

Executive Summary

This project was executed under a partnering agreement between the:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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