<0.4	226	260	<40	<40	68	64
7	NS	NS	NS	NS	96	1,730	524	4,190	<5	<5	<0.4	<0.4	95	362	<40	<40	72	<50
29	8.3	8.1	1,280	3,180	252	464	2,000	3,740	6	18	<0.4	<0.4	405	727	<40	<40	92	286
32	NS	NS	NS	NS	49	77	850	9,820	<5	<5	<0.4	<0.4	125	206	<40	<40	89	65
34	NS	NS	NS	NS	88	293	762	1,320	<5	<5	<0.4	<0.4	227	599	<40	<40	51	<50
36	8.2	8.0	3	210	4	98	162	466	<5	<5	<0.4	<0.4	73	174	<40	<40	<50	<50
Mean	***8.5***	***8.3***	***414***	***1,020***	***93***	***417***	***5,430***	***2,930***	***1.3***	***1.9***	***<0.4***	***<0.4***	***219***	***297***	***<40***	***<40***	***55***	***50***
Std. Dev.	***0.4***	***0.3***	***710***	***1,350***	***140***	***490***	***11,880***	***2,400***	***4.7***	***4.9***	***NA[5]***	***NA***	***208***	***183***	***NA***	***NA***	***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.

At Site 129-3, very little EDTA remained in the 0-12-inch or the 12-24-inch soil levels (7 and 18 mg/kg, respectively, Table 5-13), as compared to levels found in post-amendment soil samples for corn of 302 and 118 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 12-24-inch level were higher than at the 0-12-inch depth. Apparently, a large portion of the water-soluble lead and EDTA moved out of the top 24 inches within the ten weeks between the corn harvest and pre-amendment soil sampling for white mustard. This is also indicated by the high concentration of EDTA in the lysimeter samples taken three weeks after soil amendments were applied for corn on August 6, 1998 (Section 5.3, Table 5-22). However, sorption of EDTA in the top 12 inches must also be considered since the iron oxide content in the layer would be fairly higher.

At Site C, the average total lead concentration was 5,430 mg/kg at the 0-12-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 12-24-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.

Concentrations of the other contaminants of concern 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 - 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 on 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.

Table 5-13

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

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

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. A drip delivery system was used to apply EDTA to the soil over a 7-hour period. This allowed the EDTA to infiltrate into the soil slowly, minimizing runoff, compared to the hose application method for corn, which allowed runoff to occur. 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, 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 water-soluble 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; the average concentration for the 0- to 12-inch depth was 358 mg/kg, but the high concentrations in grids 30 and 32 skewed this value upwards. Water-soluble lead concentrations were also very low, likely due to the low concentrations of EDTA. In a number of the grids, concentrations of water-soluble lead were non-detectable.

Table 5-14

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

Grid No.	pH		Water-Soluble EDTA[1], mg/kg		Water-Soluble Pb mg/kg		Pb[1,2] 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	0-12	12-24
1	8.0	8.2	3,650	1,620	773	488	759	3,470	<5[3]	<5[3]	11	<0.4[3]	172	246	<40[3]	<40[3]	<50[3]	<50[3]
2	8.4	7.9	3,500	1,050	1,700	434	1,440	2,280	<5	<5	4	<0.4	232	259	<40	<40	250	265
5	8.3	7.9	11,800	2,840	918	488	1,610	1,710	5.2	6	<0.4[3]	<0.4	278	407	<40	<40	305	368
6	8.6	8.5	4,360	2,080	907	941	10,300	9,490	<5	<5	<0.4	<0.4	268	482	<40	<40	293	244
7	8.2	8.2	6,070	431	633	146	702	479	<5	<5	26	<0.4	125	231	<40	<40	79	53
8	8.1	8.6	5,380	963	865	430	895	3,190	<5	<5	<0.4	<0.4	149	248	<40	<40	<50	<50
12	8.4	8.1	8,900	1,450	1,320	764	1,620	2,780	<5	<5	<0.4	<0.4	172	185	<40	<40	<50	<50
13	8.0	8.3	9,240	502	821	205	1,720	469	<5	<5	<0.4	<0.4	152	182	<40	<40	<50	<50
14	8.3	8.5	760	1,520	274	463	745	5,910	<5	<5	<0.4	<0.4	132	232	<40	<40	<50	<50
15	NS[4]	NS	NS	NS	172	1,140	2,210	10,300	<5	<5	<0.4	<0.4	98.3	284	<40	<40	70	77
18	8.4	7.9	2,770	2,090	1,200	1,000	1,800	2,300	<5	<5	<0.4	<0.4	144	246	<40	<40	<50	<50
19	8.9	8.6	4,820	811	1,650	419	4,440	1,310	<5	<5	<0.4	<0.4	1,140	140	<40	<40	<50	<50
20	9.0	8.5	1,130	1,770	609	969	2,860	5,400	<5	<5	<0.4	<0.4	159	198	<40	<40	84	56
21	NS	NS	NS	NS	517	2,120	659	4,210	17.3	<5	<0.4	<0.4	166	326	<40	<40	55	58
24	8.8	8.4	3,970	1,050	1,370	502	1,860	3,910	<5	<5	<0.4	<0.4	246	153	<40	<40	64	53
25	8.8	8.4	2,740	1,470	1,240	748	4,800	4,140	<5	<5	<0.4	<0.4	155	250	<40	<40	51	62
26	8.8	8.1	1,000	2,510	444	885	5,850	9,600	<5	<5	<0.4	<0.4	187	318	<40	<40	62	54
27	NS	NS	NS	NS	346	1,290	1,110	6,790	<5	<5	<0.4	<0.4	164	250	<40	<40	<50	<50
29	8.6	8.3	7,960	8,190	671	1,130	867	2,180	<5	6	<0.4	<0.4	152	486	<40	<40	68	161
30	8.6	8.0	2,390	1,220	532	254	2,900	428	<5	<5	<0.4	<0.4	134	179	<40	<40	52	<50
35	8.4	8.0	7,210	1,530	928	432	1,140	3,280	<5	<5	<0.4	<0.4	219	327	<40	<40	89	89
36	8.7	8.5	12,600	1,650	672	803	691	1,330	<5	<5	<0.4	<0.4	146	241	<40	<40	75	63
Mean	***8.5***	***8.2***	***5,280***	***1,830***	***844***	***730***	***2,320***	***3,860***	***1.2***	***0.8***	***2.7***	***<0.4***	***218***	***267***	***<40***	***<40***	***76***	***73***
Std. Dev.	***0.3***	***0.2***	***3,510***	***1,660***	***422***	***449***	***2,290***	***2,960***	***4.2***	***2.0***	***6.5***	***NA[5]***	***211***	***94***	***NA***	***NA***	***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, Water-Soluble EDTA, Water-Soluble Pb, and Contaminants of Concern in Soil at Site 129-3 After Soil Amendment Additions to White Mustard

Grid No.	pH		Water-Soluble 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
1	NS[3]	NS	NS	NS	<0.3[4]	<0.3[4]	314	330	212	267	<40[4]	<40[4]
2	8.2	8.0	3	2	<0.3	2	266	305	192	221	<40	<40
3	NS	NS	NS	NS	3	<0.3	288	274	198	231	<40	<40
4	8.2	8.1	3	3	<0.3	<0.3	219	248	208	219	<40	<40
5	NS	NS	NS	NS	6	6	97	130	218	242	<40	<40
6	8.3	8.6	<0.3[4]	<0.34[4]	2	2	73	71	476	300	<40	<40
7	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	28	27	223	259	<40	<40
9	NS	NS	NS	NS	5	9	123	91	168	276	<40	<40
10	8.3	8.7	3	2	7	4	55	35	168	233	<40	<40
11	NS	NS	NS	NS	4	2	37	35	206	606	<40	<40
12	8.3	8.6	<0.3	<0.3	3	3	23	25	268	314	<40	<40
13	NS	NS	NS	NS	160	4	314	37	208	266	<40	<40
14	8.3	8.5	209	57	119	14	351	76	217	311	<40	<40
15	NS	NS	NS	NS	10	2	259	74	175	458	<40	<40
16	8.2	8.4	<0.3	3	<0.3	<0.3	68	40	197	350	<40	<40
17	NS	NS	NS	NS	<0.3	<0.3	21	27	208	491	<40	<40
18	8.3	8.2	<0.3	5	<0.3	<0.3	26	39	190	274	<40	<40
19	NS	NS	NS	NS	348	104	1236	669	241	196	<40	<40
20	8.3	8.5	128	78	100	19	1382	80	185	178	<40	<40
21	NS	NS	NS	NS	<0.3	<0.3	43	26	165	236	<40	<40
22	8.3	8.4	5	2	2	<0.3	62	60	188	231	<40	<40
23	NS	NS	NS	NS	8	1	24	73	188	190	<40	<40
24	8.4	8.7	<0.3	2	<0.3	<0.3	18	142	213	302	<40	<40
25	NS	NS	NS	NS	15	23	499	187	209	212	<40	<40
26	8.5	8.4	2	32	4	74	234	471	226	250	<40	<40
27	NS	NS	NS	NS	260	116	797	374	225	238	<40	<40
28	8.4	8.5	12	4	5	3	145	64	226	266	<40	<40
29	NS	NS	NS	NS	<0.3	<0.3	81	9	191	196	<40	<40
30	8.3	8.3	985	3	14	<0.3	10	12	176	314	<40	<40
31	NS	NS	NS	NS	<0.3	<0.3	11	9	198	207	<40	<40
32	7.7	8.2	2940	187	34	7	12	9	130	1557	<40	<40
33	NS	NS	NS	NS	<0.3	1	11	8	230	321	<40	<40
34	8.3	8.3	2	2	1	1	14	9	193	232	<40	<40
35	NS	NS	NS	NS	1	2	11	3	187	254	<40	<40
36	8.4	8.5	3	3	1	<0.3	12	7	146	230	<40	<40
Mean	***8.3***	***8.4***	***358***	***21***	***31***	***11***	***199.7***	***113.7***	***209.0***	***309.4***	<40	<40
Std. Dev	***0.2***	***0.2***	***713***	***47***	***77***	***28***	***321.0***	***152.0***	***54.3***	***231.0***	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.

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 or that lead moved out of the top 12 inches of soil due to EDTA complexation and leaching. 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.

5.2.5 1998 White Mustard Crop - Plant Sampling

5.2.5.1 Plant Growth

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.

5.2.5.2 Pre-Amendment Plant Sampling

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 COC 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

Table 5-16

White Mustard 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

White Mustard 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 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.

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, so EDTA uptake over the growing season could have caused some level of toxicity to the plants. This could have weakened the plants so that reduced lead uptake by the plants (discussed in Section 5.2.5.3) occurred when EDTA was applied.

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).

5.2.5.3 Post-Amendment Plant Sampling

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 Sunflower AAP Treatability Study conducted at TVA.[ref. 1] 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.

Table 5-19

Contaminants of Concern in 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***

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

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 Sunflower AAP greenhouse studies were 15,000 mg/kg.[ref. 1] The average EDTA concentrations in white mustard at Site C and Site 129-3 of 88,800 mg/kg and 54,400 mg/kg, respectively, were higher than concentrations of 40,000 mg/kg observed in white mustard in the Sunflower 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 carryover EDTA and water-soluble lead from the corn amendment application, or may be a natural trait of white mustard grown in these plots. The greenhouse studies of white mustard grown in pots did not indicate the type of rooting that would occur 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.

5.3 Soil Solution Data for Sites C and 129-3

Soil solution sample collection from lysimeters began 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 contaminants of concern 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

Table 5-20

EDTA and Contaminants of Concern in White Mustard From Site C After Soil Amendment Additions

Grid No.	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]	629	<4.5[3]	0.4	152	<40[3]	<50[3]
2	80,000	627	<4.5	0.7	121	<40	<50
5	NS	651	<4.5	<0.35[2]	127	<40	<50
6	100,000	811	<4.5	<0.35	93	<40	<50
7	NS	356	<4.5	<0.35	88	<40	<50
8	80,800	934	<4.5	<0.35	131	<40	<50
12	NS	602	<4.5	<0.35	99	<40	<50
13	105,000	582	<4.5	<0.35	87	<40	<50
14	NS	1,025	<4.5	<0.35	82	<40	<50
18	78,900	937	<4.5	<0.35	129	<40	<50
19	98,200	824	<4.5	<0.35	85	<40	<50
20	NS	1,963	<4.5	<0.35	110	<40	<50
24	NS	1,240	<4.5	<0.35	148	<40	<50
25	NS	636	<4.5	<0.35	85	<40	<50
26	84,800	1,438	<4.5	<0.35	131	<40	<50
29	82,800	597	<4.5	<0.35	78	<40	<50
30	NS	589	<4.5	<0.35	81	<40	<50
35	NS	787	<4.5	<0.35	94	<40	<50
36	89,100	514	<4.5	<0.35	93	<40	<50
Mean	***88,800***	***829***	***<4.5***	***<0.35***	***106***	***<40***	***<50***
Std. Dev.	***9,800***	***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.

Table 5-21

EDTA and Contaminants of Concern in White Mustard From Site 129-3 After Amendment Additions

Grid No.	EDTA, mg/kg	Pb, mg/kg	Mn[1], mg/kg	Sb[1], mg/kg
1	NS[2]	108	143	<40[3]
2	NS	76	133	<40
3	NS	128	197	<40
4	40,200	95	231	<40
5	NS	159	301	<40
6	NS	216	481	<40
7	NS	59	145	<40
8	31,500	129	201	<40
9	NS	238	254	<40
10	NS	105	348	<40
11	NS	76	324	<40
12	57,900	47	613	<40
13	NS	238	850	<40
14	NS	236	220	<40
15	NS	1,532	419	<40
16	67,900	101	335	<40
17	NS	90	432	<40
18	NS	108	478	<40
19	NS	1,526	124	<40
20	36,300	719	274	<40
21	NS	239	189	<40
22	NS	88	261	<40
23	NS	87	222	<40
24	53,700	44	368	<40
25	NS	1,082	377	<40
26	NS	532	347	<40
27	NS	1,730	331	<40
28	73,100	261	359	<40
29	NS	226	301	<40
30	NS	83	275	<40
31	NS	274	247	<40
32	64,700	308	309	<40
33	NS	411	331	<40
34	NS	439	322	<40
35	NS	151	362	<40
36	64,200	232	343	<40
Mean	***54,400***	***338***	***318***	***<40***
Std. Dev.	***15,000***	***437***	***139***	***NA[4]***

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

Table 5-22

EDTA and Contaminants of Concern in Soil Solution From Lysimeters

Date	Site	Sample Event	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	Per-Amendment Corn	<0.1	<0.1[2]	<0.3[2]	<0.01[2]	1	<0.6[2]	<1.0[2]
08/01/98	C	Post-Amendment Corn	40	10	<0.3	<0.01	2	<0.6	<1.0
08/06/98	C	Post-Amendment Corn	54	7	<0.3	<0.01	2	<0.6	<1.0
08/11/98	C	Post-Amendment Corn	40	10	<0.3	<0.01	2	<0.6	<1.0
08/25/98	C	Growing-Season Mustard	516	131	<0.3	<0.01	16	<0.6	<1.0
09/04/98	C	Growing-Season Mustard	488	260	<0.3	<0.01	21	<0.6	<1.0
09/11/98	C	Growing-Season Mustard	1,890	270	<0.3	<0.01	19	<0.6	<1.0
09/18/98	C	Growing-Season Mustard	73	17	<0.3	<0.01	1	<0.6	<1.0
09/25/98	C	Growing-Season Mustard	2,170	644	<0.3	<0.01	24	<0.6	<1.0
10/02/98	C	Growing-Season Mustard	2,500	900	<0.3	<0.01	32	<0.6	<1.0
10/19/98	C	Post-Amendment Mustard	1,946	783	<0.3	<0.01	34	<0.6	<1.0
08/06/98	129-3	Post-Amendment Corn	1,430	14	<0.3	<0.01	10	<0.6	NA
09/04/98	129-3	Growing-Season Mustard	380	155	NA[3]	NA	16	<0.6	NA
09/18/98	129-3	Growing-Season Mustard	5	2	NA	NA	<0.01	<0.6	NA

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

obtained during corn growth due to water use by the deep rooting system of corn which prevented water from moving below the rooting zone. Lead, EDTA, and manganese were detected in the samples at Site C beginning on August 1, 1998, about two weeks after amendment addition and harvest of the corn. The concentrations of EDTA and lead at Site C reached a maximum of 2,500 mg/L and 900 mg/L, respectively, on October 2, 1998. Samples could not be obtained from lysimeters at Site 129-3 until August 6, 1998. EDTA and lead were also detected in lysimeter samples at Site 129-3 beginning on August 6, 1998.

The sandy soils at both sites were conducive to the leaching of EDTA and lead after the corn crop was harvested and the roots were no longer using water. There was a delay of about a month after application of soil amendments before the concentrations in the solutions began to significantly increase. A series of tillage and irrigation cycles conducted between the corn harvest and planting of white mustard most likely caused movement of EDTA and lead down to the lysimeters. The tillage and irrigation cycles were conducted to promote EDTA degradation.

A sample collected from the lysimeter in the northwest corner of Site C 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 collected from the lysimeter showed copper concentrations ranging from 3 ppm up to 267 ppm over the 8-week period in which they were collected (Table 5-23). 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. Since copper was detected at only one lysimeter, it is likely there was a localized copper source in the soil in the immediate vicinity of that lysimeter. This episode seemed to be an isolated event from a single source and the reduction in concentration at subsequent sampling events (Table 5-23) indicated that copper persistence in the soil solution would probably diminish with time.

5.4 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

Table 5-23

Results of Copper Analysis on Water Collected From Lysimeter at Site C

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

- 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, 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.)

The *in situ* technologies, except containment, provide a clean site and normally avoid future liability and restrictions to site use. Among the lowest cost options to date is phytoextraction, 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. However, some of the operating parameters are still in need of refinements. These include growing practices, including plant species selection, amendment application methods, and amendment application rates.

Section 6.0
Cost Assessment

6.1 Cost Performance

For estimating purposes, TVA assumed that a phytoremediation project would be conducted in a soil with moderate levels of lead contamination such as the conditions encountered at Site C. Under these circumstances, it was assumed that:

- The growing season would be shorter than for sites located further south
- Two crops would be grown per year (one corn crop and one white mustard crop)
- Soil conditions would be less than optimum
- The level of lead in the soil would be about 2,500 ppm
- Five years of remediation would be required to meet the regulatory standard.

Based on these assumptions, TVA estimated that a typical project cost would be $30.61 per cubic yard of soil per year or about $153 per cubic yard of soil over the entire life of the project (Table 6-1). This estimate is preliminary in nature and will be refined as the project progresses.

6.2 Cost Comparisons to Conventional and Other Technologies

Cost comparisons to several *ex situ* and *in situ* procedures for remediating metals-contaminated soil sites were examined. Conventional *ex situ* methodologies compared included:

- Landfilling of contaminated soil
- Soil washing (separation)
- Incineration
- Solidification

In situ methods compared included:

- *In situ* soil flushing
- Solidification/Stabilization
- Containment
- Electrokinetics
- Phytoremediation

Literature data indicate that phytoremediation is among the lowest cost options at $25 to $127 per cubic yard (Table 6-2). Comparison of these figures with TVA's preliminary estimate of $30.61 per cubic yard of soil per year suggests that TVA's preliminary estimate is reasonable.

Table 6-1

Preliminary Estimate of the Annual Cost of a Five-Year Phytoremediation Project

Startup		Operation & Maintenance		Demobilization	
Activity	**$/acre per yr.**	**Activity**	**$/acre per yr.**	**Activity**	**$/acre per yr.**
Labor	$0	Labor		Removal of equipment and structures	$200
Planning & Contracting		Site Management	$2,308	Site restoration	
Remediation Work Plan	$5,000	Planting	$2,000	Soil Sampling	$2,365
Site Preparation	$2,000	Soil Amendment Application	$1,200	Decontamination	$400
Capital Equipment		Harvesting	$2,000	Demobilization of personnel	$0
Initial Capital Investment	$3,187	Subtotal	$7,508		
Construction		Monitoring			
Fencing	$668	Monitoring Wells	$0		
Permitting & Reg. Reqd.	$1,000	Analytical Services			
		Plant Sampling	$1,300		
		Equip. or facility modification			
		Annual Capital Invest.	$1,300		
		Utilities			
		Water	$950		
		Training reqd. to operate equip.	$600		
		Effluent treatment and disposal			
		Disposal Cost	$17,800		
		Personal Protective Equip.	$2,000		
		Subtotal	$19,800		
		Ancillary Equipment	$0		
		Consumables & Supplies			
		Fertilizers and Pesticides	$500		
		EDTA	$40,000		
		Acetic Acid	$12,000		
		Subtotal	$40,500		
Total Startup, $/acre per year	$11,855	Total O&M, $/acre per year	$83,958	Total Demobilization, $/acre per year	$2,965
				Grand Total, $/acre per year	$98,778
				Grand Total, $/yd^3 per year	$30.61
				Grand Total, $/yd^3 (over five years)	$153

Table 6-2

Comparison of Remediation Costs

Remediation Method	Cost of Remediation Technique ($ per cubic yard)
Ex situ Methods	
Landfilling	$165 - $410 [refs. 17,18]
Soil Washing	$175 - $390 [ref. 11]
Incineration	$300 - $1,500 [ref. 32]
Solidification	$150 [ref. 32]
In situ Methods	
In situ Soil Flushing	$300 - $380 [ref. 11]
Solidification/Stabilization	$150 [ref. 32]
Containment	$100 - $175 [ref. 11]
Electrokinetics	$40 and up [ref. 32]
Phytoremediation/Phytoextraction	$25 - $127 [refs. 17,18]

Section 7.0
Regulatory Issues

To gain acceptance for the demonstration from the regulatory agencies, the draft Technology Demonstration Plan (TDP) was provided to both USEPA Region 4 and the Minnesota Pollution Control Agency (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 4 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 demonstration plan. The project team then worked on revising the 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. By the time field work began, the MPCA and USEPA Region 4 had their concerns addressed.

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 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 demonstration plan was revised, written responses to the RAB's comments were prepared by the project team. 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.

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. There were 319 sites that have shown lead contamination above the industrial cleanup levels.

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 DSERTS data, there are 889 sites with metals contamination that exceed the risk-based levels.

Of the 889 sites, there are 451 sites that are currently scheduled to be cleaned up because of metals contamination. According to a query of the DSERTS database, these 451 sites have approximately 2,062 cubic yards of soil that will require remediation at an estimated cost of $1,116 million.

8.2 Transition

Some of the problems encountered in the application of the field demonstration need to be addressed. The current scope of work and funding levels would need to be expanded to pursue the causes of these field problems and their solution. Phytoextraction technology as implemented under the conditions at TCAAP will require at least an additional year, preferably two, of field operation to refine techniques and incorporate lessons learned during the first year of the demonstration conducted in 1998. Due to the extreme variability of lead in the soil across the plot areas, TVA intended to evaluate removal of lead from the sites primarily through the lead concentration in the biomass, and 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. Lead soil variability was complicated by the fact that large quantities of particulate contaminants and solid refuse 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. Had the sites been

more homogeneous with respect to lead, it is quite likely such a change could have been seen, and more meaningful results could have been obtained for the first year.

Regulatory approval was granted for the demonstration. However, there are environmental concerns which need to be addressed, such as potential movement of EDTA below the rooting zone, which may be of concern to regulatory agencies. However, even though vertical movement of EDTA did occur, there was little evidence of vertical lead migration, and this movement was *within the two foot deep rooting zone*. This indicated that movement of EDTA in and of itself was not environmentally detrimental. Nonetheless, rates and methods of amendment application will be refined to minimize environmental impacts while providing adequate phytoextraction results. A water balance simulation was suggested to accomplish this, but was deemed impractical within the existing budget and project logistics constraints.

Instead, lysimeters were installed to monitor potential EDTA or lead movement through the soil. A water balance simulation would have required 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). Data lacking for the water balance was hydraulic conductivity of site soils. Because of the heterogeneous texture of the soil, sampling to adequately determine the overall hydraulic conductivity of the sites to perform a mass water balance would have been impractical and prohibitively expensive. These demonstration sites are comprised of a variety of soil textures as well as debris from burning or disposal activities. Texture variability, at Site C for instance, resulted from a hard-pan road under the surface and debris ranging from bullet jackets to broken concrete, sheet metal scrap and wire, and railroad ties. An accurate assessment of the hydraulic conductivity of this site would essentially require samples to be taken in close proximity (sample to sample) to account for the varying texture and varying soil infiltration rates. Mass water balances have been performed for some phytoextraction studies, but these have been in more uniform soils of a consistent texture or in situations where liners were applied under the soil to be treated.

The cropping scheme and plant species need to be changed for optimum results in 1999. This will be explored through a review of the literature, consultation with professional growers and plant breeders, and greenhouse testing of alternative species.

8.3 Draft Implementation Guidance Document

The procedures outlined in this document are based on the first-year results of a two-year demonstration. Therefore, recommendations such as crop selection, cultural practices, types of soil amendments, and methods of application may need to be modified for maximum treatment effectiveness. Several factors should be carefully considered when planning a phytoextraction project at any given site to ensure good results. Phytoextraction is a living, dynamic system which will be implemented and conducted under very heterogeneous chemical, physical, and environmental conditions. In many areas where contamination is present, the circumstances may 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 will 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 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 receive 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.

Phytoremediation offers the potential as an inexpensive remediation method. However, it will not be applicable to all situations. Factors such as soil type, soil fertility levels, soil lead concentration, nature of contamination, and the presence of other contaminants will directly control the success of the technology. 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, and sunflower. Other crops that may be used to remediate other heavy metals include amaranthus (radioactive cesium and strontium), oat and barley (zinc), Alpine pennycress (cadmium), Indian mustard (copper and selenium), and Alyssum species (nickel). Quite likely, there are 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.

1. The 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 COC, type and concentration of COC, climate, geology, hydrogeology, etc.

2. Determine the extent of past site characterization and the extent of future characterization that may be required.

3. Obtain a soil characterization for other contaminates 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, and infiltration rates, etc.

5. Determine if phytoextraction is suitable based on:

    - type and concentration of COC, i.e., contaminant in ionic form and present at a concentration that can be remediated within a reasonable timeframe;

    - depth and extent of COC, i.e., accessibility of COC to plant rooting system;

    - other contaminants present, e.g., beryllium (Be) or thallium (Tl), 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.

6. Consult with appropriate regulatory agencies (State and Federal, and local if required) as to permitting and legal requirements and obtain clearance to proceed.

7. 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 leaching, 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 (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S), 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 (Cu), iron (Fe), manganese (Mn), and zinc (Zn). 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 (Pb). 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 (As) and selenium (Se), 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 COC (Pb). However, a point for consideration is that there may be significant variability, or heterogeneity, in COC 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.

8. 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.

9. 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 pounds per acre basis. This amount of acetic acid will be diluted approximately 1:7 with water for application to the field.

10. Calculate the amount of EDTA to add to the soil. This is based on the contaminant (Pb) concentration in the soil. The amount of EDTA should be adequate to solubilize sufficient lead across the remediation area for plant uptake while minimizing chelate leaching. The ideal amount is a 1:1 molar ratio of EDTA-to-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 lead across the field, then basing the EDTA application on a rate that provides a 1:1 ratio for 75% of the field. This will mean that in some areas, the chelate is under-applied, while in other areas, it will be over-applied. Another method which may prove useful would be to base the amount of EDTA added on the amount of plant-available, or potentially plant-available, lead in soil as determined by a sequential extraction analysis of the soil, rather than on the total amount of lead. 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 more easily extractable forms of lead would also be the form most likely solubilized by EDTA. The amount of EDTA to add would be based on the amount of lead in these fractions.

11. 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. This will be done in consultation with 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.

12. 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 (particularly of N and P) then will be adjusted upward in order to maximize vegetative biomass yield at the expense of potential grain 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.

13. Install protective fencing around the area, if required, and establish work and decontamination zones.

14. Eradicate existing vegetation and remove trees as needed.

15. To facilitate farming operations, visible obstructions, such as large rocks and metal scrap, should be removed from the area.

16. Till the area with commercial farming equipment. For proper seed bed preparation, it is recommended that tillage be to a depth of at least two feet, if possible. Tillage should be done in at least two passes at right angles to each other. Depending on the soil type, this may be done with a tractor-mounted, power takeoff-driven Rototiller (in a sandy soil without appreciable large rock content) or with a conventional moldboard breaking plow (in a silty or clay soil). Where a hardpan or clay lenses are present, a subsoil attachment may be necessary to suitably penetrate the recalcitrant areas.

17. Apply and incorporate fertilizer using commercial farming equipment. This step may also be performed simultaneously with planting.

18. Install irrigation systems. 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.

19. 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.

20. 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.

21. 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.

22. 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.

23. Commence pre-amendment sampling immediately before addition of soil amendments to solubilize lead. This will involve obtaining a limited number (6-12, depending on the size of the area) of soil samples at 0- to 12-inch and 12- to 24-inch depths across the entire remediation area. Obtain whole plant samples from the same locations as the soil samples. This sampling will be done only once at the beginning of the project to establish background concentrations of COCs in plant tissue and soil before adding soil amendments. Thereafter, this sampling will not be necessary.

24. 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. The acetic acid and EDTA should be added to acidify the soil and solubilize lead to a depth of two feet.

25. 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.

26. 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. Soil sampling will not be required at this point since 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. 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.

27. Harvest the crop, either by hand for small (0.2-acre) remediation areas or with commercial harvesting equipment such as combines for larger areas of one acre or more. Experience has shown that 0.2 acre is the maximum area that can be efficiently and cost effectively harvested by hand. 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.

28. 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, then re-weighing to determine the amount of moisture lost.

29. 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.

30. 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 a depth of two feet or more 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.

Section 9.0
Lessons Learned

Procedures and methodology that could be modified to improve the technology application are as follows:

In order for the phytoextraction technology to be applicable on a larger scale, agronomic practices need to be conducted using mechanized agricultural equipment. In this demonstration, due to the size of the demonstration plots, a hand planter was used for sowing corn and mustard and fertilizer was applied using a lawn spreader.

The geology of the demonstration sites made soil sampling labor intensive and time consuming and the staff and time allocated in the budget were inadequate for the task. An approach which utilized mechanized soil sampling equipment was employed during the sampling for the mustard crop. Additional personnel and time have been allocated and budgeted for sampling activities in the 1999 demonstration plan.

The yields expected from corn were based on literature values for these crops, but actual yields were lower than expected. At best, the soil conditions at the demonstration areas are suboptimal for maximum crop yields, and the disposal of a diverse mixture of wastes on the areas resulted in a further decline in potential productivity. Production of a large biomass is one of the critical components of a successful lead phytoextraction scheme. Fertilizer was applied at recommended agronomic rates for normal grain production of field crops. Instead, fertilizer amounts, particularly of nitrogen and phosphorus, should be applied to achieve maximum vegetative production. This would constitute an over-application from an agronomic perspective since these rates would be higher than rates recommended for grain or seed production. In addition, use of higher yielding varieties of corn and mustard may be necessary to increase biomass yield. Plant screening to select species that have higher biomass than the crops used in this study and which also exhibit high lead accumulation may also be required to increase the effectiveness of this methodology.

Rigorous greenhouse studies were conducted by TVA prior to the 1998 field activities at TCAAP. These studies showed efficient concentration of lead in corn (up to 1.3%) when the soil was amended with an acidifier and a chelate. In many cases, results in this field demonstration approached the results obtained in the greenhouse studies, although the overall average in the field study was lower. The concentration of lead taken up into plant tissue was a function of the concentration of lead in the soil, and the extreme variability in soil lead was reflected by the variability of lead concentrations in the plant tissue. This variability contributed to the overall lower average lead concentration in the plants. The studies also showed white mustard to be an efficient accumulator of lead when a chelate was used to solubilize soil lead into a form available to the plant. Acidifying the soil, a step required with other plant species, was not necessary to achieve maximum lead concentrations (2 %) in the white mustard. Elimination of this step conserves implementation costs in the field and appeals to regulators, the installation, and the community. However, the white mustard subsequently did not perform well in the field, due to a

limited rooting system resulting from field and environmental conditions. Accordingly, a search will be conducted for a deeper rooted variety of cool season crop for use in the 1999 demonstration and greenhouse testing will be performed to validate the species selected.

Phytoremediation is an emerging technology, and there is not an extensive reported database on performance of mustard crops in the field. Also, the reported database for crops other than mustard is scanty. TVA will consult with professional growers and extension agronomists in the Minnesota/North Dakota area for recommendations for alternative cool season crops. Plant species to be considered for potential use at TCAAP may be varieties of brown and oriental mustard, as well as safflower. These plants may produce a deeper and more extensive rooting system than white mustard, as well as a higher biomass. These cultivars are very drought tolerant, and as such have a good water extraction rate which would reduce the sensitivity to overwatering. These plants also have a high transpiration rate, which would be conducive to plant uptake of large quantities of water-soluble lead. A greenhouse study would determine the following: 1) lead uptake capacity; 2) growth habit; 3) need for soil acidification; and 4) tolerance to other contaminants in the soil from TCAAP. (The greenhouse study was completed and has been inserted as Appendix G).

In this demonstration, the chelate was applied in amounts to supply a molar ratio of chelate to soil lead of 1:1. However, this ratio cannot be consistently achieved on areas such as those in this demonstration due to the high variability of soil lead concentrations across the plots. This was evidenced by the wide range of soil lead concentrations observed in the individual grids. The amount of chelate applied should be adequate to solubilize sufficient lead for plant uptake in all or most of the area while minimizing vertical movement of the chelate. For the first year of this study, the amount of chelate applied was based on the average lead concentration of bulk soil samples. However, a more practical application rate may be achieved by examining the mean, the median, and the frequency distribution of the grid lead concentrations. Chelate application may then be based on a rate that, for example, provides at least a 1:1 ratio for 75% of the grids.

Another potentially useful tool that could be employed in the 1999 demonstration season is a sequential extraction technique for metals-contaminated soils. This method 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. This fraction is usually less than the total concentration of lead in the soil. The molar ratio of EDTA-to-soil lead then can be equalized to match only the plant-available fraction of soil lead, which will reduce the amount of chelate required to solubilize lead for plant uptake.

The method of chelate application to the soil needs refinement in order to supply chelate solution at a rate that will rapidly saturate the soil without causing runoff, a problem that occurred during acetic acid application for corn. However, the amount of runoff was negligible compared to the total volume of acetic acid applied. There was an unknown hard-pan road running just under the soil surface across and out of the plot area which served as a natural conduit for the acetic acid solution. The very heterogeneous soil texture at the site resulted in differential infiltration rates across the plot. The presence of clay lenses restricted infiltration and promoted surface flow, whereas the sandier areas within the plot exhibited rapid infiltration and no surface movement

occurred. This variability in texture will always be encountered within a natural soil body, but it was especially pronounced at the demonstration sites. Berms were constructed in this area to prevent any potential future occurrence of a runoff during soil amendment application, and the amendment delivery system was modified to allow more controlled application. This situation offered a valuable insight into the necessary site preparation assessment in the implementation of the technology.

Results of the demonstration strongly suggested that rapid soil saturation may be required for maximum lead uptake by mustard. Chelate application using the drip delivery system for the mustard crop required approximately 7 hours to complete. This eliminated problems with runoff, but apparently did not saturate the soil rapidly enough to allow the mustard plants to take up an appreciable amount of lead. To rectify this problem, a drip delivery system will be used in the second year of the demonstration (1999) that will deliver the amendments at a more rapid rate.

The soil at both sites will be deep-tilled to a depth of two feet or more to bring any lead that may have moved downward within the root zone in these sandy soils back closer to the surface. This will allow more extensive root contact with soil lead. Deep tillage is a commonly accepted farming practice. In this application, deep tilling is not an additional step, but the least obtrusive method of mixing the soil *in situ* to make soil-bound lead more accessible to plant roots throughout the two-foot treatment zone and homogenize the soil. In many cases before treatments were applied, as shown in the initial soil characterization, there was more lead in the lower depths of the treatment zone (top two feet) than in the upper depths. As mentioned previously, the vertical movement of soil lead that did take place occurred within the two foot rooting zone. The tillage step mixes soil lead as much as possible to reduce variability and places lead in the upper, more dense rooting zone, allowing for more efficient phytoextraction. Deep tillage would be recommended for phytoextraction and is not related to estimation of EDTA application rates. The additional costs for deep tilling are insignificant, even for "low-cost" phytoremediation systems.

The irrigation cycles employed after corn harvest as an attempt to stimulate EDTA degradation may have enhanced vertical movement of EDTA and some water-soluble lead. However, the amount of lead movement was negligible, as eighty-five percent of water-soluble lead remained in the top two feet of soil, which is considered the rooting zone, ten weeks after adding EDTA to the soil at Site C. The total average lead concentrations at both Site C and Site 129-3 for 0-to-12-inch and 12-to-24-inch soil depths at the end of the growing season (after mustard) were within the concentration ranges found for the initial sampling and for sampling taken during the growing season (after corn and before mustard).

Although lead was found in lysimeter samples, the source could not be pinpointed, as lead contamination in the soil was present throughout down to 5 feet; and the lysimeters were placed at 4 feet. After soil acidification, about 50-60 percent of soil lead will be complexed with EDTA. Once the soil returns to the indigenous pH (within 72 hours), EDTA would be complexed with other soil cations, such as iron or calcium, and lead would be re-precipitated in the soil. However, the EDTA-metal complex would exist in a constantly changing equilibrium which is

governed by the amounts of elements such as calcium, iron, or lead within soil microsites. EDTA that moved downward in the soil would complex with some of the soil lead in addition to other cations, since lead was present down to five feet. Complexation of lead from the 2-to-4-foot soil depth did occur as indicated by the difference in the EDTA-to-lead ratio found in the upper soil compared to that found in the lysimeters. At Site C, the EDTA-to-lead ratio was 1:1 at the 0-to-24-inch soil depth, whereas in the lysimeters this ratio ranged from 1.2 to 5.3. At site 129-3, only a few samples were collected, with ratios varying from 1.1 to 6.3, so an assessment of EDTA to lead ratio could not be accurately made. The practice of intensive irrigation in concert with deeper tilling to return water-soluble EDTA and lead closer to the surface with each cycle is currently under consideration.

In summary, the actions listed below will be implemented in the 1999 demonstration year. The original Demonstration Plan will be modified in accordance with these changes:

- Crops will be planted by commercial mechanical seed planter rather than by hand planter
- Soil sampling will be done with mechanized equipment rather than by manual samplers
- A silage variety of corn concomitant with increased planting density and increased fertilization will be used to increase biomass production
- Chelate application rates will be based on the frequency of lead concentration across the plot area rather than on the mean lead concentration in the entire plot, or, if deemed suitable, will be based the amount of lead that either is, or is potentially, plant-available, as determined by a soil sequential extraction procedure
- A rapid-delivery drip system will be used for application of soil amendments
- Irrigation and tillage practices will be modified to maintain lead within the rooting depth of plants
- A deeper rooted variety of mustard or a similar cool season will be used instead of white mustard

More details are provided in Appendix F for the 1999 corn crop. A report on the greenhouse study of potential cool season crops is in Appendix G.

Section 10.0
References

1) Behel, A. D., R. A. Almond, D. A. Kelly, P. A. Pier, W. J. Rogers, and D. F. Bader; "*Results of a Greenhouse Study Investigating the Phytoextraction of Lead From Contaminated Soils Obtained From the Sunflower Army Ammunition Plant, Desoto, Kansas.*" Report No. SFIM-AEC-ET-CR-98036; August 1998.

2) Department of the Navy, Naval Facilities Engineering Command; "*1994 Tri-Service Environmental Quality Strategic Plan (EQ Strat Plan) Report.*" March 16, 1995.

3) Huang, J. W., J. Chen, W. R. Berti, and S. D. Cunningham; "*Phytoremediation of Lead-Contaminated Soils: Role of Synthetic Chelates in Lead Phytoextraction.*" Environ. Sci. Technol. 31, pp. 800-806; 1997.

4) Cunningham, S. D. and D. W. Ow; "*Promises and Prospects of Phytoremediation.*" Plant Physiol. 110:715-719, 1996.

5) Cunningham, S.; "*Phytoremediation of Lead-Contaminated Soils and Sludges. 14th Annual Symposium of Current Topics in Plant Biochemistry, Physiology, and Molecular Biology: Will Plants Have a Role in Bioremediation?.*" University of Missouri, Columbia, Missouri, April 19-22, 1995.

6) Nanda Kumar, P.B.A., V. Dushenkov, H. Motto, and I. Raskin; "*Phytoextraction: The Use of Plants to Remove Heavy Metals From Soils.*" Environ. Sci. Technol. 29:1232-1238, 1995.

7) Raskin, I; "*Phytoremediation: In Search of a Green Solution. Symposium on Phytoremediation-Principles and Emerging Technologies.*" Alabama A&M University, Huntsville, AL, March 28-29, 1996.

8) Comis, D.; "*Green Remediation: Using Plants to Clean the Soil.*" J. Soil Water Conserv. 51:184-187, 1996.

9) Rufus L. Chaney, United States Department of Agriculture, personal communication.

10) Brown, S. L., R. L. Chaney, J. S. Angle, and A. J. M. Baker; "*Phytoremediation Potential of Thlaspi Caerulescens and Bladder Campion for Zinc- and Cadmium-Contaminated Soil.*" J. Environ. Qual. 23:1151-1157, 1994.

11) Smith, L. A., J. L. Means, A. Chen, B. Alleman, C. C. Chapman, J. S. Tixier, Jr., S. E. Brauning, A. R. Gavaskar, and M. D. Royer; "*Remedial Options for Metals-Contaminated Sites.*" CRC Lewis Publishers, Boca Raton, FL., 1995.

12) Blaylock, M. J.; "*Phytoremediation of Lead-Contaminated Soil at a Brownfield Site in New Jersey - A Cost-Effective Alternative.*" International Business Communications Second Annual Conference of Phytoremediation, DoubleTree Guest Suites Hotel, Seattle, WA, June 18-19, 1997.

13) Black, Harvey; "*Absorbing Possibilities: Phytoremediation;*" Innovations, Vol. 103, No. 12, pp. 1-6. 1997.

14) Rock, Steve, and Scott Beckman; "*Phytoremediation Field Demonstrations in the U.S. EPA Site Program. In Situ and Onsite Bioremediation;*" Volume 3. Fourth International *In Situ* and Onsite Bioremediation Symposium. New Orleans, LA, April 28-May 1, 1997.

15) Lasat, M.M., M. Fuhrmann, S.E. Ebbs, J.E. Cornish, and L.V. Kochian, "*Phytoremediation of a radiocesium-contaminated soil: Evaluation of cesium-137 bioaccumulation in the shoots of three plant species*". J. Environ. Qual. 27:165-169, 1998.

16) Dushenkov, S, A. Mikheev, A. Prokhnevsky, M. Ruchko, and B. Sorochinsky, "*Phytoremediation of radiocesium-contaminated soil in the vicinity of Chernobyl, Ukraine*". Environmental Sci. and Tech. 33, no. 3: 469-475, 1999.

17) Boyd, V.; "*Pint-Sized Plants Pack a Punch in Fight Against Heavy Metals.*" Environmental Protection (May 1996):38-39; 1996.

18) Salt, D. E., M. Blaylock, P.B.A. Nanda Kumar, V. Dushenkov, B. D. Ensley, I. Chet, and I. Raskin; "*Phytoremediation: A Novel Strategy for the Removal of Toxic Metals From the Environment Using Plants.*" Bio-Technology 13:468-474, 1995.

19) Federal Remediation Technologies Roundtable, "*Guide to Documenting and Managing Cost and Performance Information for Remediation Projects,*" Revised Version, USEPA Contract No. 68-W5-0055, October 1998.

20) Army Corps of Engineers' Toxic and Hazardous Materials Agency; "*Installation Restoration Program: Remedial Investigation Report for the Twin Cities Army Ammunition Plant (Final Report),*" April 1991.

21) Behel, A. D, D. A. Kelly, P. A. Pier, W. J. Rogers, R. A. Westmoreland; "*Test Plan for the Demonstration of Phytoremediation of Lead-Contaminated Soil at the Twin Cities Army Ammunition Plant;*" USAEC Report No. SFIM-AEC-ET-98008; March 1998.

22) "*Health and Safety Plan, Environmental Field Activites, Twin Cities Army Ammunition Plant, New Brighton, MN 55112,*" September 1996.

23) Kabata-Pendias A. and H. Pendias; Elements of Group V. In "*Trace Elements in Soils and Plants,*" CRC Press, Boca Raton, FL., pp. 171-177, 1984.

24) Shacklette, H. T. and Boerngen, J. G; "*Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States and Partial Data on Cadmium,*" U.S. Geol. Surv. Prof. Pap., 1270, p. 149, 1984.

25) Kabata-Pendias A. and H. Pendias. Elements of Group VII. In "*Trace Elements in Soils and Plants,*" CRC Press, Boca Raton, FL., p. 226; 1984.

26) Kabata-Pendias A. and H. Pendias. 1984. Elements of Group VII. In "*Trace Elements in Soils and Plants,*" CRC Press, Boca Raton, FL., p. 177.

27) Laul, J. C., W. C. Weimer, and L. A. Rancitelli, Biogeochemical distribution of rare earths and other trace elements in plants and soils. In "*Origin and Distribution of the Elements,*" Vol. II, Ahrens, L. H., Ed., Pergamon Press, Oxford, p. 819, 1979.

28) Gough, L. P., H. T. Shacklette, and A. A. Case, "*Element Concentrations Toxic to Plants, Animals, and Man.*" U.S. Geol. Surv. Bull. 1466, p. 80, 1989.

29) Lehn, H. and J. Schoer; "*Thallium Transfer From Soils to Plants: Correlation Between Chemical Form and Plant Uptake.*" Plant and Soil. 97, p. 253, 1987.

30) Jones, K. CV., N.W. Lepp, and J. P. Obbard; Other Metals and Metalloids. In "*Heavy Metals in Soils.*" B. J. Alloway, Ed. Blackie and Son Ltd, Bishopbriggs, Glascow, and Leicester Place, London, pp. 280-315, 1990.

31) Smith, I. C., and B. L. Carson. "*Trace Metals in the Environment.*" Vol. 1, Ann Arbor Scientific Publications, Ann Arbor, MI., p. 394, 1977.

32) USAEC, "Remediation Technology Screening Matrix and Reference Guide," USAEC Report Number SFIM-AEC-ET-CR-97053, 1997.

Appendix A
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APPENDIX B
Data Archiving and Demonstration Plans

Copies of the project's demonstration test plan demonstration 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
5179 Hoadley Road
SFIM-AEC RM-TIC (Ms. Julia Tracy)
Aberdeen Proving Ground, Maryland 21010-5401

The demonstration test plan is entitled "*Test Plan for the Demonstration of 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, telephone (410) 436-6861, at Aberdeen Proving Ground, Maryland, or by writing to the following address:

Commander
U.S. Army Environmental Center
5179 Hoadley Road
SFIM-AEC RM-TIC (Ms. Darlene Bader)
Aberdeen Proving Ground, Maryland 21010-5401

APPENDIX C
Quality Assurance

SECTION C

Quality Assurance Plan

C.1 Purpose and Scope of the Plan

The purpose of the quality assurance plan outlined 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.

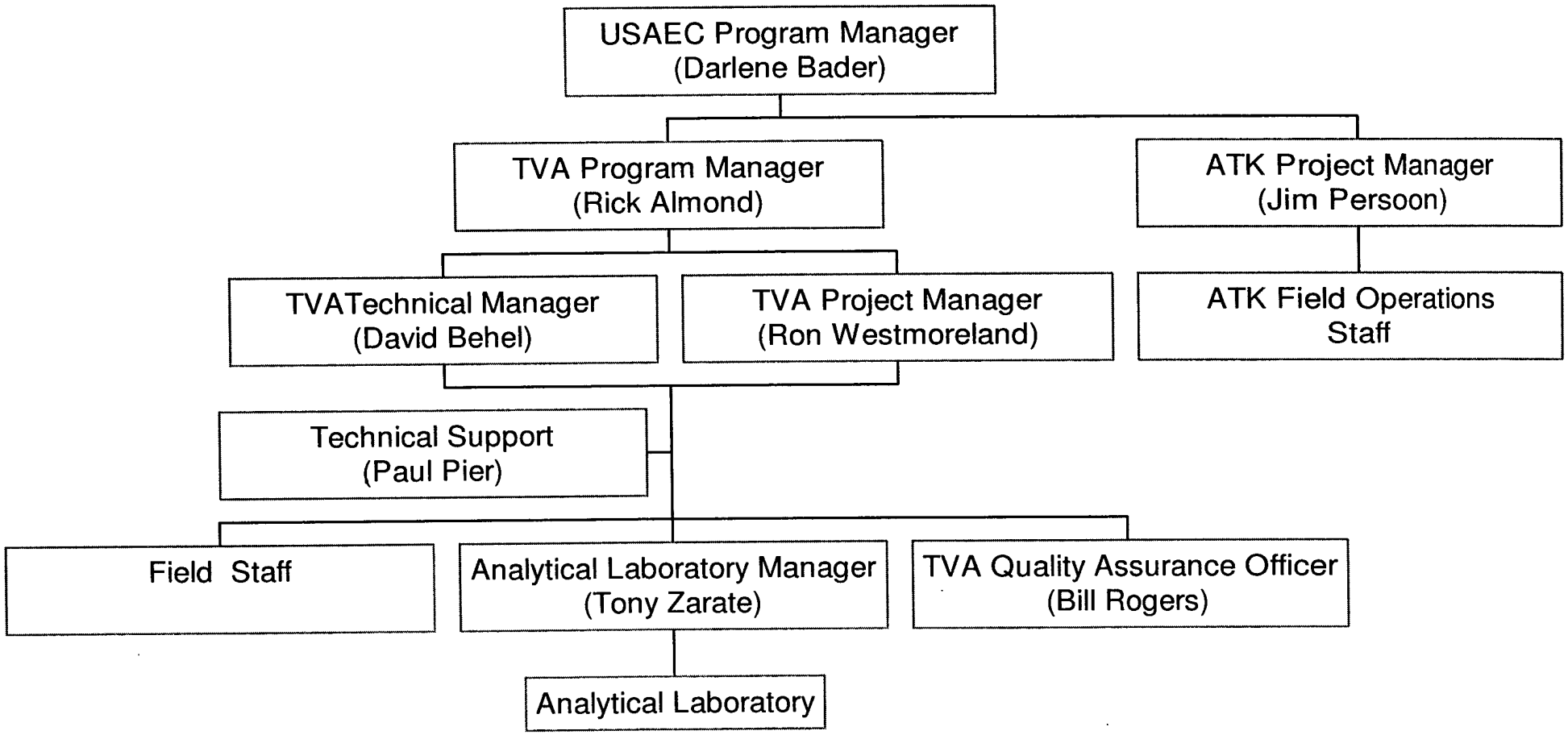

Figure C-1

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 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 Analytical Laboratory ran appropriate method blanks for the procedures used in this portion of the project. Method accuracy and precision were demonstrated by running quality control samples. Analysts demonstrated the ability to generate acceptable results with the methods by utilizing appropriate proficiency samples or standard reference materials. The Analytical Laboratory determined Method Detection Limits for target compounds.

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

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 and reduced on vendor-supplied chromatographic software for HPLC systems and on vendor-supplied analysis software for FIA systems. These systems typically 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 Onsite 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-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.

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 % =(meq $K_2Cr_2O_7$ - meq $FeSO_4$)(0.003)(100)(1.30)/(g water-free soil)

=(10.0 - meq Fe SO_4)(0.003)(100)(1.30)/(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.

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.
LACHAT INSTRUMENTS DIVISION
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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 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.

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.

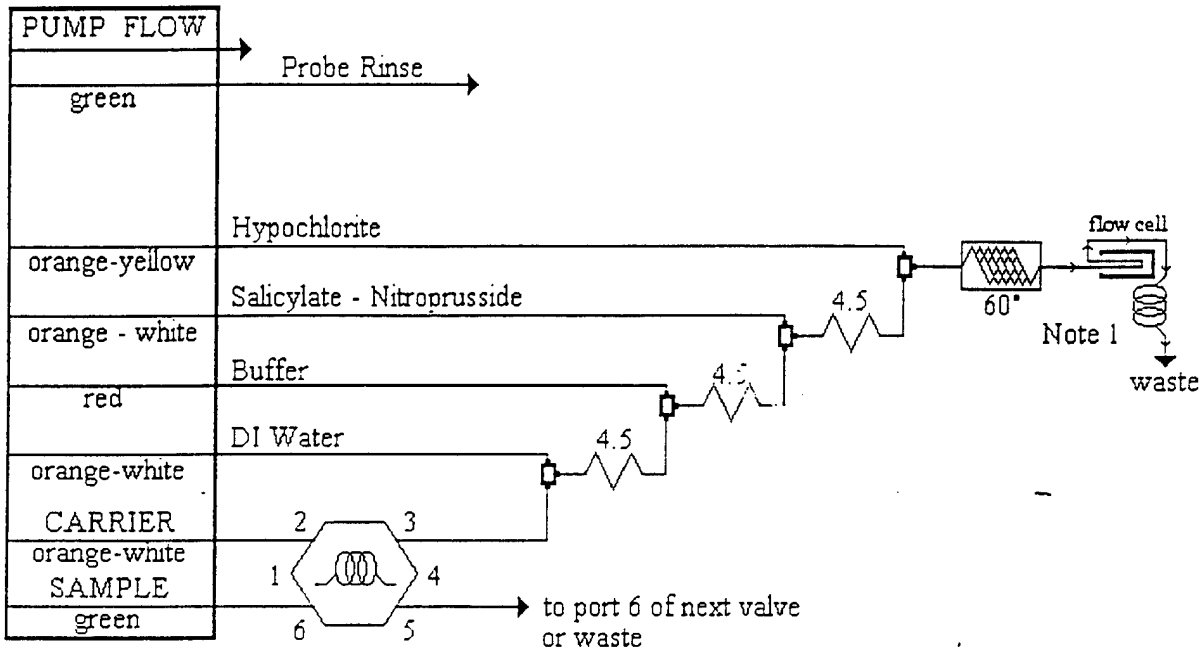
10.2. Correspondence, Allen Doyle, University of Alaska, Fairbanks, Institute for Arctic Biology, 4/20/92.

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:

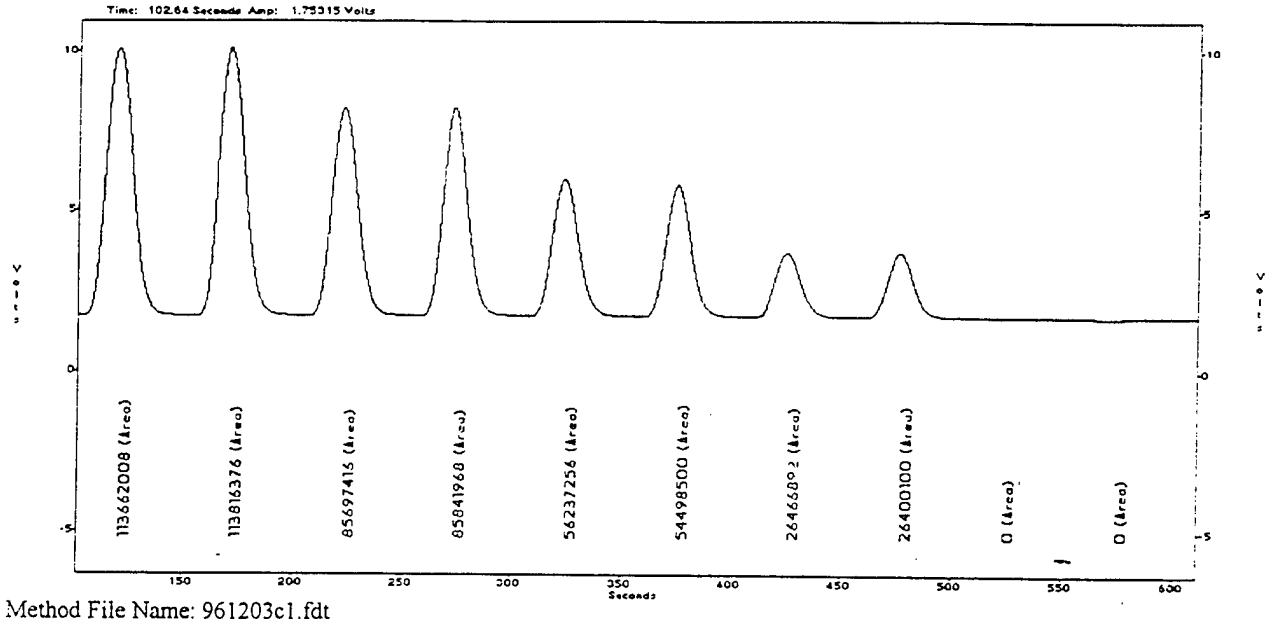
Min Probe in Wash Period:	5 s
Probe in Sample Period:	30 s

Valve Timing:

Load Time:	0.0 s
Load Period:	20 s
Inject Period:	30 s

11.3. SUPPORT DATA FOR QUIKCHEM 8000

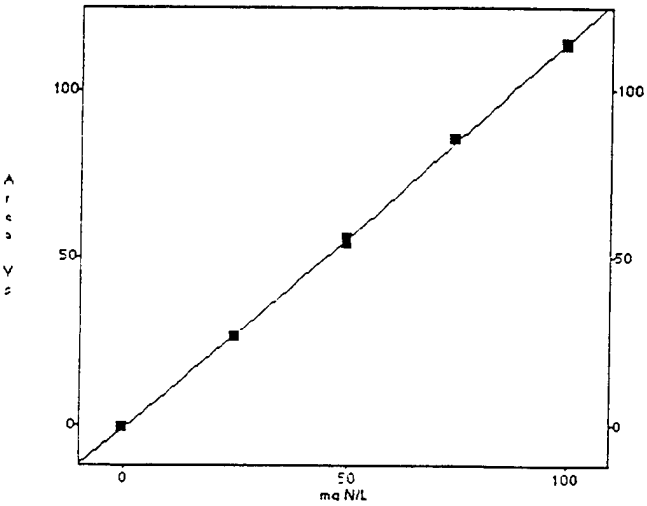
Calibration Data for Total Kjeldahl Nitrogen



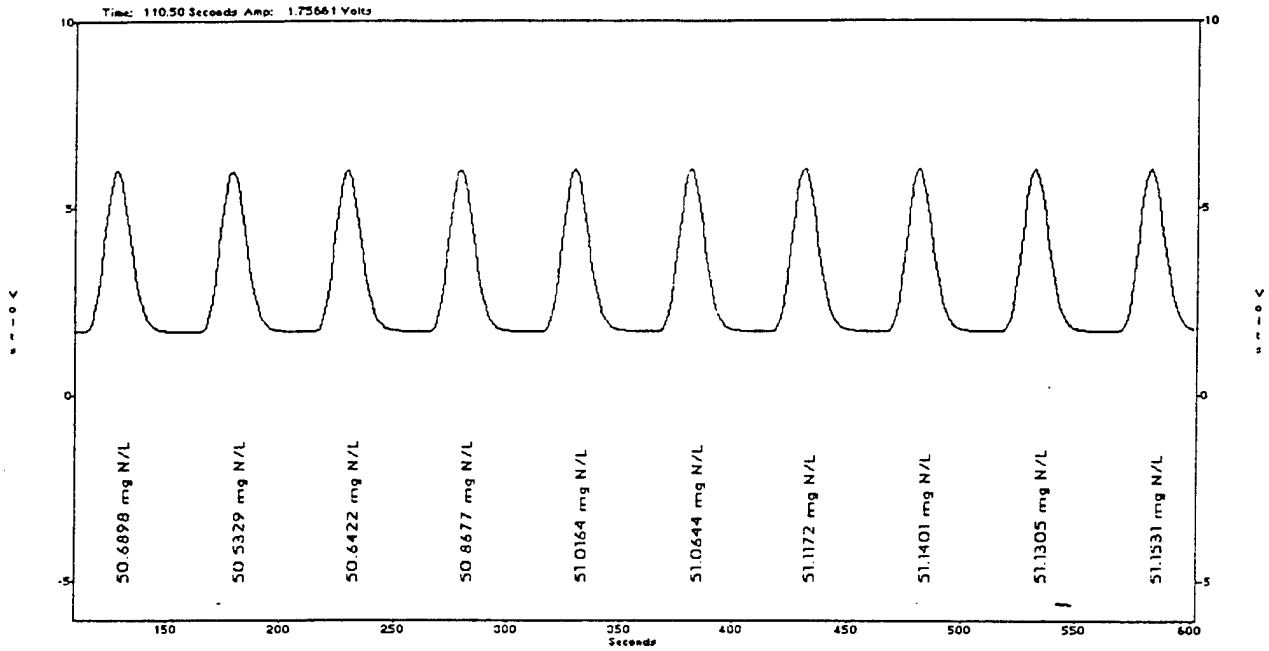
Method File Name: 961203c1.fdt
Acq. Date: 03 December 1996

Calibration Graph and Statistics

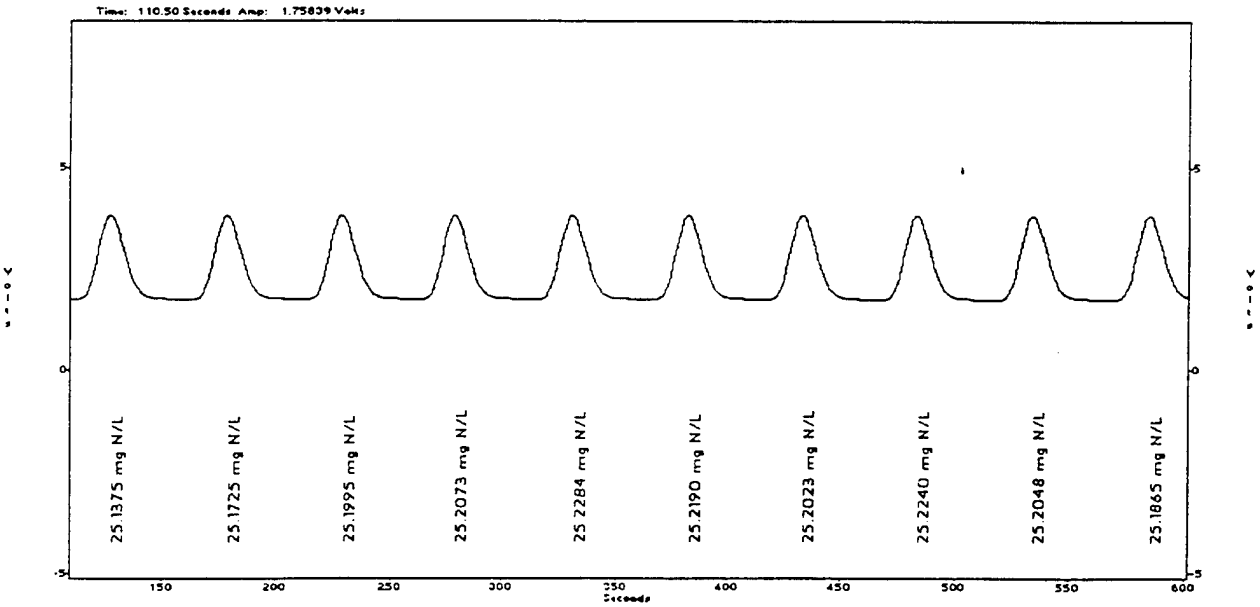
Level	Area	mg N/L	Determined	Replicate %RSD	% residual
1	113739192	100.	99.5	0.1	0.5
2	85769696	75.0	76.0	0.1	-1.3
3	55367880	50.0	49..8	2.2	0.4
4	26433496	25.0	24.3	0.2	3.0
5	0	0.0	0.0	0.0	—



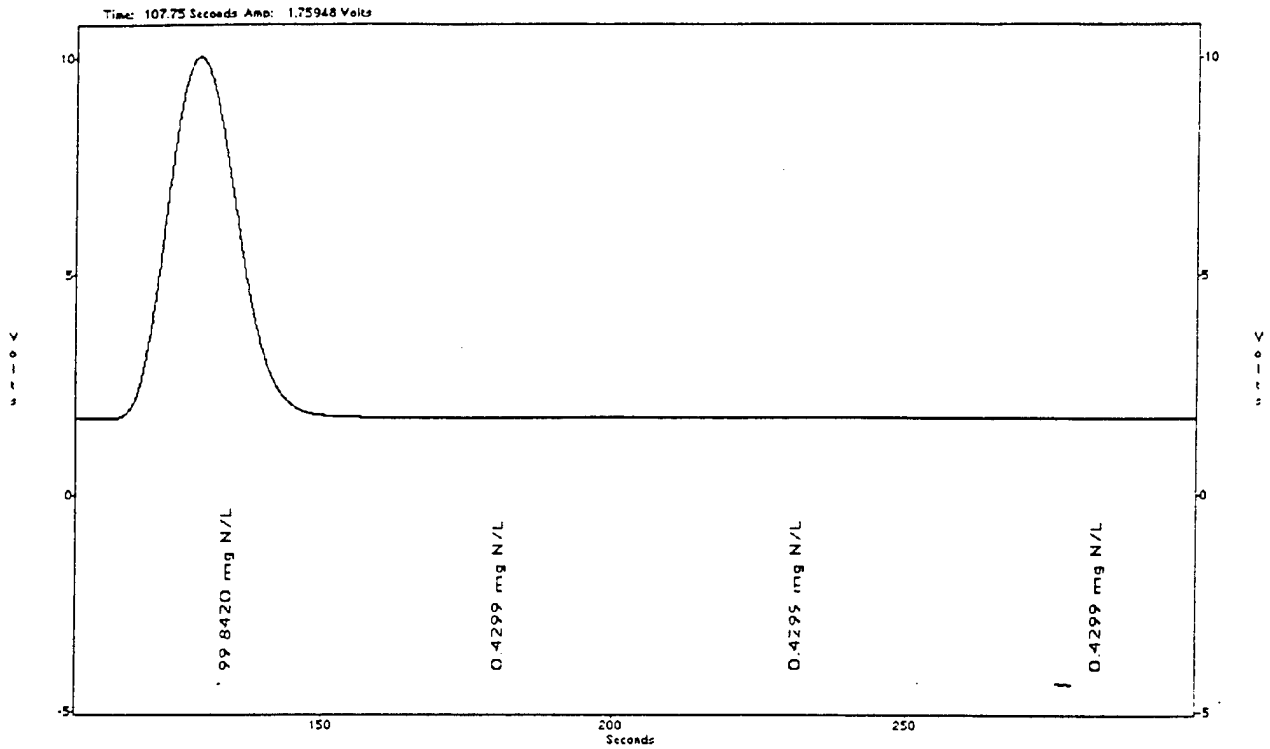
Scaling: None
Weighting: None
2nd Order Poly
Conc = -3.473e-016 Area² + 9.108e-007 Area + 4.299e-001
R^2 = 0.9997



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

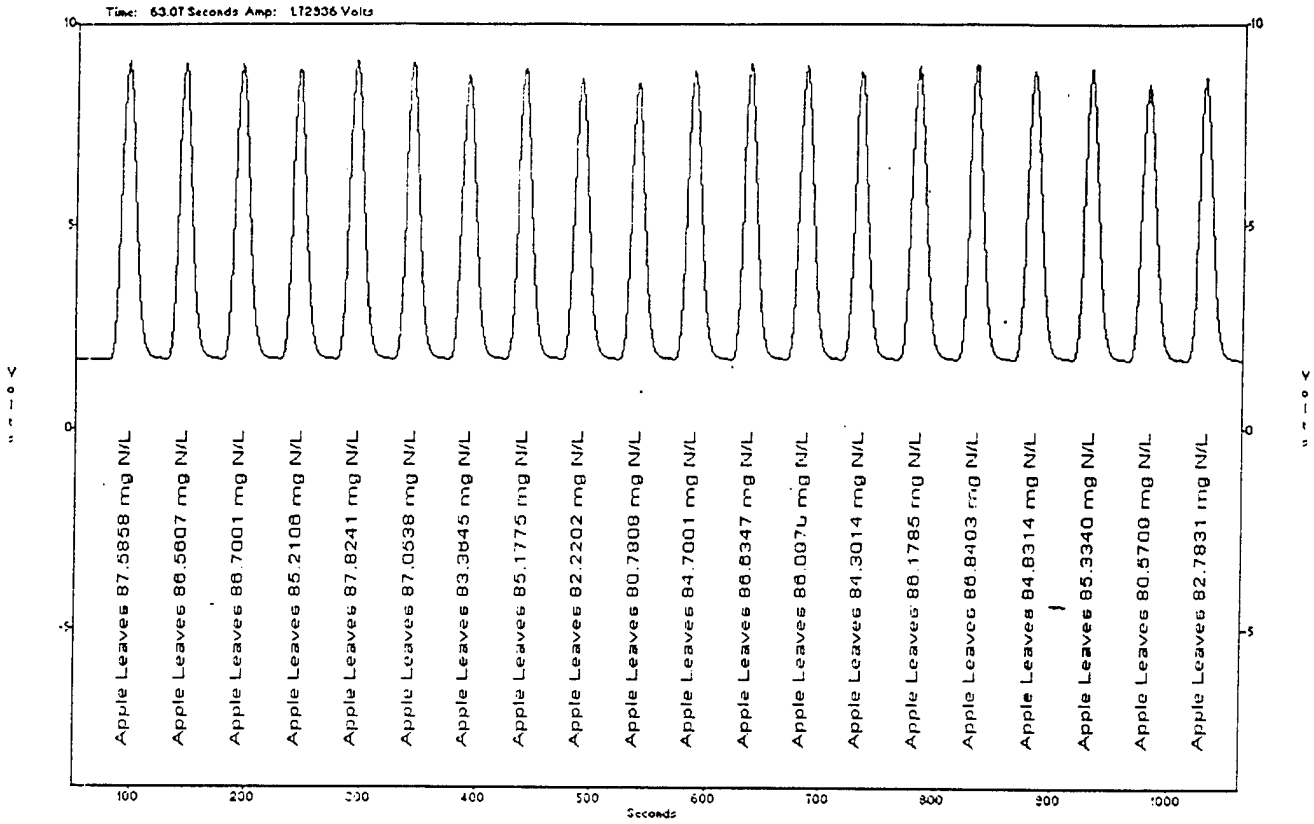


Precision data for total kjeldahl nitrogen using 25.0 mg N/L standard
% RSD = 0.11
Standard Deviation (s) = 0.027, Mean (x) = 25.20, Known value = 25.0 mg/L
Data File name 961203m1.fdt
Acq. Date: 03 December 1996



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

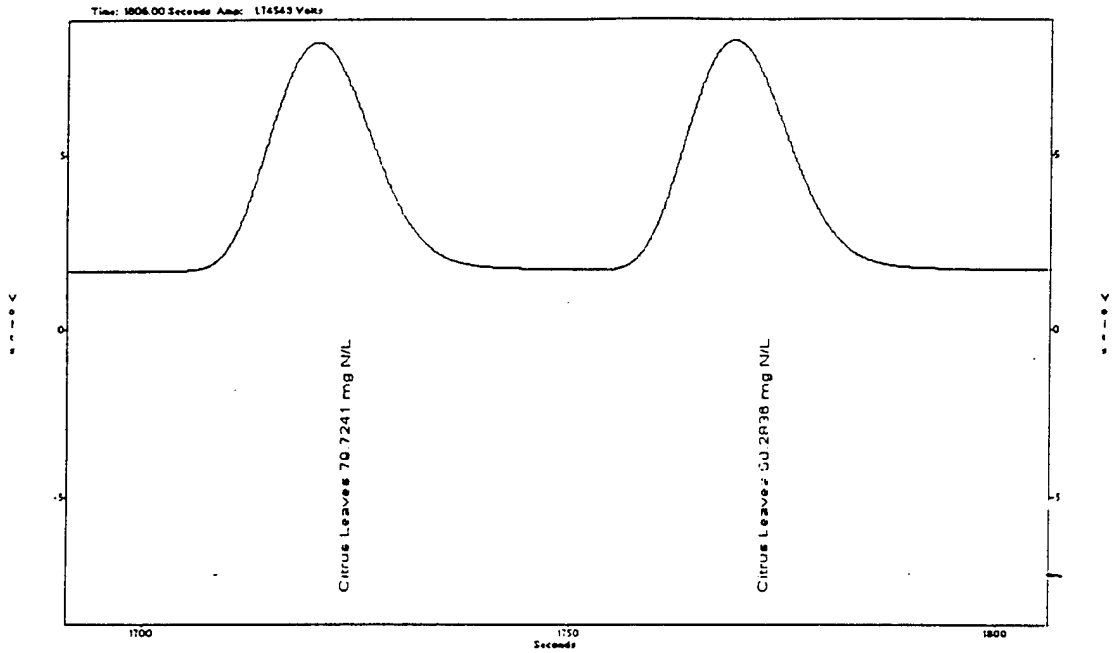
Mean (x) = 2.09 % N, Standard Deviation (s) = 0.0293; Known Value = 2.31 % N

Datafile Name: 961205s2.fdt

Acq. date: 5 December 1996

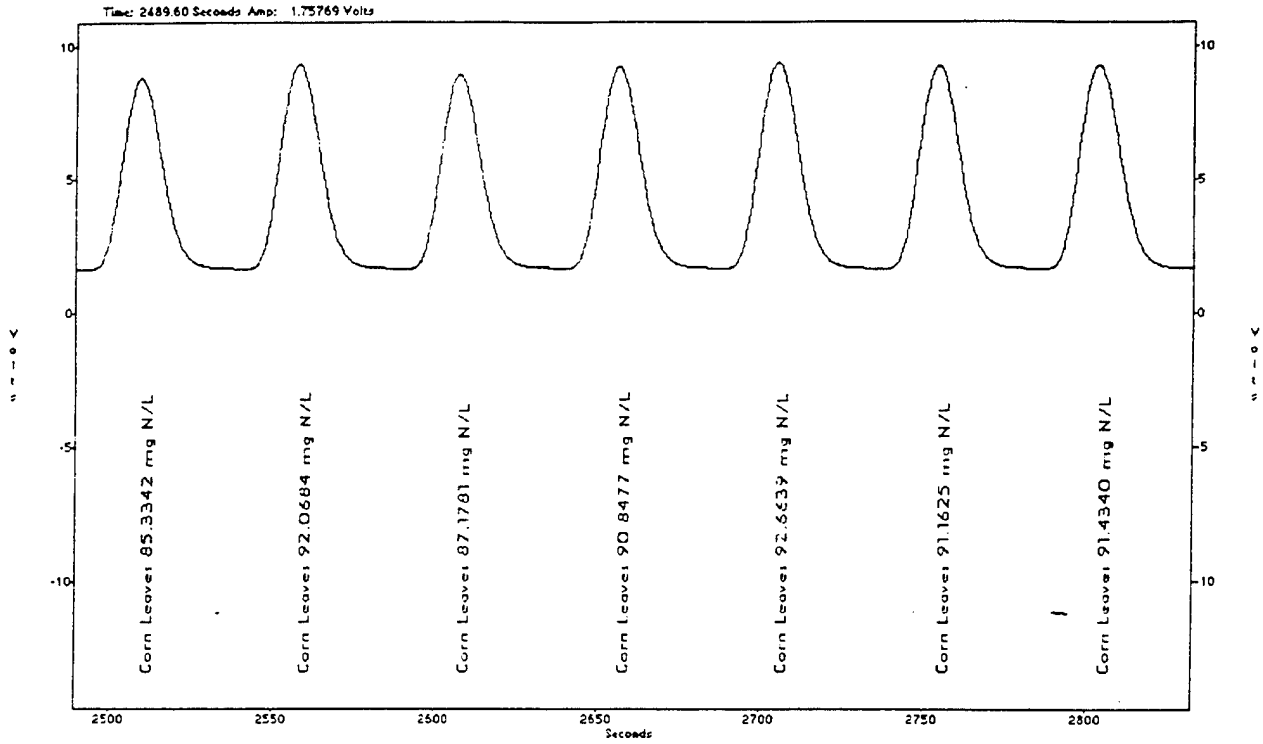
Tube Number	Mean conc. of 2 reps (mg N/L)	Mean conc. of 2 reps (% N)	Recovery (%)
1	87.1	2.05	88.8
2	86.0	2.11	91.5
3	87.4	2.13	92.0
4	84.3	2.08	89.9
5	81.5	2.08	90.0
6	85.7	2.09	90.6
7	85.2	2.10	90.8
8	86.5	2.10	91.1
9	85.1	2.12	91.9
10	81.7	2.04	88.2

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

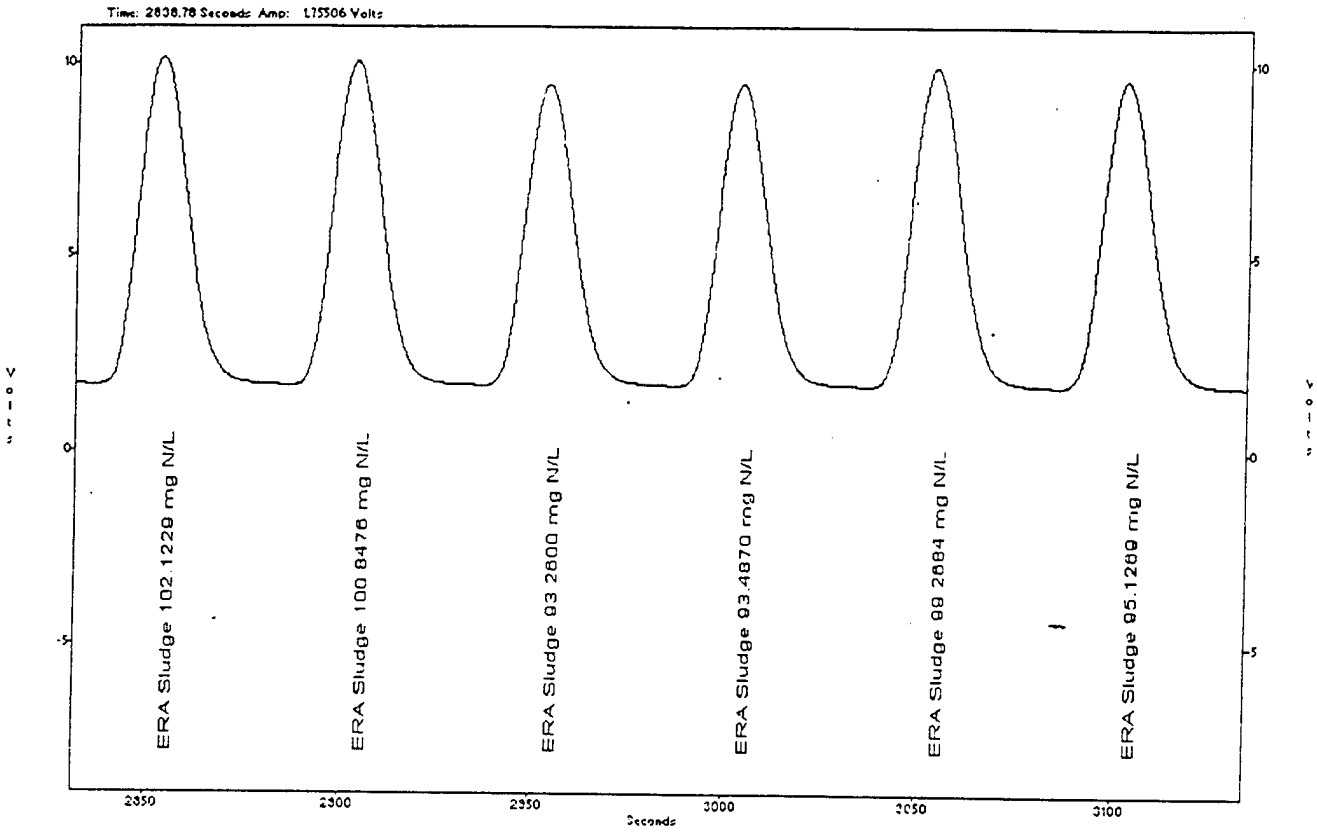
Mean (x) = 2.48 % N, Standard Deviation (s) = 0.0754, Known Value = 2.71 % N

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.

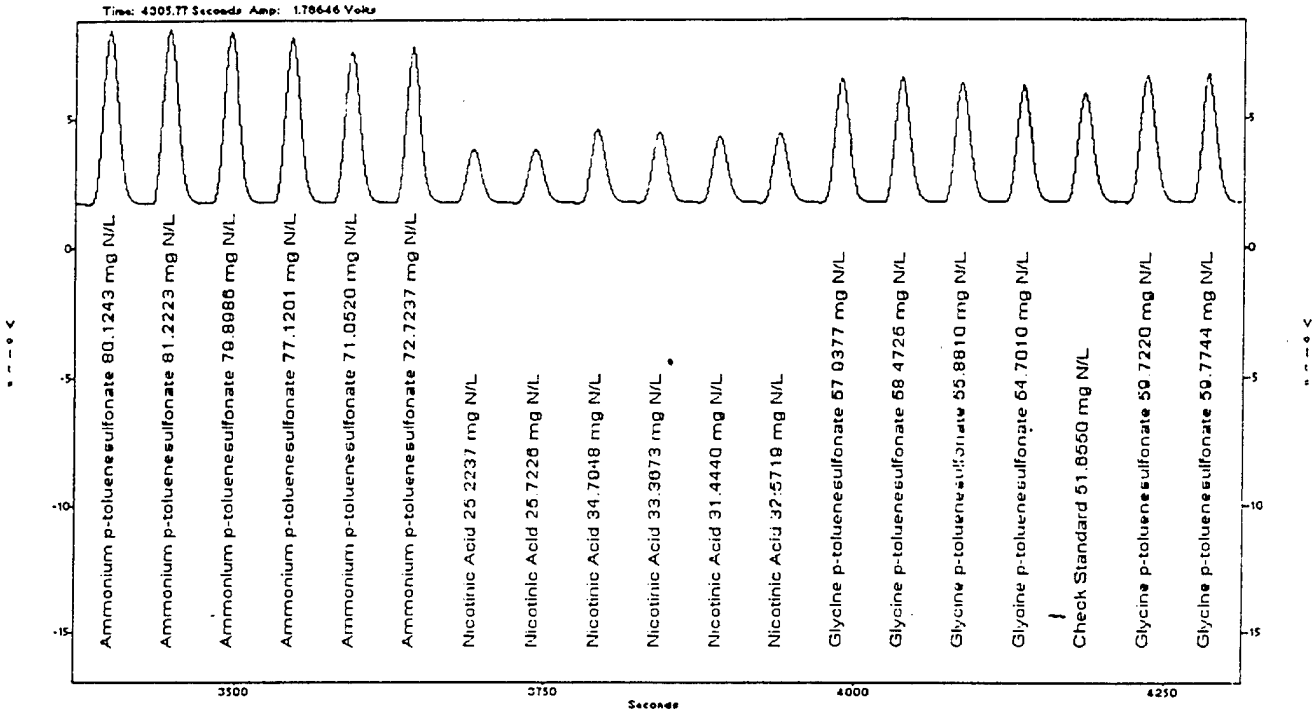
Digestion %RSD = 1.41, n = 3

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**

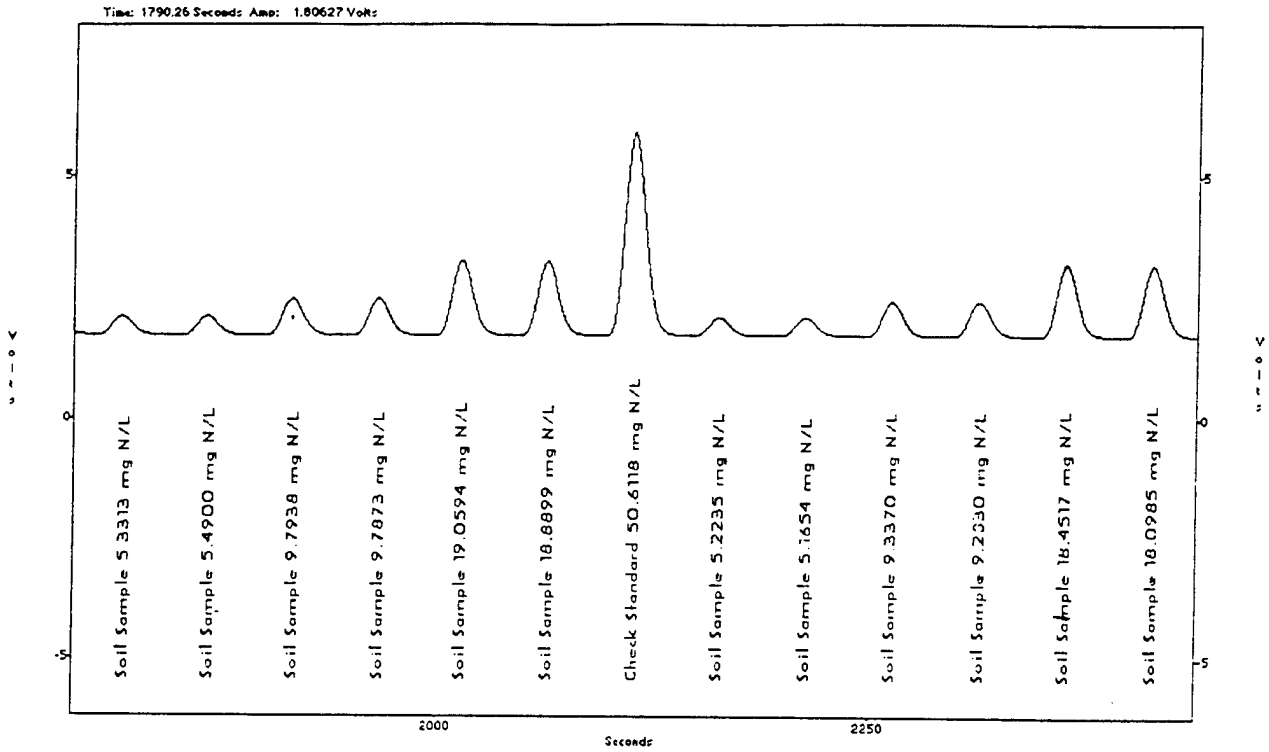
PRIMARY STANDARDS



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

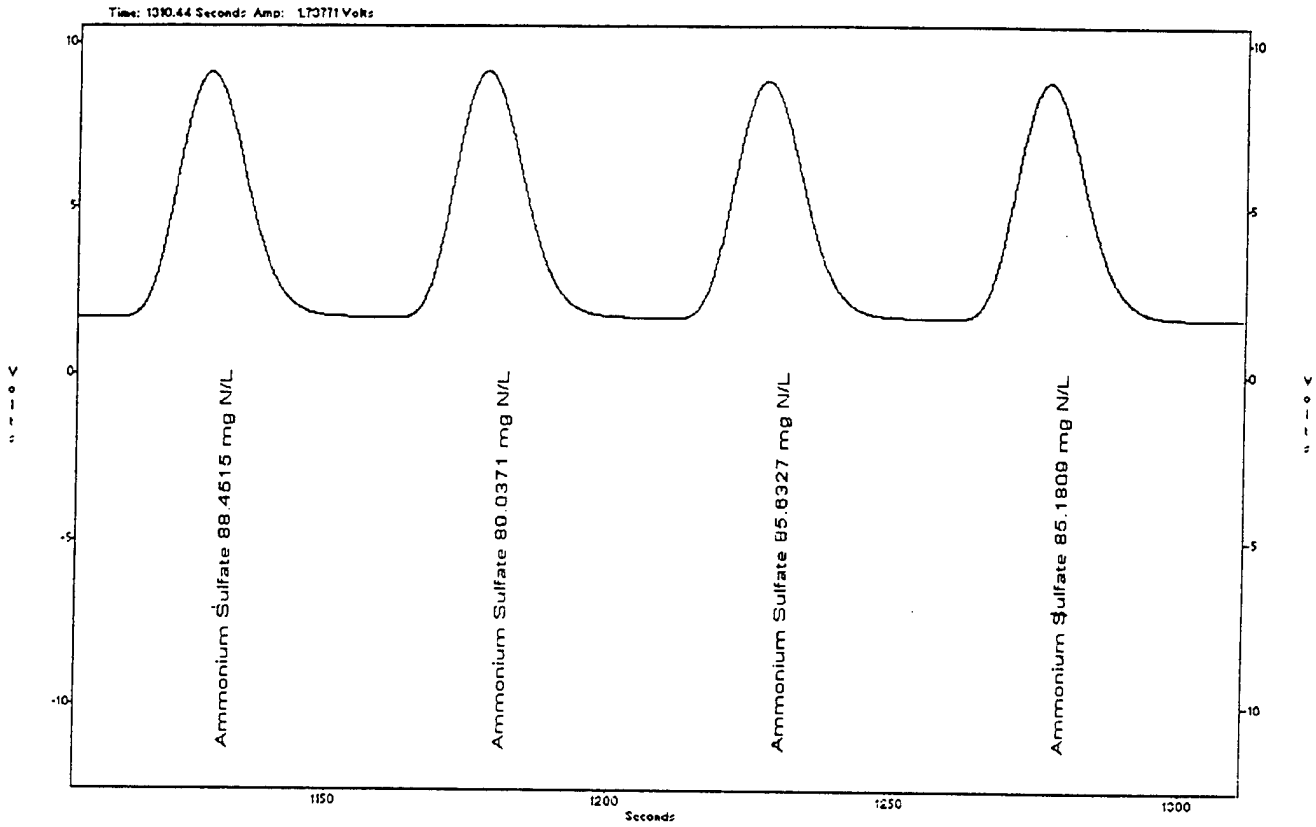
Mean (x) = 0.243 % N, Standard Deviation (s) = 0.014

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

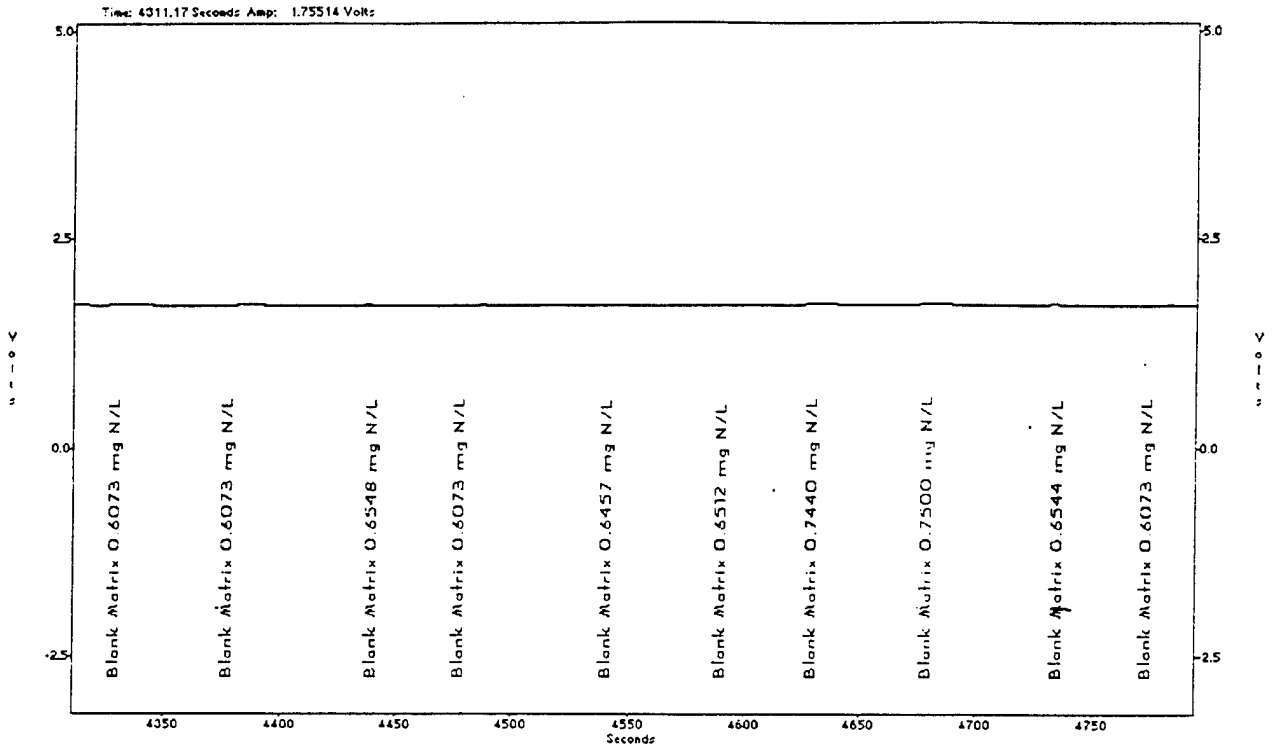
Mean (x) = 20.59 % N, Standard Deviation (s) = 0.199, Known Value = 21.26 % N

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 $BeSO_4 \cdot 4H_2O$ (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.

2. Sampling and Analysis Methods for Hazardous Waste Combustion; U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory, Office of Research and Development: Research Triangle Park, NC, 1984; Prepared by Arthur D. Little, Inc.

3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

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	Tl -	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

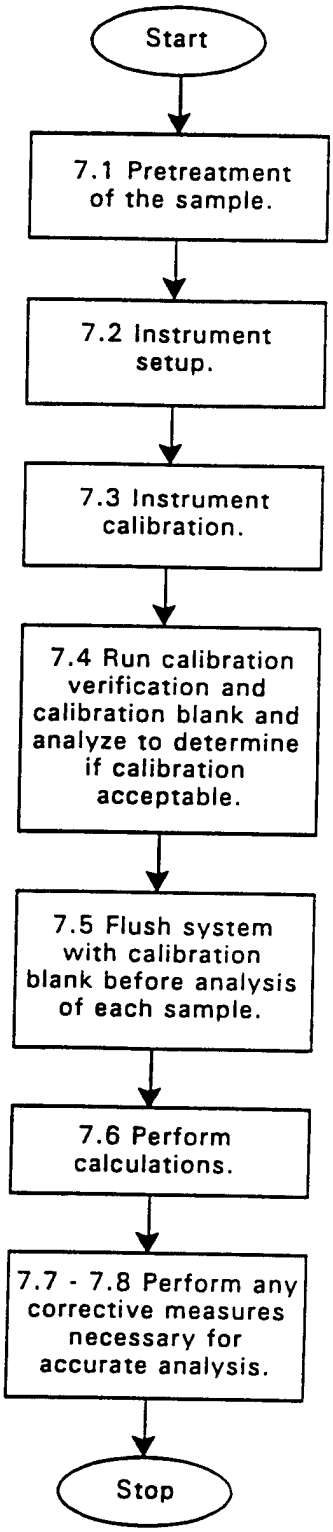
[a]These performance values are independent of sample preparation because the labs analyzed portions of the same digests.

[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.

METHOD 6010B

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 Soil 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

Analyte	Percent Recovery[a,c]							
	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.

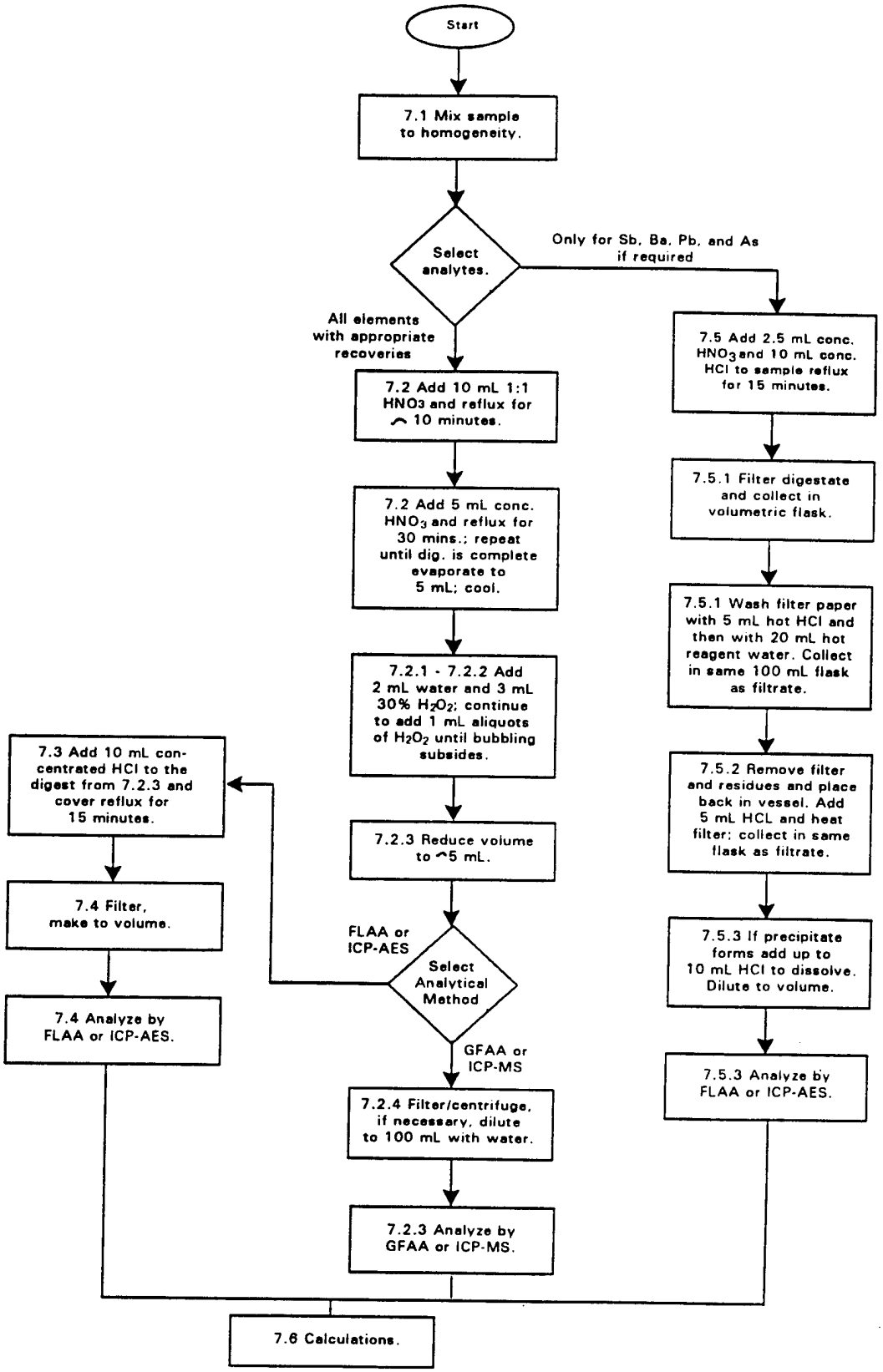
Table 5

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.

METHOD 3050B
ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS



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

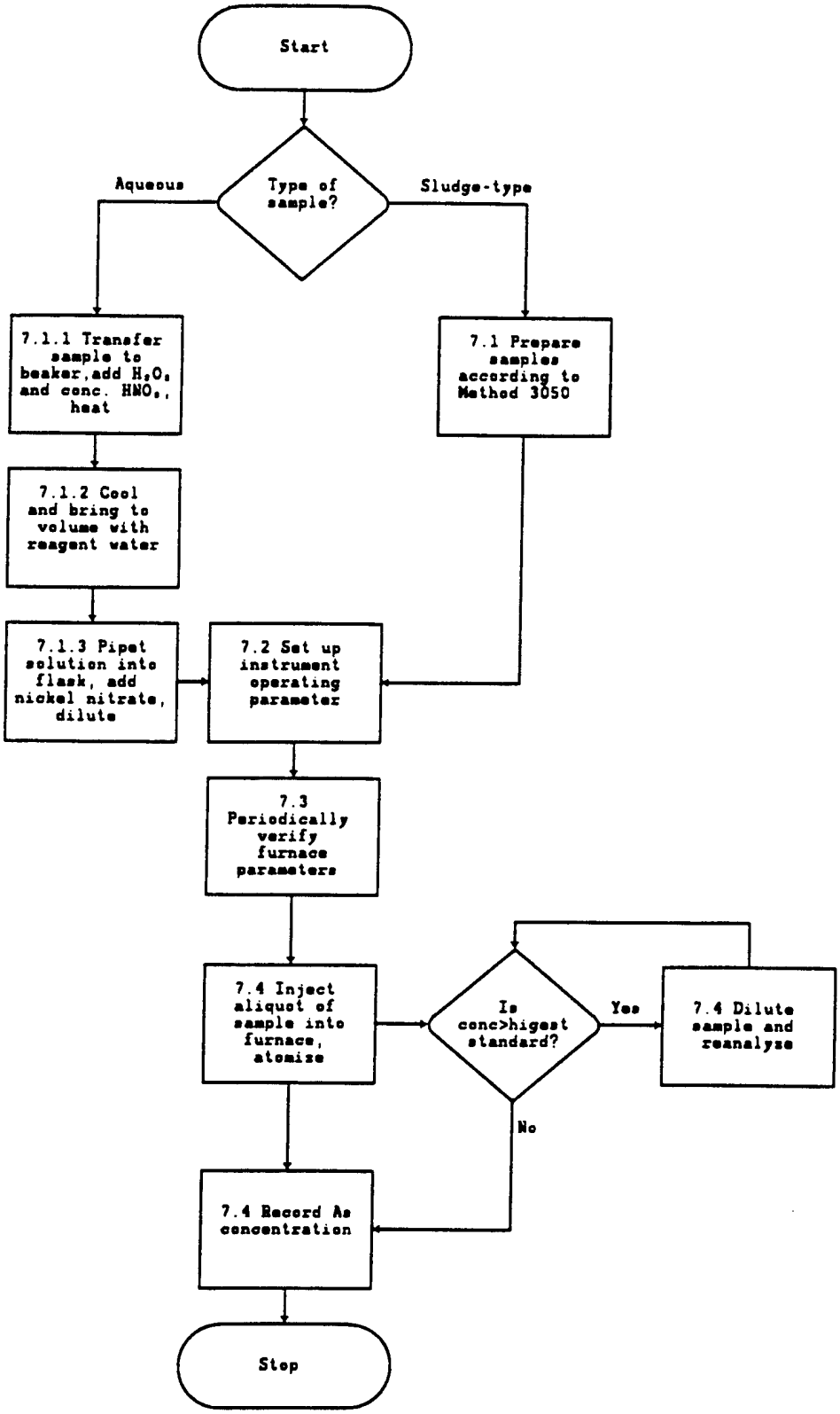
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

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-μm 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-μm 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.

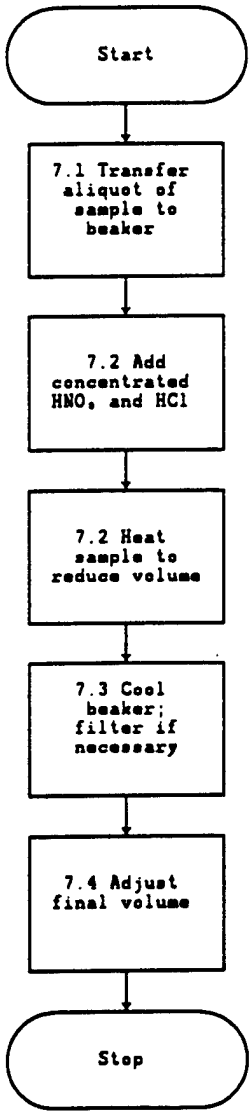
9.0 METHOD PERFORMANCE

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_3 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	-	28.66		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
[illegible]-Trimethylbenzene	99	1.2	-	-
[illegible],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

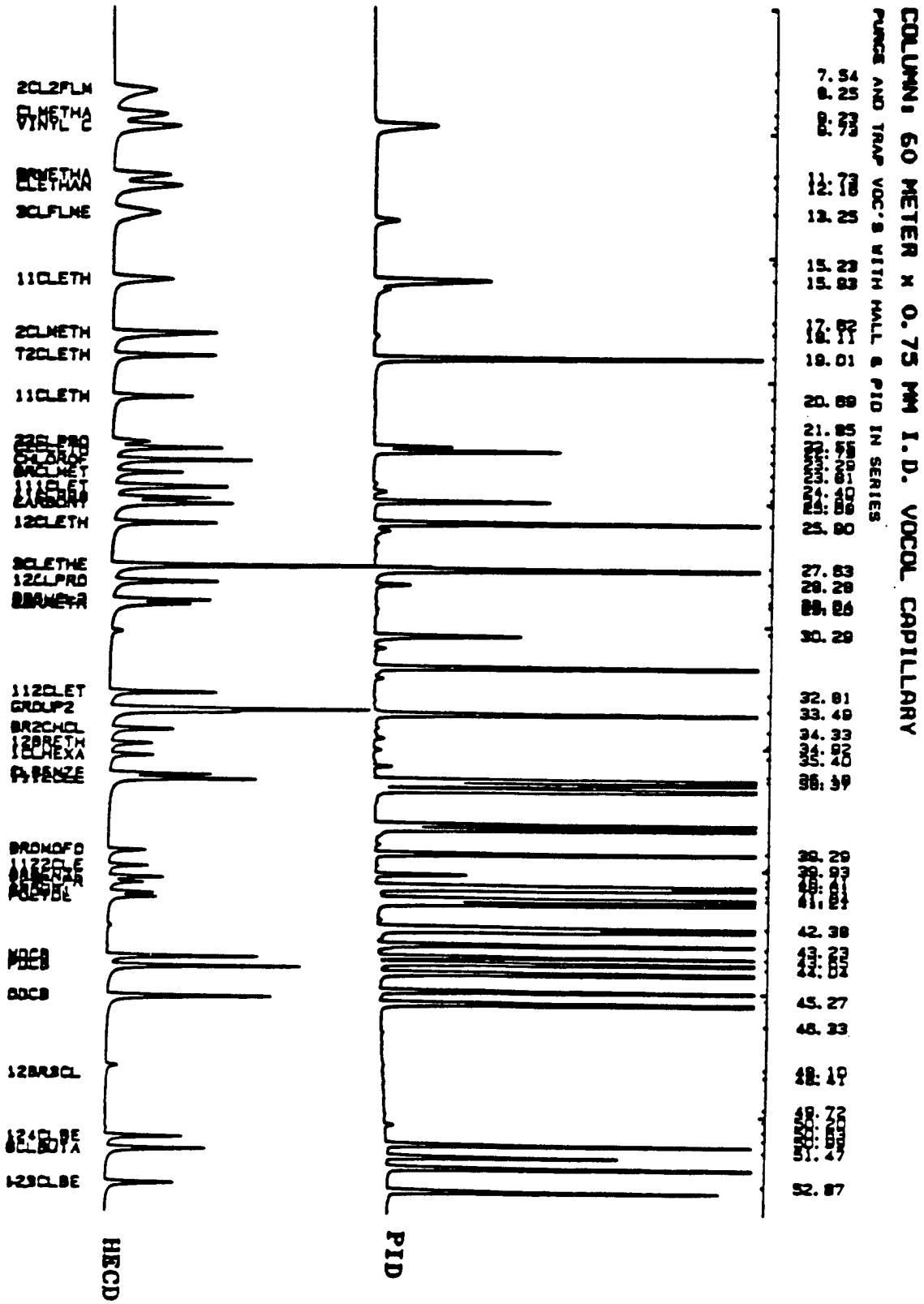
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

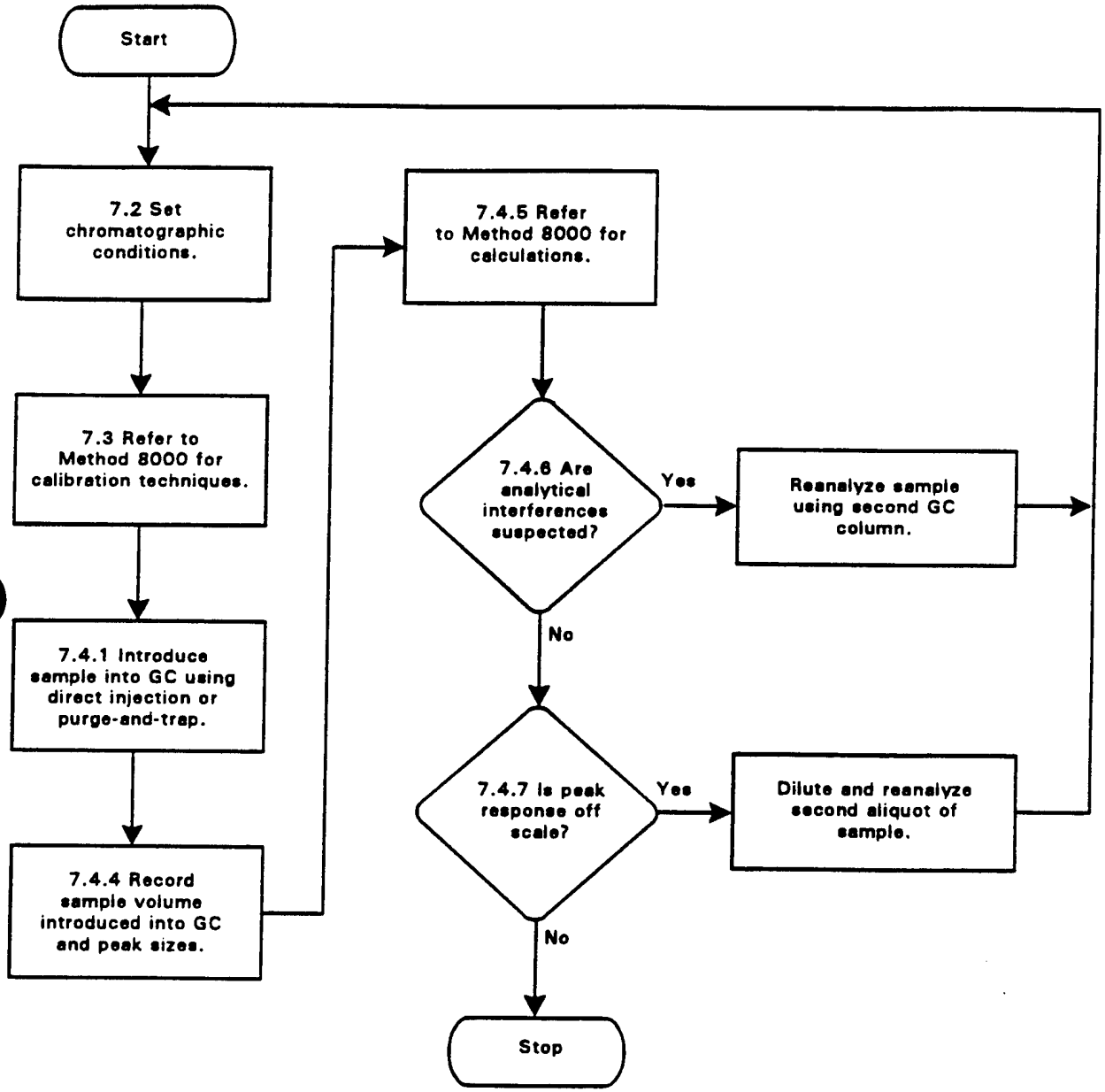
Matrix	Factor[b]
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

[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
Preparation Procedure for CEC: Method ASA 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-17
Chain of Custody Procedure

"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.

"Sample Chain of Custody"

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	REMARKS

RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME	RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY (SIGNATURE)	DATE/TIME
RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME	RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY (SIGNATURE)	DATE/TIME
RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED FOR LABORATORY BY: (SIGNATURE)	DATE/TIME	LABORATORY (NAME, CITY, STATE)			

TVA 29203 B (RG-CTR 4-94)

•COPY 1 - FIELD INVESTIGATOR •COPY 2 - FIELD INVESTIGATOR •COPY 3 - RETAINED BY LABORATORY

"Sample Chain of Custody"

10.2 Sample custody form - General

Sample Chain of Custody
Tennessee Valley Authority
Environmental Applications 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						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
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-18
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 25^0C).

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-19
Analytical Procedure for EDTA in Soil: 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:

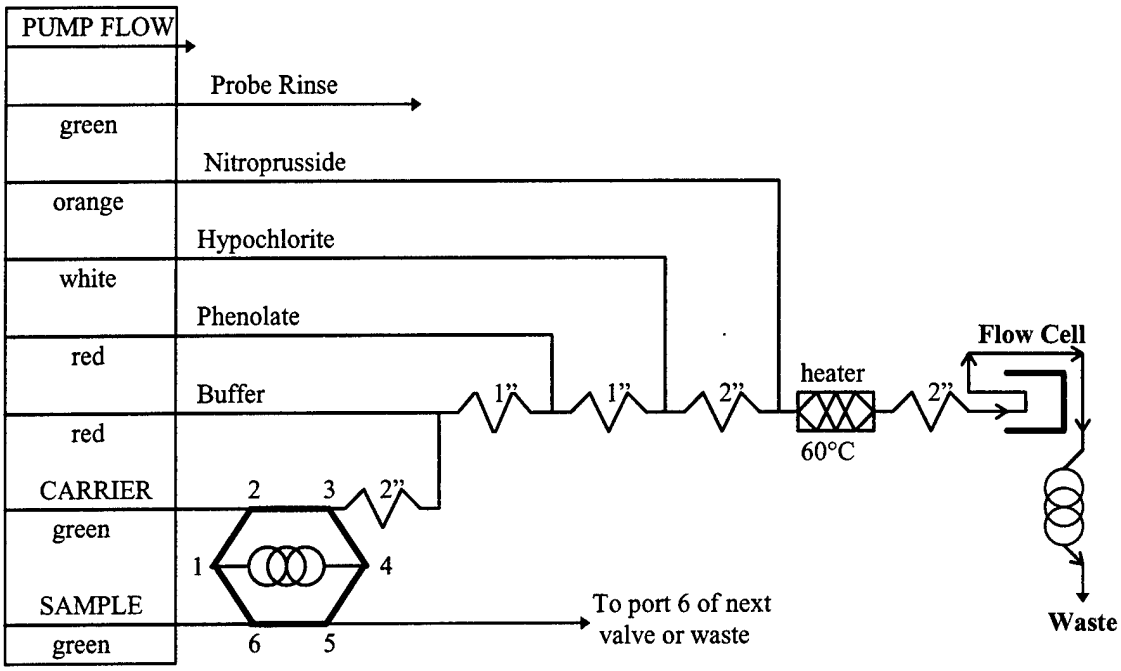
Method Cycle Period:	70.0
Min. Probe in Wash Period:	9.0
Probe in Sample Period:	30.0

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 0-12-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., fifteen-inch row spacing vs thirty-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 two-and one-half inches to the side, and two 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 twenty to thirty percent 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' 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°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°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 ten percent 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 ten-fold lower than had been expected, compared to results from the Sunflower experiments. Although the soils in the two studies were of similar pH and lead content, the Sunflower 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 Sunflower 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 Sunflower 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 percent 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 percent 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 percent 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 kriged 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

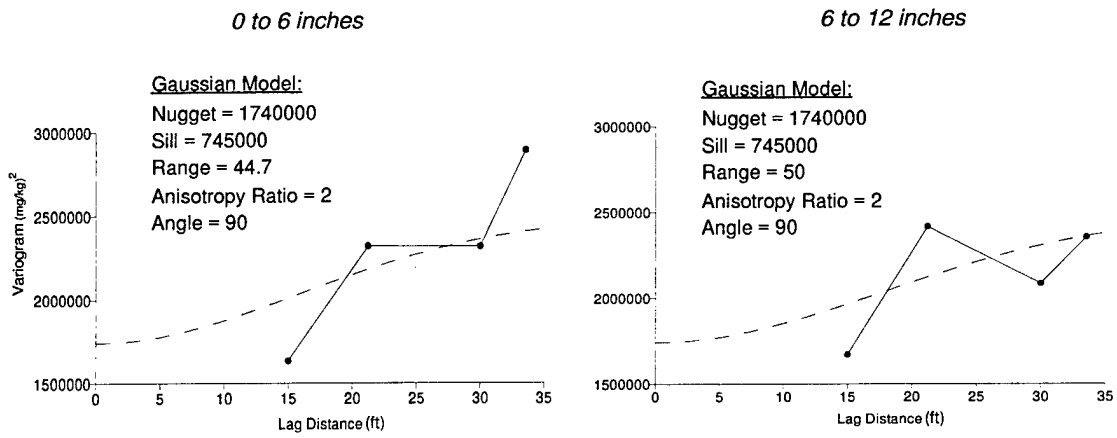
Table 1 presents summary statistics or total lead in soil at Site C from initial and post-mustard sampling events. As shown, although samples were obtained from every cell (36 each) before remediation began at the site, only 22 samples could be collected following the mustard crop amendment. The standard 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 $[mg/kg]^2$).

(a) Initial Lead



(b) Post-Mustard

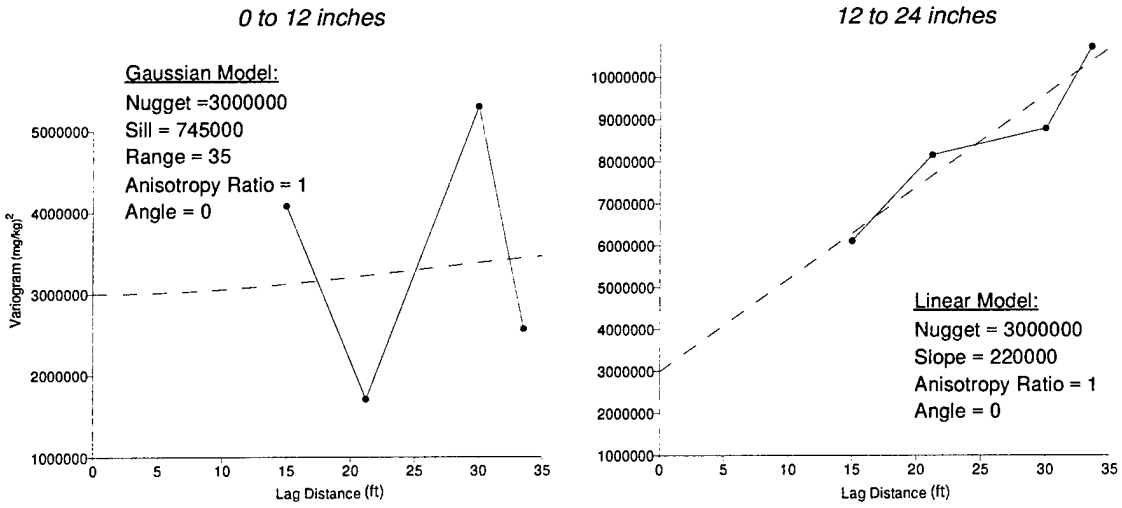


Figure 1
Variograms of Site C Analytical Data from
(a) Initial Soil Lead Sampling and (b) Post-Mustard Amendment Soil Lead Sampling

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.

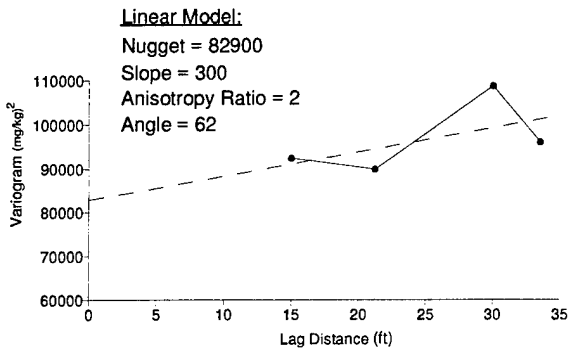
Table 2
Summary Statistics of Total Lead in Soil (mg/kg) at Site 129-3
From Initial and Post-Mustard Sampling Events

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

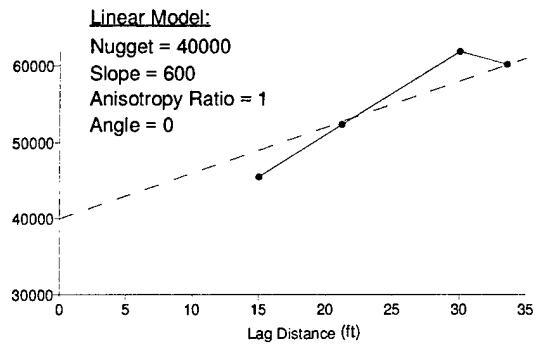
Figure 2 shows variograms developed for Site 129-3 soil sampling results. Variograms for the initial lead sampling event (by depth interval) were fit to a linear model. The nugget effects of both initial lead (Figure 2a) and post-mustard (Figure 2b) variograms are high as found with Site C.

(a) Initial Lead

0 to 6 inches

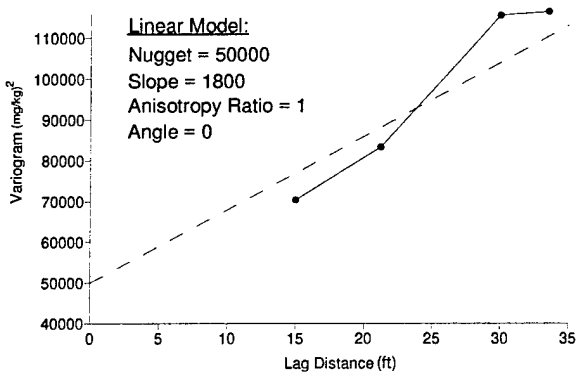


6 to 12 inches



(b) Post-Mustard

0 to 12 inches



12 to 24 inches

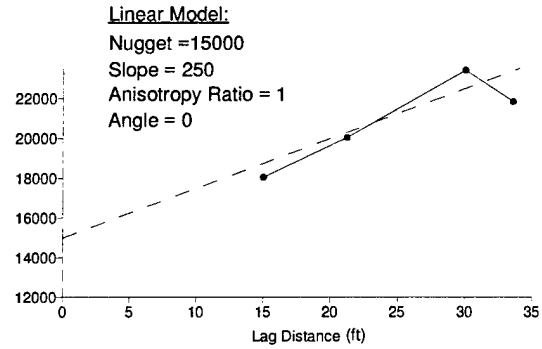


Figure 2
Variograms of Site 129-3 Analytical Data from
(a) Initial Soil Lead Sampling and (b) Post-Mustard Amendment Soil Lead Sampling

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.

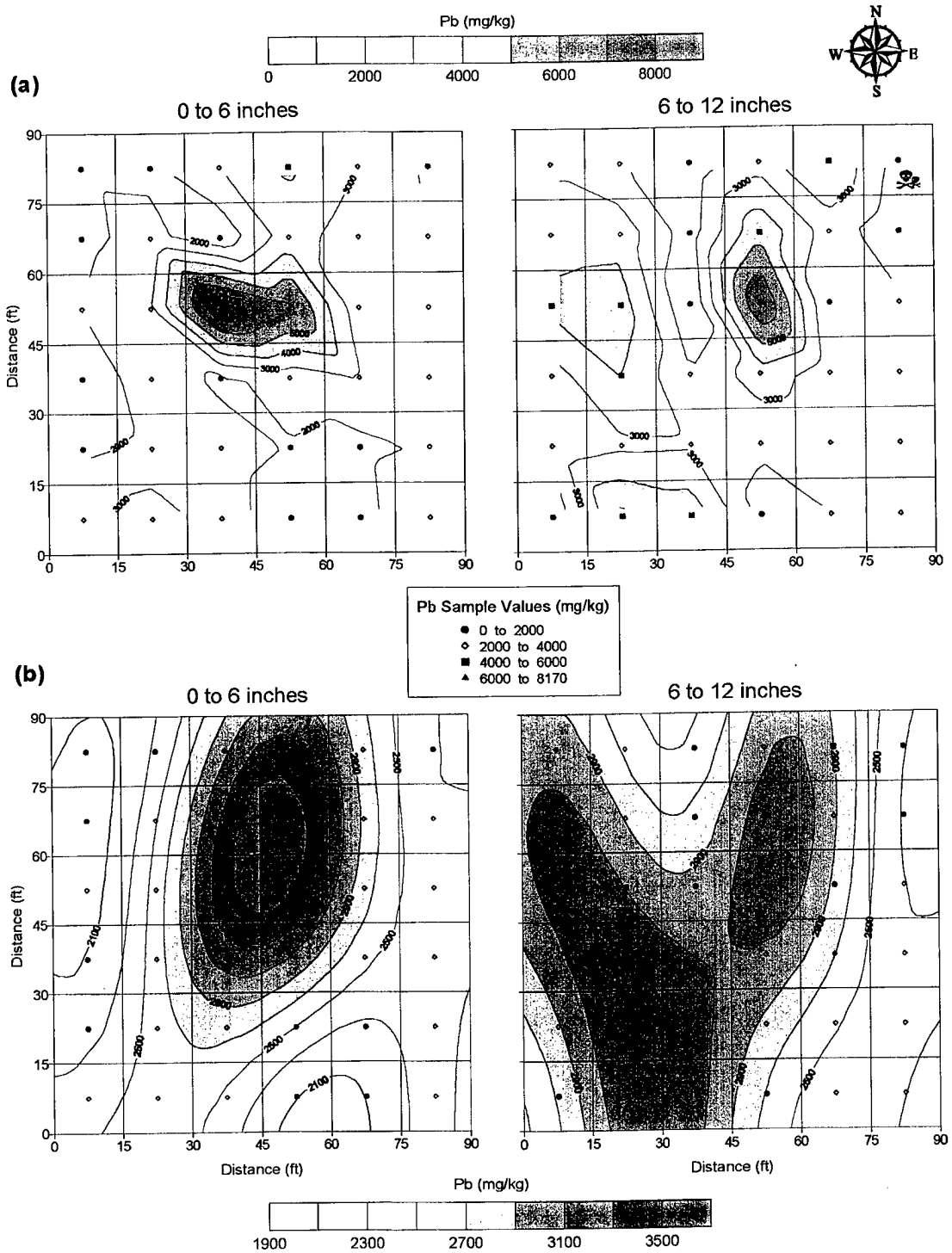


Figure 3
Maps of Site C Initial Soil Lead Based on (a) Triangulation with Linear Interpolation and (b) Kriging Interpolation

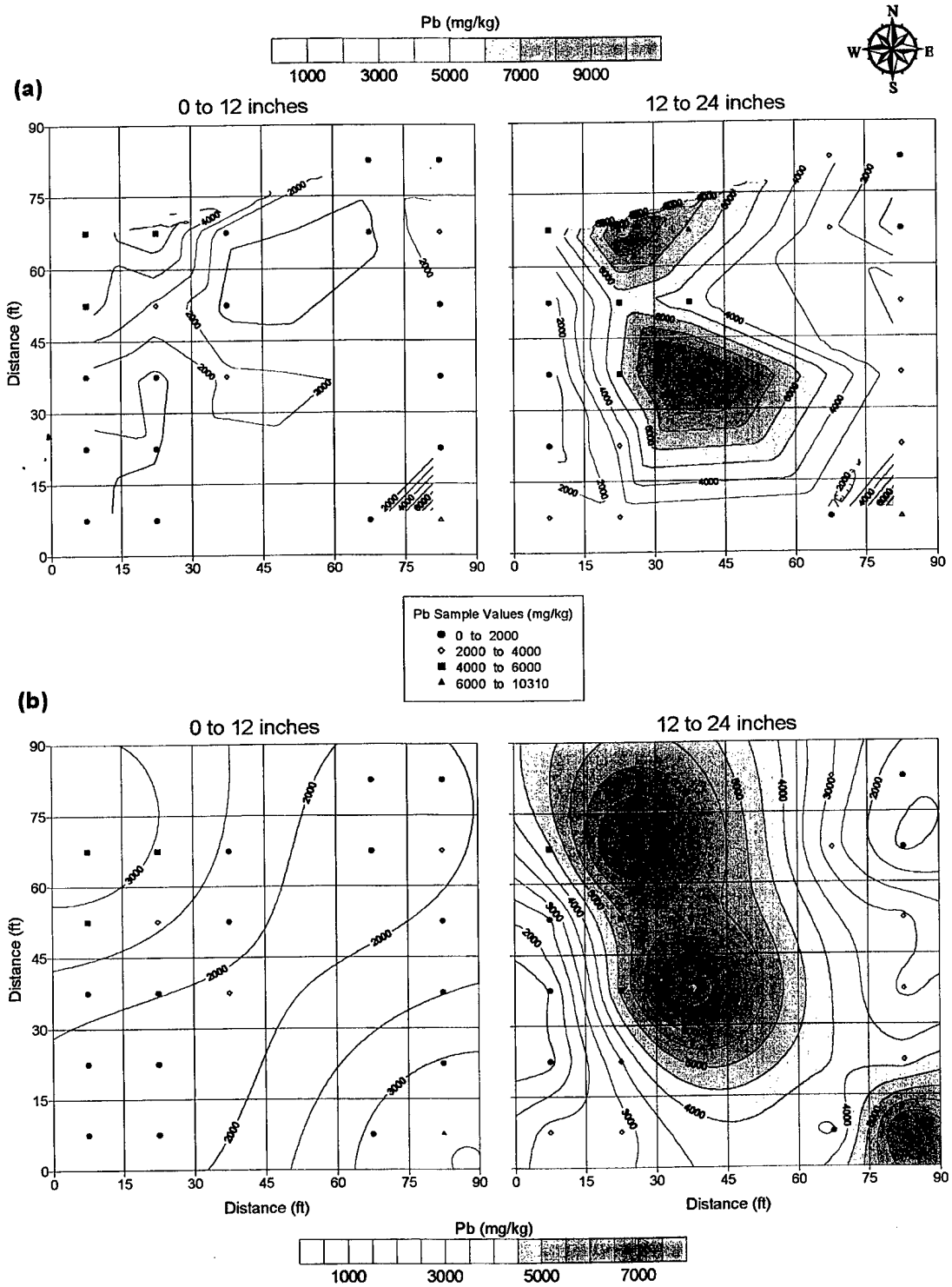


Figure 4
Maps of Site C Post-Mustard Soil Lead Based on (a) Triangulation with Linear Interpolation and (b) Kriging Interpolation

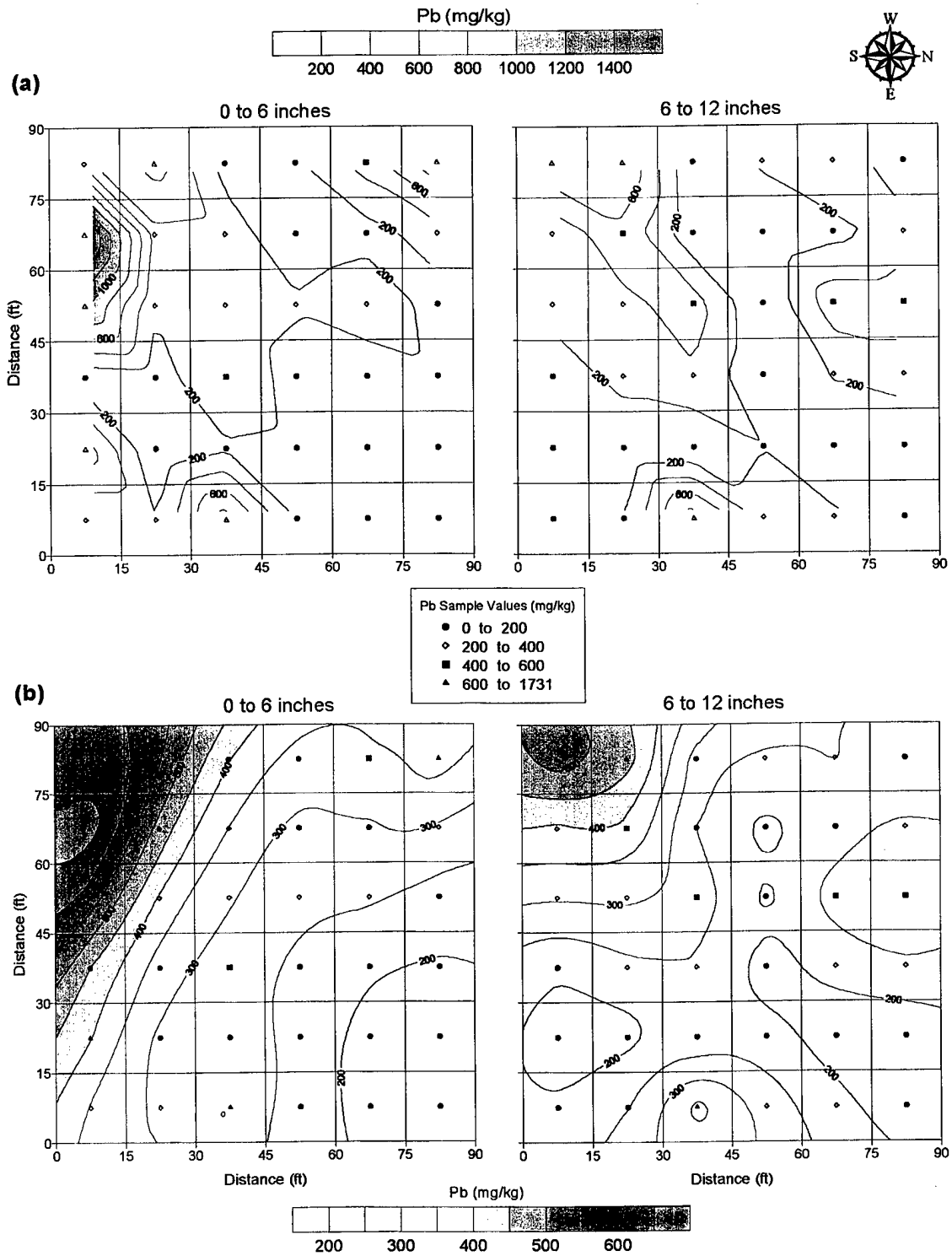


Figure 5
Maps of Site 129-3 Initial Soil Lead Based on (a) Triangulation with Linear Interpolation and (b) Kriging Interpolation

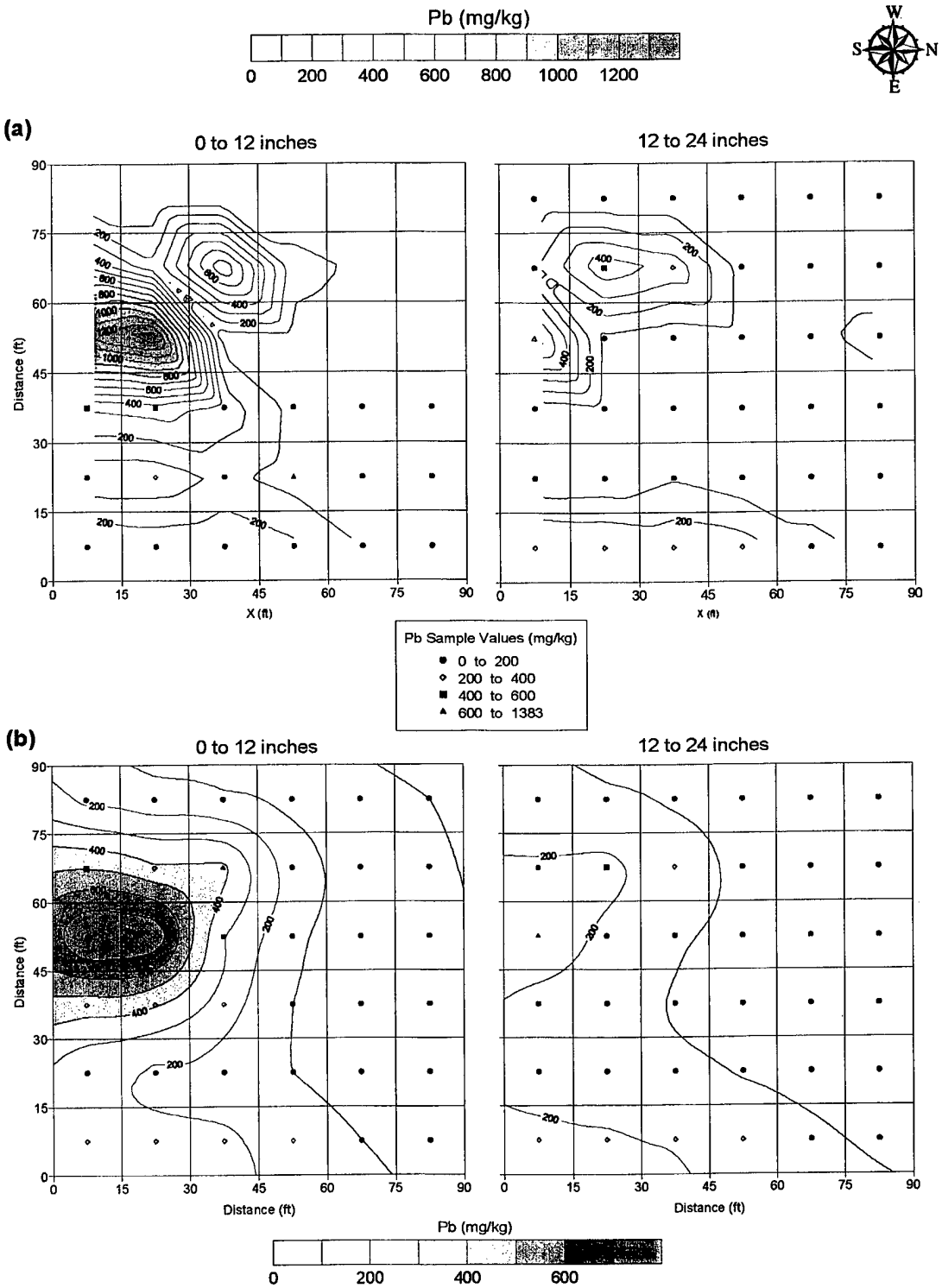


Figure 6
Maps of Site 129-3 Post-Mustard Soil Lead Based on (a) Triangulation with Linear Interpolation and (b) Kriging Interpolation