Section 1.0
Introduction

1.1 Background Information

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

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

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

- Landfilling of contaminated soil

- Soil washing (separation) - excavation of soil followed by soil washing, return of clean soil to the site, and landfilling of soil which is still contaminated

- Incineration - excavation and incineration, with the remaining mineral fraction returned to the original site, or landfilling if decontamination is not complete

- Solidification - excavation and *ex situ* solidification with pozzolanic agents and landfilling of the stabilized material

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

In situ methods include:

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

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

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

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

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

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

1.2 Official DoD Requirement Statement

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

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

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

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

1.2.1 How Requirements Were Addressed

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

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

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

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

DOD PILLAR 1: Cleanup

PROGRAM THRUST 1.N: Inorganic-Contaminated Soils

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

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

TRI-SERVICE REQUIREMENTS

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

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

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

1.3 Objectives of the Demonstration

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

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

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

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

The project was executed in seven phases, these being:

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

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

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

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

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

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

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

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

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

In contrast, the demonstration within the second site, Site 129-3, was intended to illustrate the effectiveness of phytoextraction methods near the conclusion of a remediation program, or for situations in which the level of contamination is low and the use of a "polishing treatment" is desirable. Lead concentrations ranged from 23 to 740 ppm at the site. Demonstrating remediation at low-end concentrations was considered to be important because the effectiveness of a phytoextraction technique can vary with soil lead concentration. Consequently, it was important to identify any problems that may be encountered at low lead concentrations which are not observable at high concentrations.

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

1.4 Regulatory Issues

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

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

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

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

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

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

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

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

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

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

1.5 Previous Testing of the Technology

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

In 1996, the USAEC funded a greenhouse study at TVA to determine whether the effectiveness of phytoextraction techniques could be increased. The primary goal of that project was to determine whether enhancing the water solubility of soil-borne lead would be a practical method for improving the phytoextraction of lead-contaminated soils. The greenhouse study was conducted by TVA using soil from the Sunflower Army Ammunition Plant (SFAAP) located at Desoto, Kansas. TVA provided technical expertise and conducted the greenhouse study at the TVA greenhouse and environmental growth chamber facilities in Muscle Shoals, Alabama. The results of this study can be found in the report "*Results of a Greenhouse Study Investigating the Phytoextraction of Lead From Contaminated Soils Obtained From the Sunflower Army Ammunition Plant, Desoto, Kansas*," USAEC Report No. SFIM-AEC-ET-CR-98036. [Ref. 2]

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

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

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

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

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

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

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

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

Table 1-1

List of Promising Research With Synopsis of Findings

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

Table 1-2

List of Known Phytoremediation Field Trials With Synopsis of Findings

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

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

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

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

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

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

Table 1-2 (Continued)

List of Known Phytoremediation Field Trials With Synopsis of Findings

• A field study investigated the potential of red root pigweed, Indian mustard, and tepary bean for phytoextraction of radioactive ^{137}cesium from contaminated soil. Pigweed showed much higher potential for removing cesium from the soil than mustard and bean (40-fold more), with approximately 3% of the total ^{137}cesium being removed from the top 15 cm of soil. The project is continuing to investigate the effect of inorganic and organic soil amendments on potential for leaching of ^{137}cesium.[Ref. 15]
• A field study is ongoing at a site in Chernobyl, Ukraine, using sixteen high biomass cultivars of amaranthus, amaranthus x Jerusalem artichoke hybrid, sunflower x Jerusalem artichoke hybrid, corn, peas, sunflower, and Indian mustard in combination with 20 different soil amendments to remediate soil contaminated with radioactive ^{137}cesium. Soil amendments included chelates, surfactants, organic and inorganic acids, and salts. Amaranthus showed the highest bioaccumulation coefficients for cesium and the highest yields, with significant variation within cultivars. Indian mustard was intermediate in cesium bioaccumulation, but lowest in yields; sunflower showed a low bioaccumulation coefficient and low yields. Of the soil amendments, only ammonium salts were effective in increasing extraction of ^{137}cesium from the soil by the plants. Cropping resulted in only a small decrease in ^{137}cesium activity in the soil.[Ref. 16]