

## **Section 4.0**

### **Demonstration Approach**

#### **4.1 Performance Objectives**

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

- The concentration of lead in plants (corn and white mustard) after lead uptake was induced. Desired lead concentrations were 1% in corn and 2% in white mustard, based on a previous greenhouse treatability study<sup>Ref. 2</sup> for remediation within a reasonable timeframe.
- Crop total uptake of lead as calculated on the basis of aboveground total biomass production. At the initiation of this project, a desired biomass production target was 6 tons per acre of corn stover prior to grain production and 7 tons per acre for white mustard as cited in the literature<sup>Ref. 6</sup>. The 6 tons of corn stover per acre figure is approximately equivalent to 18 tons per acre of mature corn, including grain.
- The concentrations of lead remaining in the soil after each harvest. The industrial regulatory target for lead concentration at TCAAP is 1,200 mg Pb/kg soil, and the regulatory target for residential use is 400 mg Pb/kg soil. Lead concentrations at Site 129-3 are already below the industrial use standard. The demonstration at Site 129-3 was intended to illustrate remediation at lower lead levels.
- The concentration of lead in soil solutions beneath the plant rooting zone. A soil solution target concentration was not set at Site C due to elevated lead concentrations, up to 49,000 ppm, at deeper (≥3 foot) soil depths.

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

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

#### **4.2 Physical Setup and Operation**

##### **4.2.1 Introduction**

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

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

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

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

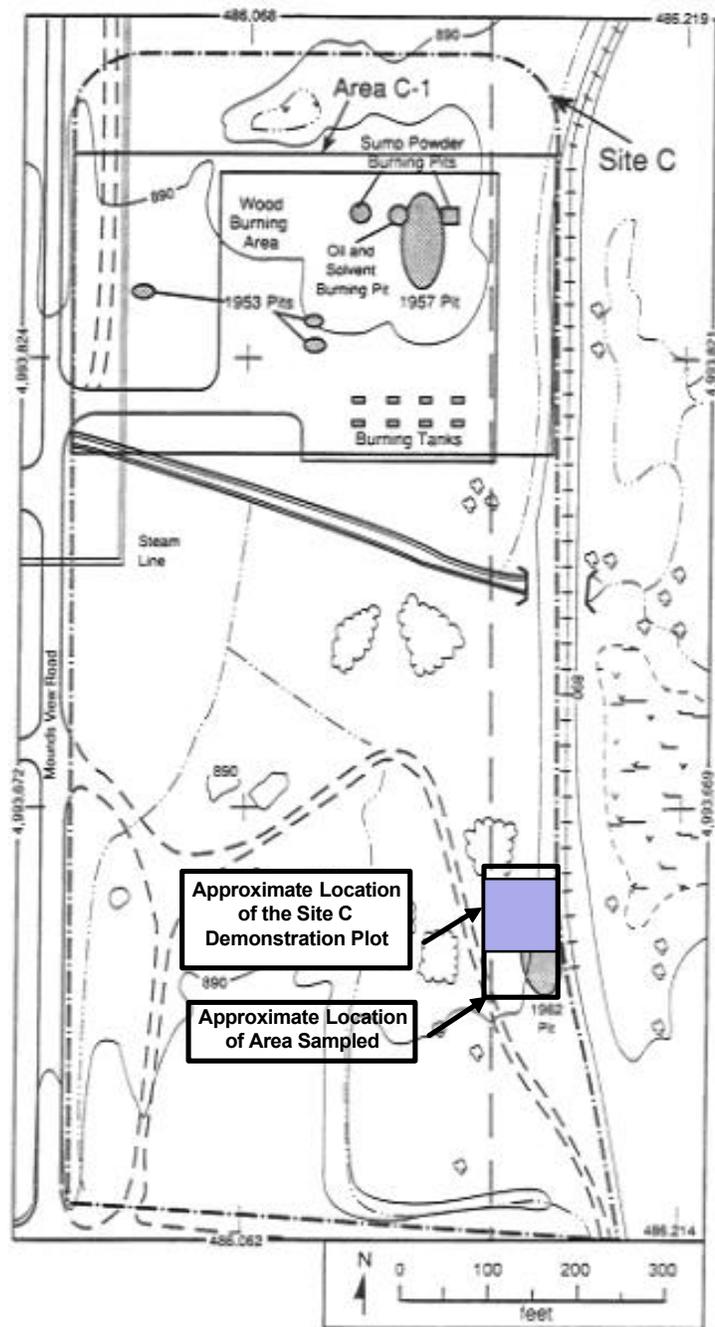
Following the selection of the two demonstration sites, the sites were prepared for use. This task involved installing controlled access zones, eradicating existing grass, installing fences and irrigation systems, and a pre-operational inspection of the site.

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

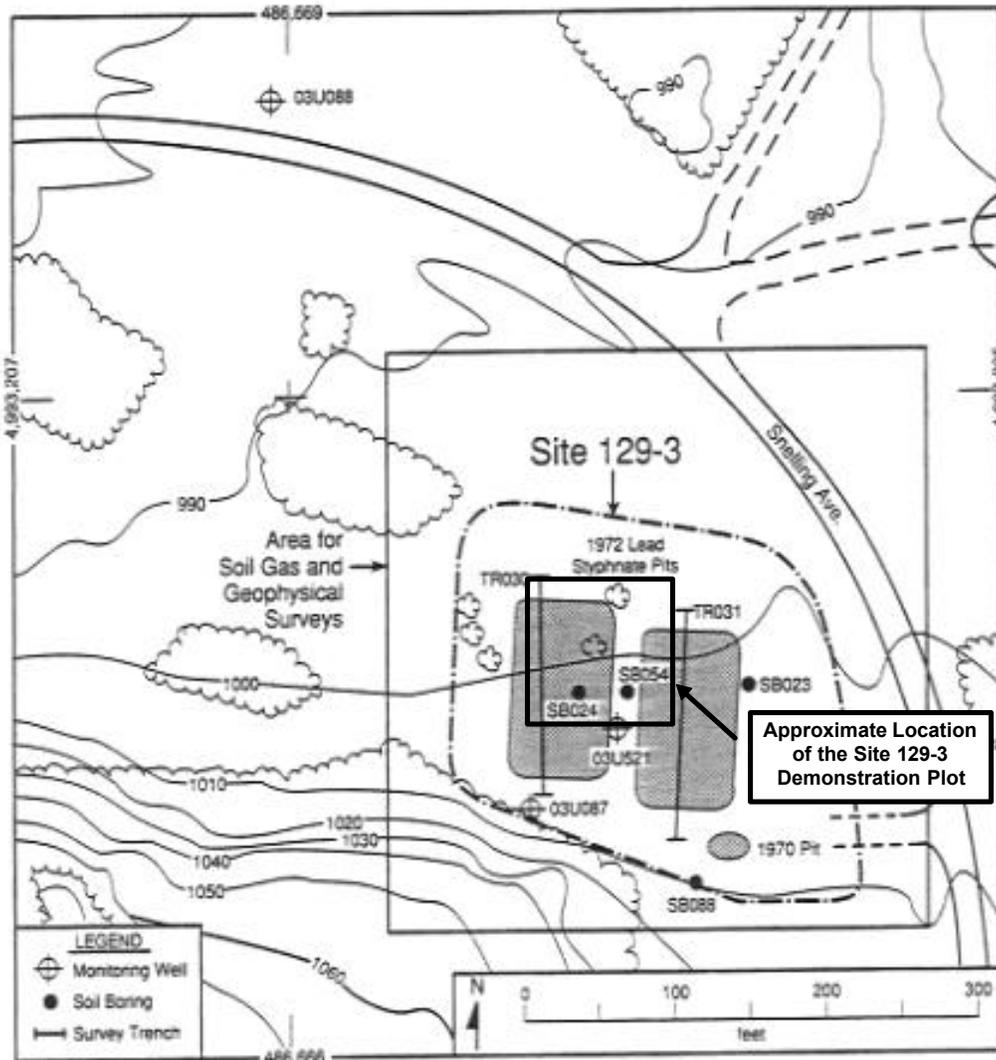
All field operations work on this project were conducted in Modified Level D or Level C personal protective equipment (PPE), as specified in the demonstration Health and Safety Plan located in Appendix B of the Technology Demonstration Plan.<sup>Ref. 21</sup>

#### **4.2.2 Site Characterization**

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



**Figure 4-1**  
**Demonstration Site at Site C**



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

**Figure 4-2**  
**Demonstration Site at Site 129-3**

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

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

1. A selected area of Site C (Figure 4-1) was divided into two areas: Site C-North and Site C-South. Site 129-3 was sampled in only one area. The dimensions of these areas were 150 feet x 90 feet at C-North, 90 feet x 90 feet at C-South, and 90 feet x 90 feet at Site 129-3.
2. The C-North Site was subdivided into sixty 15- x 15-foot grids.
3. The C-South and 129-3 sites were subdivided into thirty-six 15- x 15-foot grids.
4. Each 15- x 15-foot grid was further subdivided into four 7.5- x 7.5-foot quadrants.
5. Each 7.5- x 7.5-foot quadrant was sampled to a depth of 12 inches by taking one soil core using a hand-held soil sampling probe. NOTE: during the winter of 1997 and spring of 1998, it was not necessary to wet the soil to prevent the production of Pb-laden dust, as per the demonstration Health and Safety Plan due to the damp condition of the soil.
6. The sample core was subdivided into two portions. One portion represented the depth from 0 inch to 6 inches and the second from 6 inches to 12 inches. Each half core had an approximate wet weight of 100 grams.
7. The quadrant samples from each grid were composited. The 0-inch to 6-inch samples, one from each quadrant of the grid, were composited by placing the four quadrant samples into a single OneZip™ plastic bag. The 6-inch to 12-inch samples from the four quadrants of each grid were composited by placing these samples into another OneZip™ plastic bag (i.e., two 400-gram samples were obtained per grid; 120 soil samples from Site C-North, 72 samples from Site C-South, and 72 samples from Site 129-3). Each plastic bag containing a 400-gram composite sample was labeled as in the following example:

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

8. After sampling all four quadrants in each 15- x 15-foot grid, the soil sampling probe was cleaned by moving to the next grid, taking a soil sample, and discarding the sample collected. The soil sample was discarded within the grid. A field blank was collected by sampling a clean area outside the plot area in the same manner in which other samples were taken.
9. Upon completion of the sampling program, hand tools and all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.
10. Field wastes were packaged in heavy-duty plastic bags and disposed of by ATK.
11. The 400-gram composite samples were packaged for shipment to the TVA Analytical Laboratory in Muscle Shoals, Alabama, in accordance with the TVA chain of custody procedures (Appendix D-17).
12. Upon receipt at TVA, the 400-gram samples were air dried by opening the plastic bag and folding down the top to permit sufficient air movement. The opened bags were placed on tables in a TVA greenhouse and allowed to dry for one week with periodic mixing of the soil in the bag.
13. Upon drying, the soil samples were analyzed for pH and total lead (Table 4-1) by the methods listed in Table 4-12 (see Section 4.3.2.1).
14. After soil from the entire area of Site C was analyzed for total lead content, a 90- x 90-foot area was selected from within Site C-North for use as the demonstration area for Site C. For Site 129-3, the original 90- x 90-foot area of Site 129-3 was selected as the demonstration plot. The soil samples taken from these plots were then further analyzed to fully characterize the site. Analyses conducted are listed in Table 4-2. The methods used are listed in Table 4-12 (see Section 4.3.2.1).

#### **4.2.3 Site Preparation and Process Description**

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

**Table 4-1**  
**Chemical Analyses for the Initial Soil Characterization Work**

<b>Sample Type</b>	<b>Minimum Sample Size<sup>1</sup></b>	<b>Parameter Measured</b>
Soil	12 grams	pH Total Metals (Pb) <sup>2</sup>

- (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**

<b>Sample Type</b>	<b>Minimum Sample Size<sup>1</sup></b>	<b>Parameter Measured</b>
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) <sup>2</sup>
		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) <sup>2</sup>
		Bio-Available Pb (Water-Soluble)
		Cation Exchange Capacity (CEC)
		Soil pH
		Soil Moisture

- (1) Every twentieth sample contained twice the usual amount of sample and was submitted for use in the QC program.
- (2) The term “Total Metals” for any element refers to an analysis following an acid digestion of the sample and was used to distinguish it from metals measured following a leaching process.

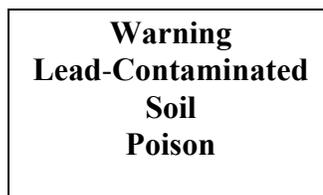
- Installation of controlled access zones
- Mowing grass
- Eradication of existing vegetation within the plots
- Installation of fences
- Installation of sprinkler irrigation systems
- Pre-operational site inspection
- Installation of the soil solution monitoring system (just after planting the 1998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

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

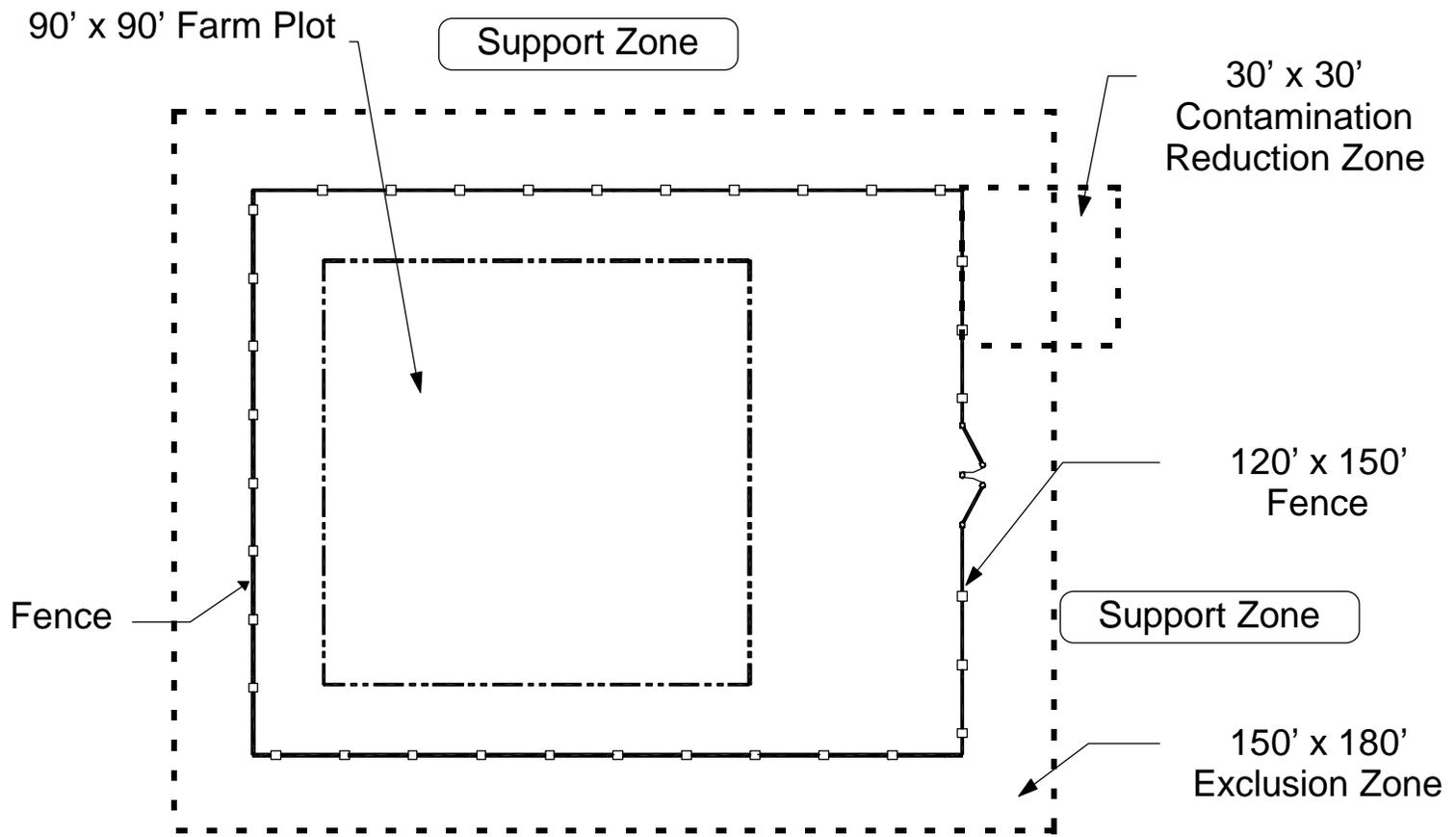
The SZ consisted of all areas outside the EZ and CRZ. This work was conducted using Modified Level D PPE. Upon setting up the controlled access zones, the area within the EZ and CRZ was mowed. Mowing was conducted using Level C PPE.

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

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



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



**Figure 4-3**  
**Layout for the Initial Site-Controlled Access Zones**

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

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

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

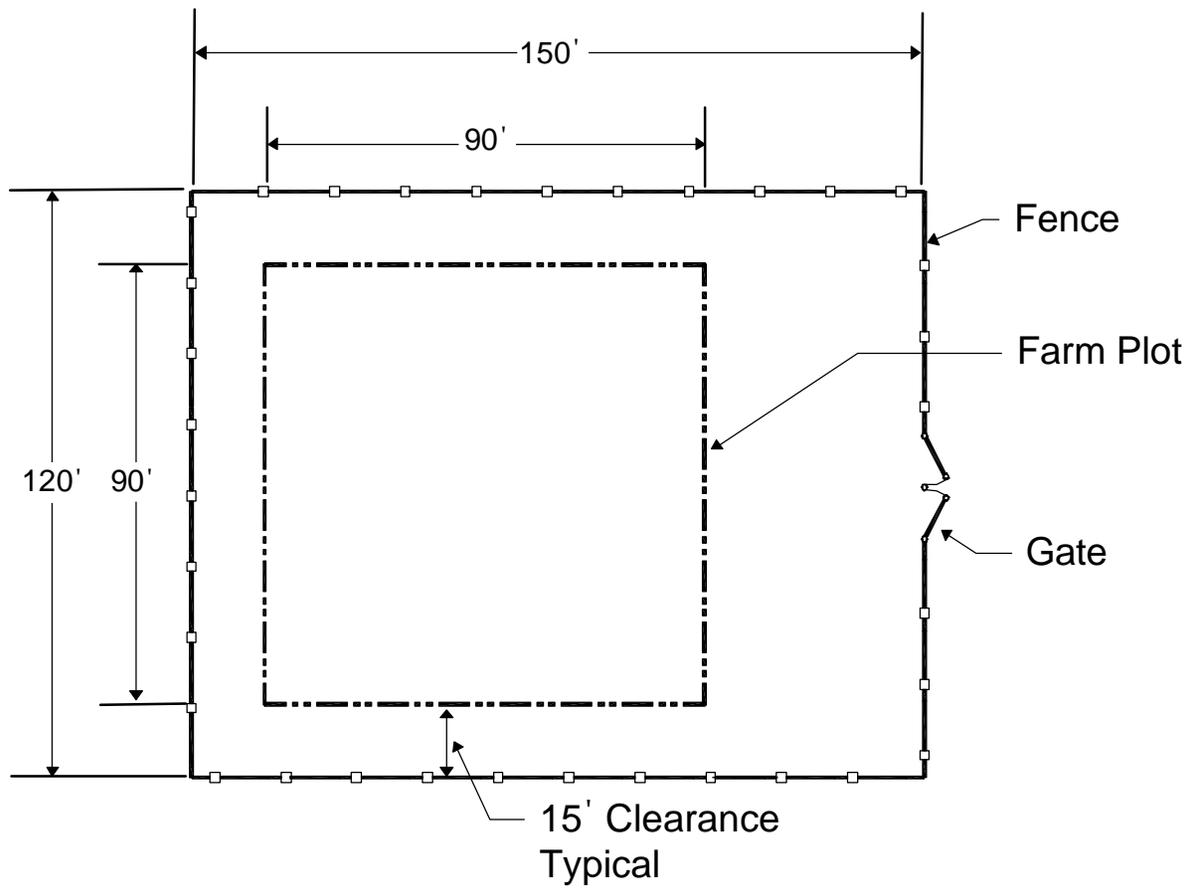
The contaminated soil was swept up and placed inside the demonstration plots. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.

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

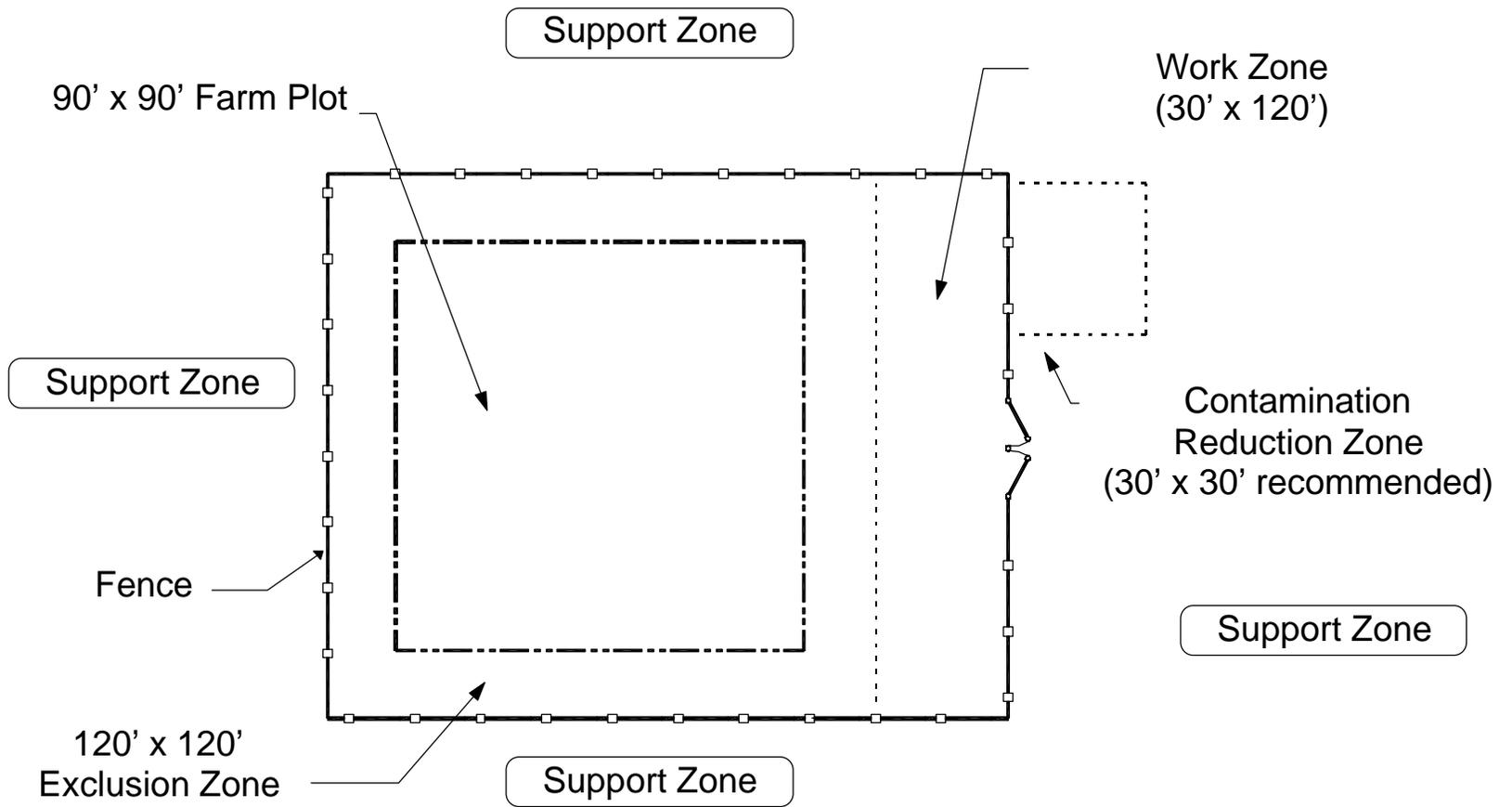
- The sprinkler irrigation systems and related subsystems were functional.
- The fences were in good order and were equipped with the proper signs.
- All tools were removed from the site.
- The controlled access areas were delineated.
- The demonstration fences were properly secured.

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

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



**Figure 4-4**  
**Layout of Demonstration Sites**



**Figure 4-5**  
**Layout for the Final Site-Controlled Access Zones**

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

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

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

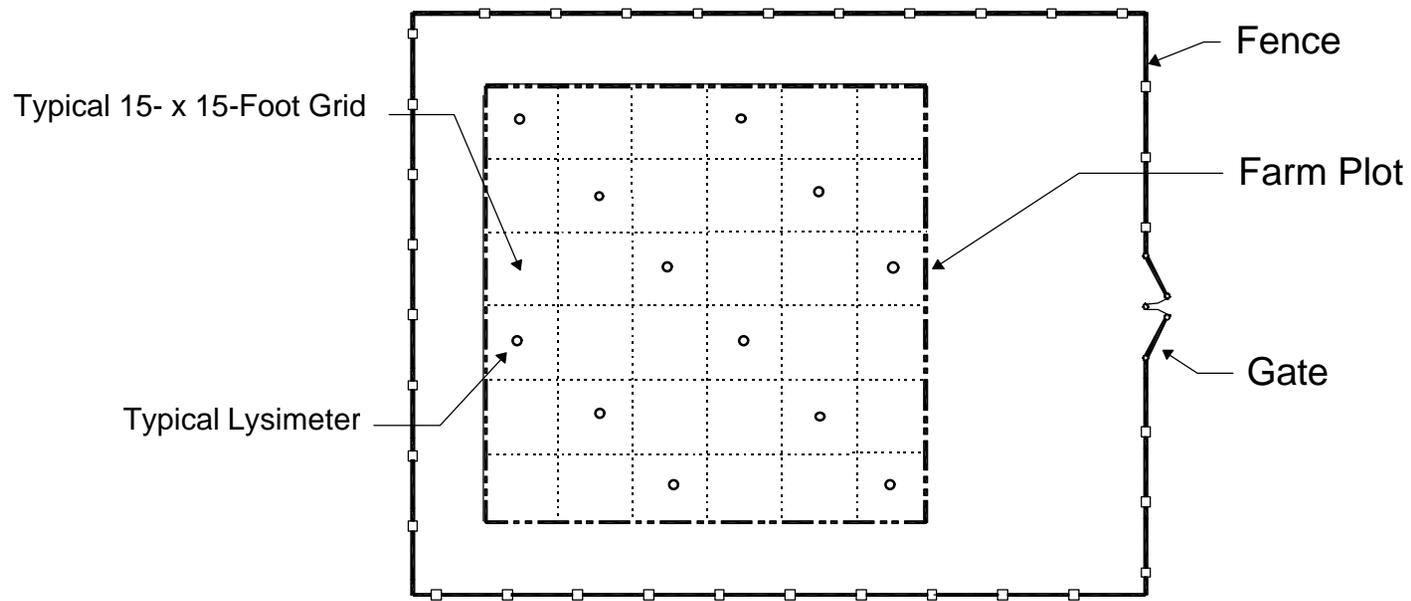
The lysimeters were installed using Level C PPE until air monitoring showed that Level D PPE was appropriate. The air monitoring was performed on June 3, 1998, and consisted of one sample collected in the morning and one sample collected in the afternoon. Under the sampling conditions (digging and rototilling),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

#### **4.2.4 Process Operations**

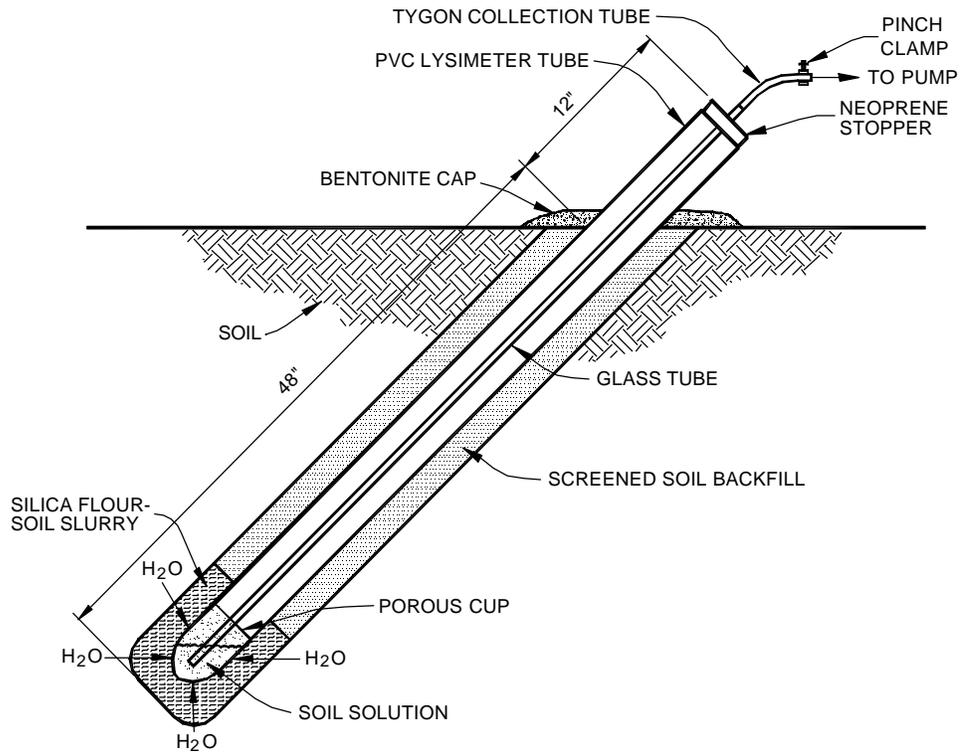
##### **4.2.4.1 1998 Demonstration**

###### **4.2.4.1.1 1998 Crop Planting**

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



**Figure 4-6**  
**Position of Lysimeters in a Soil Solution Monitoring System**



**Figure 4-7**  
**Diagram of a Lysimeter**

Tasks accomplished during the planting periods included:

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

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

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

The nitrogen fertilizer used for corn was ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , 34% N) applied at a N rate of 150 pounds per acre (88 pounds of  $\text{NH}_4\text{NO}_3$  to provide 30 pounds of N per plot). The potassium fertilizer was potassium sulfate ( $\text{K}_2\text{SO}_4$  - 45% K) applied at a K rate of 150 pounds of K per acre (67 pounds of  $\text{K}_2\text{SO}_4$  to provide 30 pounds of K per plot). Additionally, a small amount of phosphate fertilizer in the form of triple superphosphate (TSP-21% P) was band-applied as a "starter" fertilizer for corn on Site C at a rate of 14 pounds of TSP per 0.2-acre plot to provide 3 pounds of P per plot (15 pounds of P per-acre basis). Corn is more susceptible to phosphate deficiency than mustard, and phosphate levels in soil at Site C were very low (16 pounds per acre available P). The corn crop developed signs of phosphate deficiency early in the season (purple coloration of the stems and leaves) and two foliar applications of a 0.5% P solution were made to correct the problem. Phosphate was soil-applied for corn only at Site C. Phosphate levels at Site 129-3 were sufficient for corn, and no additional phosphate was applied for that corn crop. In addition, the corn at Site C exhibited iron deficiency (interveinal chlorosis - a whitening of the leaf between the leaf veins) three weeks into the growing season. This was corrected by a foliar application of a 2% iron sulfate solution.

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

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

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

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

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

#### **4.2.4.1.2 1998 Crop Tending**

Tasks accomplished during the crop-tending periods included:

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

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

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

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

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

- ◆ Presence of weeds
- The condition of the surrounding fence, including verification that the fence was intact
- The mechanical condition and maintenance requirements of the irrigation subsystem

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

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

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

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

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

#### **4.2.4.1.3 1998 Soil Amendment Addition**

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

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

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

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

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

#### 4.2.4.1.4 1998 Crop Harvesting and Processing

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

Harvesting consisted of the following tasks:

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

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

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

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

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

#### **4.2.4.2 1999 Demonstration**

##### **4.2.4.2.1 1999 Crop Planting and Tending**

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

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

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

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

##### **4.2.4.2.2 1999 Soil Amendment Addition**

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

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

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

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

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

#### **4.2.4.2.3 1999 Crop Harvesting and Processing**

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

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

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

#### **4.2.4.4 Personnel and Equipment Decontamination**

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

**Table 4-3**

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

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

**Table 4-4**  
**Plant Count and Height for Grids in Site C (1999)**

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

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

**Table 4-5**  
**Plant Count and Height in Grids at Site 129-3<sup>1</sup> (1999)**

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

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

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

#### **4.2.4.5 Record Keeping**

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

#### **4.2.4.6 Demobilization and Site Restoration**

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

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

Residuals consisted of plant tissues, contaminated plant and soil sample wastes, rinse water, and contaminated articles of clothing (Tyvek<sup>®</sup> 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<sup>®</sup> suits, booties, gloves, masks, respirator filters, etc.) were disposed of in a manner appropriate to the nature of the waste. (ATK activity)

### **4.3 Sampling Procedures**

#### **4.3.1 Introduction**

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

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

- Additionally, characterize the soils at the selected sites for other chemical and physical properties.
- Determine metal and chelate levels in the soil and plants during the demonstration period.
- Determine whether any downward movement of heavy metals, trichloroethylene, or chelate occurred at depths below the plant root structures during the demonstration period.

Field activities were conducted in 2000 to:

- Determine soil physical properties (soil types) three-dimensionally across the plot area to determine the effect on movement of water and EDTA and Pb.
- Characterize the soil profile for amount and type of debris in the subsurface soils, which potentially affect downward movement of EDTA and Pb.
- Determine the movement of lead, EDTA, and other cations in groundwater and surface water within the Site C plot and into areas adjacent to the plot.
- Determine the concentrations of cations that compete with lead for complexation by EDTA, which affects lead transport in water.

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

### **4.3.2 Experimental Design for 1998 Demonstration Phases**

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

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

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

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

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

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

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

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

#### **4.3.2.3 1998 Statistical Analysis of Data**

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

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

1. There were two treatments (amendment application). These corresponded to Site 129-3 (treatment T1), a site with low concentration of lead, and Site C (treatment T2), a site with high concentration of lead.
2. Measures of the concentration of lead in plants and soil were done on each plot.
3. Total lead uptake was estimated on each plot at harvest.
4. A normal distribution was assumed for lead concentration and total lead uptake. If high variation or a non-normal distribution was observed, a test of additivity and homogeneity of variances was done and an appropriate data transformation was then used to test the hypothesis.

Data evaluation was based on the following statistical models:

- Model 1 - A general investigation of the variability of lead content, including site effects, variability across rows within a site, and variability across columns within a site.
- Model 2 - A paired t-test to compare soil lead concentrations only in the grids analyzed before and after soil amendment additions.
- Model 3 - Changes in lead concentration in soil over the two-year period.

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

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

- Site effects: to test the hypothesis that changes in concentration or total lead uptake are due to site concentration.
- Rows within sites: to test the hypothesis of variability of concentration or total lead uptake across rows.
- Columns within sites: to test the hypothesis of variability of concentration or total lead across columns.

**Table 4-6**  
**Sampling Goals for the TCAAP Demonstration**

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

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

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

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

Table 4-7

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

Sample Location	Sample Period	Sample Type	Minimum Sample Size <sup>1</sup>	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) <sup>2</sup>
						Plant-available Pb
						pH
						Chelate (EDTA) (Except for corn)
		Plants (Aerial)	100 grams	None	9 grids for corn; 18 grids for white mustard	Total Metals (As, Be, Pb, Sb, Tl, Mn) <sup>2</sup>
						Moisture
Soil Solution	250 mL	Nitric Acid	Not Applicable	Total Metals (As, Be, Cu, Pb, Sb, Tl, Mn) <sup>2</sup>		
				40 mL	None	Not Applicable
Site C	After adding soil amendments	Soil	40 grams	None	36 grids	Total Metals (As, Be, Pb, Sb, Tl, Mn) <sup>2</sup>
						Plant-available Pb
					18 grids	pH
						Chelate (EDTA)
		Plants (Aerial)	100 grams	None	36 grids	Total Metals (As, Be, Pb, Sb, Tl, Mn) <sup>2</sup>
						9 grids
		Soil Solution	250 mL	Nitric Acid	Not Applicable	Total Metals (As, Be, Cu, Pb, Sb, Tl, Mn) <sup>2</sup>
						40 mL

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

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

**Table 4-8**

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

<b>Sample Location</b>	<b>Sample Period</b>	<b>Sample Type</b>	<b>Minimum Sample Size<sup>1</sup></b>	<b>Preservative Added</b>	<b>Number of Grids Sampled</b>	<b>Parameter Measured</b>
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) <sup>2</sup>
						Plant-available Pb
						pH
						Chelates (EDTA) (Except for corn)
		Moisture				
		Plants (Aerial)	100 grams	None	9 grids for corn; 18 grids for white mustard	Total Metals (Pb, Sb, Mn) <sup>2</sup>
		Soil Solution	250 mL	Nitric Acid	Not Applicable	Total Metals (Pb, Sb, Mn) <sup>2</sup>
			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) <sup>2</sup>
						Plant-available Pb
						Moisture
					18 grids	pH
						Chelates
		Plants (Aerial)	100 grams	None	36 grids	Total Metals (Pb, Sb, Mn) <sup>2</sup>
					9 grids	Chelate (EDTA)
		Soil Solution	250 mL	Nitric Acid	Not Applicable	Total Metals (Pb, Sb, Mn) <sup>2</sup>
			80 mL	HCl	Not Applicable	Trichloroethylene
			40 mL	None	Not Applicable	Chelate (EDTA)

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

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

**Table 4-9**  
**An Overview of Experimental Design for Soil Sampling**  
**in Sites C and 129-3 for 1998**

- 1st Planting (Corn) - before soil amendment addition - 9 grids per site for two sites with two soil depths (36 samples total).
- 1st Planting (Corn) - after soil amendment addition - 36 grids per site for two sites with two soil depths (144 samples total).
- 2nd Planting (White Mustard) - before soil amendment addition - 18 grids per site for two sites with two soil depths (72 samples total).
- 2nd Planting (White Mustard) - after soil amendment addition - 36 grids per site for two sites with two soil depths (144 samples total).

Total: 396 samples

**Table 4-10**

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

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

Total: 198 samples

**Table 4-11**  
**Experimental Design Details for 1st Growing Season (1998) for Soil and Plant Sampling**

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

**Table 4-12**  
**Methods for Analyzing Soils, Plants, and Soil Solution**

<b>Parameter Measured</b>	<b>Extraction or Preparation Method<sup>2</sup></b>	<b>Analytical Method<sup>2</sup></b>
<b>Soil and Plant Analyses</b>		
pH	N/A	ASA 12-2.6
Total Organic Carbon (TOC)	N/A	ASA 29-3.5.2
Total Kjeldahl Nitrogen (TKN)	N/A	Lachat QuikChem 13-107-06-2-D
Extractable P	ASA 24-5.2	6010B
Exchangeable K	ASA 9-3.1	6010B
Exchangeable Ca	ASA 9-3.1	6010B
Exchangeable Mg	ASA 9-3.1	6010B
Exchangeable Al	ASA 9-4.2	6010B
DTPA-Extractable Fe	ASA 17-4.3	6010B
DTPA-Extractable Mn	ASA 17-4.3	6010B
Total Metals (Be, Pb, Sb, Tl, Mn) <sup>1</sup>	3050B	6010B
Total Metals (As) <sup>1</sup>	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
<b>Soil Solution Analyses</b>		
Total Metals (Be, Cu, Pb, Sb, Tl, Mn) <sup>1</sup>	3005A	6010B
Total Metals (As) <sup>1</sup>	7060A	7060A
Chelator (EDTA)	N/A	AP-0047
Trichloroethylene	N/A	8021B

- (1) The term “Total Metals” for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.
- (2) The methods and procedures listed are provided in Appendix D.

The general model used to test the hypotheses was:

$$Y_{ijk} = \mathbf{u} + \mathbf{p}_i + \mathbf{i}_{ji} + \mathbf{F}_{ki} + \mathbf{e}_{ijk} \quad (\text{Model 1})$$

- $Y_{ijk}$ : Lead concentration in plant
- $\mathbf{u}$ : Concentration mean or uptake mean for the two sites
- $\mathbf{p}_i$ : Site effect
- $\mathbf{i}_{ji}$ : Variability of rows within sites
- $\mathbf{F}_{ki}$ : Variability of columns within sites
- $\mathbf{e}_{ijk}$ : Random variation assumed  $N(0, \sigma)$

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

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

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

and the test criterion is:

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

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

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

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

$$Y_{ijkl} = \mathbf{u} + \mathbf{y}_{ji} + \mathbf{i}_{ji} + \mathbf{F}_{ki} + \mathbf{e}_{ijkl} \quad (\text{Model 3})$$

- $\mathbf{y}_{ji}$ : Variability of periods

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

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

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

### **4.3.3 Experimental Design for 1999 Demonstration Phases**

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

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

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

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

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

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

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

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

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

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

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

#### **4.3.3.4 1999 Statistical Analysis of Data**

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

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

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

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

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

**Table 4-13**

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

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

**Table 4-13 (Continued)**

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

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

**Table 4-13 (Continued)****Chronology of Groundwater and Surface Water Sampling Events at Site C in 2000**

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

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

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

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

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

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

EDTA in all sampling results is reported as Na<sub>2</sub>EDTA and as EDTA. For EDTA, analytical results are based on comparison with Na<sub>2</sub>EDTA standards and are calculated as mg/kg or mg/L Na<sub>2</sub>EDTA. Earlier reports on this project reported EDTA results calculated as Na<sub>2</sub>EDTA without note. This Results Report shows the data calculated as Na<sub>2</sub>EDTA and as EDTA. The conversion factor is:  $(292.24\text{g/mol EDTA})/(336.21\text{g/mol Na}_2\text{EDTA}) = 0.8692$ .

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

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

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

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

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

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

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

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

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

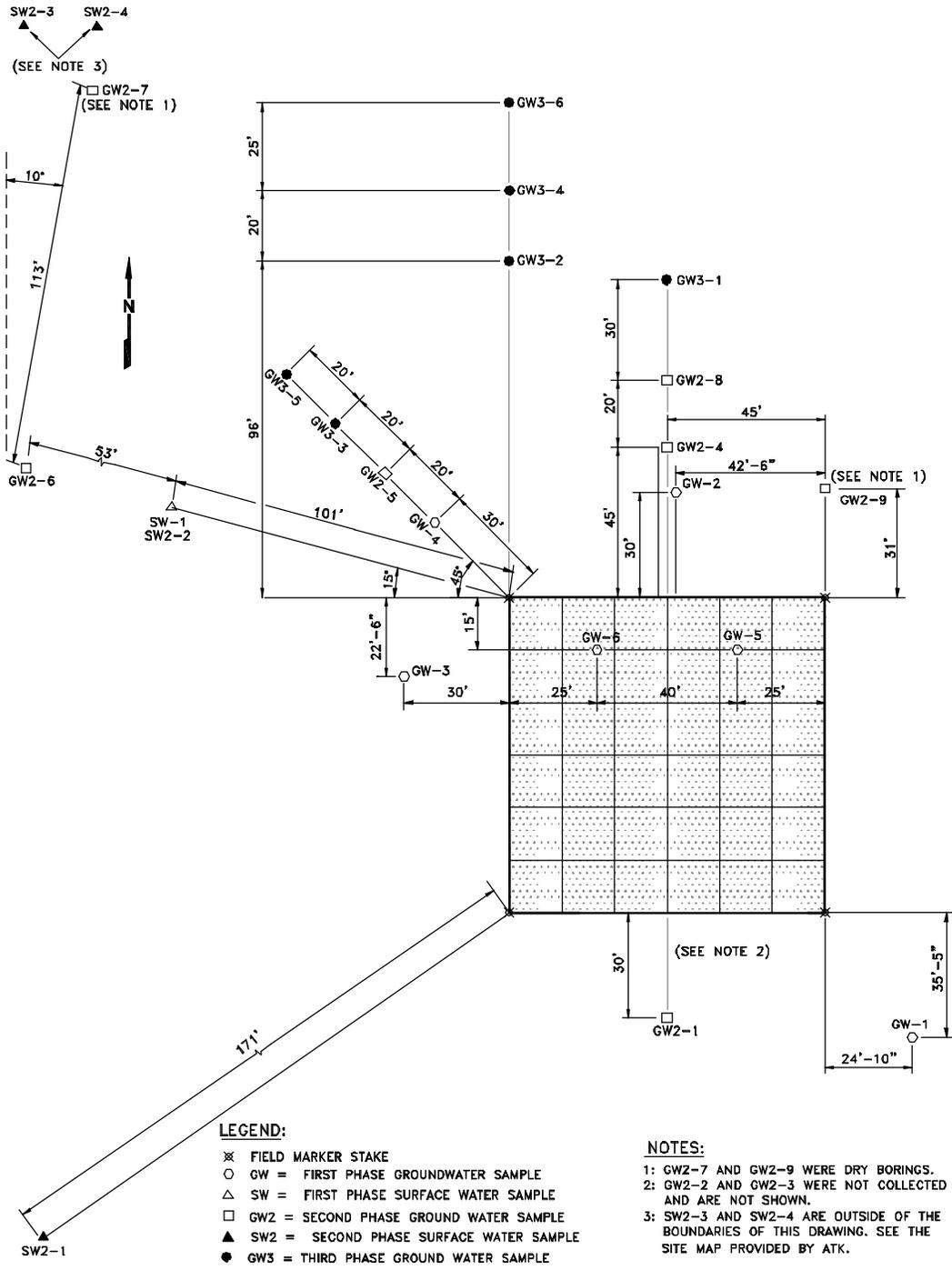
One split of each sample was sent to the TVA laboratory where the groundwater samples and blanks were filtered through a 0.2 micron pore size Millipore<sup>®</sup> syringe filter and divided into two equal portions. One portion was acidified and analyzed for lead and 19 other cations. The other, unacidified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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

#### **4.3.5 Sampling Plan**

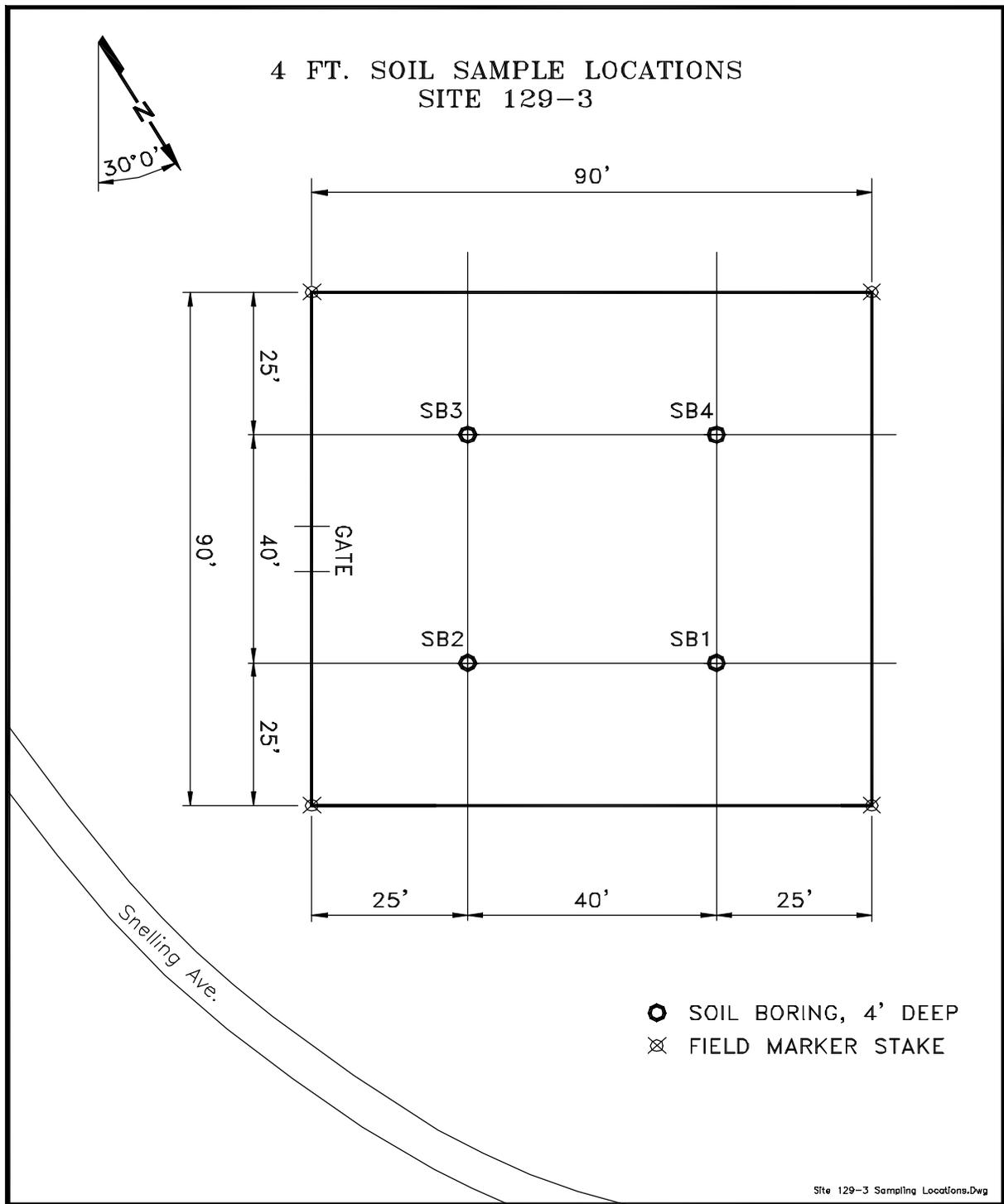
##### **4.3.5.1 Soil Sampling**

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

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

1. The Site C and 129-3 farm plots were each subdivided into thirty-six 15- x 15-foot grids, as described above in Section 4.3.2. Each 15- x 15-foot grid was then subdivided into four 7.5- x 7.5-foot quadrants.
2. All of the grids were sampled during most sampling periods during the 1998 season. However, only every second or fourth 15- x 15-foot grid was sampled during sampling periods conducted prior to the addition of soil amendments (see Tables 4-7 and 4-8). Those 15- x 15-foot grids were designated with a flag. In 1999, only twelve grids were sampled at Site C and two at Site 129-3.
3. The 0-inch to 12-inch soil sample from each grid was a composite sample comprised of soil taken from the four quadrants within each grid. Each grid quadrant was sampled by creating a 12-inch-deep hole using a power soil sampling auger and then scraping a soil sample from the length of the hole using a spoon. Each soil sample weighed approximately 200 grams. Use of the power sampling equipment was a modification of the Technology Demonstration Plan.
4. The four 0-inch to 12-inch soil samples from each grid were composited by placing the four quadrant samples into a single OneZip™ plastic bag. Each plastic bag contained approximately one 800-gram composite sample and was labeled, as indicated in Section 4.3.5.7.
5. A 12-inch to 24-inch soil sample was obtained from each quadrant of each grid sampled above. Each 12-inch to 24-inch quadrant sample was obtained from the sampling hole used to obtain the 0-inch to 12-inch sample by placing the soil auger into the original hole, drilling a 24-inch deep hole, and then scraping a soil sample from the length of the 12- to 24-inch hole using a spoon. Each soil sample weighed approximately 200 grams.
6. The 12-inch to 24-inch soil samples from each grid were composited by placing the four quadrant samples into a single OneZip™ plastic bag. Each plastic bag contained approximately one 800-gram composite sample and was labeled, as indicated in Section 4.3.5.7.





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

7. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.<sup>Ref. 21</sup>
8. Field wastes were packaged in suitably sized heavy-duty plastic bags and placed in a designated satellite area until disposal in a hazardous waste landfill.
9. The soil samples were packaged for shipment to the TVA Analytical Laboratory in Muscle Shoals, Alabama, in accordance with the TVA chain of custody procedures (Appendix D-17).
10. Upon receipt at the TVA facility, the 800-gram soil samples were air-dried by opening the plastic bag and folding down the top to permit sufficient air movement. The opened bags were placed on tables in a greenhouse and allowed to dry for one week with periodic mixing of the soil in the bag.
11. Upon drying, the soil samples were analyzed, as outlined in Tables 4-7 and 4-8. The specific analytical methods used are shown in Table -12. A total of 396 soil samples were taken during the 1998 demonstration year (Table 4-9). Fifty-six samples were taken during the 1999 season.

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

#### **4.3.5.1.2 Soil Sampling in 2000**

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

The sampling procedure was as follows:

1. The sample locations were determined as shown in Figure 4-9 and 4-10.
2. 48" Geoprobe<sup>®</sup> Macro-Core Sample Tubes with liners (MC PETG Liner, heavy duty) were used to sample continuously to depth of exactly 4 feet from ground surface. If significant obstructions were encountered (evidenced by lifting of Geoprobe<sup>®</sup>), then the sample tube was removed, the liner discarded, and the sampling point was offset 1 to 2 feet.
3. Compression of the soil in the tubes to less than 40 inches necessitated collection of two separate samples at each of the sample locations. One sample was collected from the ground surface to exactly 2 feet deep. The second sample was collected from 2 feet to 4 feet via the same sample hole (the probe was inserted through the void left by the 0- to 2-foot sample collection).
4. Probe rods were retracted and the sample liner removed. Length of sample material within the liner was measured to the nearest inch and recorded. Before cutting, a permanent marker was used to write "Top" and "Bottom" directly on the sample liner. Any empty liner material was cut away, (use Macro-Core Circular Cutting Tool or knife) and a black (black, b for bottom) vinyl end cap was placed on the end with the deepest soil and a red vinyl end cap on the end with the shallowest soil. A permanent marker was used to label each tube.

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

5. Each deep core soil sample (i.e., MC PETG Liner) was labeled as to
  - Site C or Site 129-3
  - Sample location
  - Top or bottom of sample
  - Date
  - Depth range at which sample was collected
  - Sampler's initials
6. Any soil from the outside of the sample liner was wiped away with a dry cloth or paper towel. Up to six core samples (12 liner halves) were placed in a large plastic bag and a knot was tied in the opening. This bag was placed in a 2<sup>nd</sup> plastic trash bag, which was knotted, and then again in a third bag, which was knotted. The triple-bagged samples were placed in a cooler on top of Blue Ice.
7. Immediately before relinquishing samples to the shipping company (UPS or FEDEX), the old Blue Ice was removed and new frozen Blue Ice was added. The chain of custody form was completed and placed in a sealable bag inside cooler. The custody seal was applied across the opening of the cooler and signed and dated. The ice chests were shipped over night for delivery by 10:00 a.m. to:

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

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

<u>Date</u>	<u>Location</u>	<u>Start Time</u>	<u>End Time</u>	<u>Recovery (inches)</u>	<u>Comments</u>
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#### **4.3.5.2 Plant Sampling**

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

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

2. A 15- x 15-foot (minimum) plastic tarp was placed on an area within the WZ (see description of WZs in Section B 6.4 of the demonstration Health and Safety Plan<sup>Ref. 21</sup>).
3. All of the grids were sampled during most sampling periods in 1998. However, only every second or fourth 15- x 15-foot grid was sampled during sampling periods prior to the addition of soil amendments (see Tables 4-7 and 4-8). These 15- x 15-foot grids were designated with a flag. In 1999, only twelve grids were sampled at Site C and two at Site 129-3.
4. Two plants from each of the four 7.5- x 7.5-foot quadrants were harvested by cutting the plant at the stalk near the base (eight plants total). Each plant was cut down by carefully holding the plant to prevent contact with contaminated soil, cutting the stalk using a corn knife or shears, and carrying the harvested plants to the tarp in the WZ.
5. At the WZ, the eight plants harvested from each grid were cut into small pieces using hand tools and placed into large paper bags. Each paper bag was labeled, as indicated in Section 4.3.5.7. After processing the plants from each grid, but prior to processing plants from the next grid, the plant debris on the tarp was brushed into a dust bin using a broom and deposited into the paper bag. Each paper bag was folded at the top and sealed (stapled).
6. Upon completion of the sampling program, hand tools were decontaminated by either wiping off the tool or rinsing with potable water.
7. Upon leaving the sampling site, all personnel involved in the sampling procedure underwent decontamination in accordance with the demonstration Health and Safety Plan.<sup>Ref. 21</sup>
8. The plant samples were packaged for shipment to the TVA Analytical Laboratory in Muscle Shoals, Alabama, in accordance with the TVA chain of custody procedures (Appendix D-17).
9. Upon receipt at the TVA facility, the plant tissue samples were oven-dried for 72 hours at 55°C in the original paper bags. The tissue was then ground to less than 2.0-mm particle size using a Wiley Mill. The dried, ground tissue was stored in large glass bottles and labeled.
10. A representative plant sample was obtained from the glass bottles and analyzed, as outlined in Tables 4-7 and 4-8. The specific analytical methods that were used are provided in Table 4-12. A total of 198 plant samples were taken in 1998 (Table 4-10). Twenty-eight plant samples were taken in 1999.

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

#### **4.3.5.3 Soil Solution Sampling**

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

#### **4.3.5.3.1 Soil Solution Sampling at Site C**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

##### **4.3.5.4.1 Groundwater Sampling at Site C**

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

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

1. Using the Geoprobe® sampling equipment in accordance with manufacturer's instructions, the access hole was bored or drilled to the expected subsurface water level.
2. After location of water was achieved, a water sample of at least 200 mL in volume was withdrawn from the collection device and placed in the sample container.
3. Care was taken to ensure that no soil or other solid or liquid contaminant was introduced into the sample or sample bottle. However, if such contamination had occurred, the contaminated sample would have been discarded and another sample obtained.
4. The sample was not filtered, acidified, or altered in any way from the natural state.
5. Each sample was labeled as to the following:
  - a) Site C
  - b) sample location
  - c) date
  - d) time
  - e) depth at which sample was collected
  - f) physical appearance of sample, i.e., clear, turbid, etc.
  - g) name of person collecting the sample

6. Each sample bottle label was covered with plastic tape so that moisture would not obliterate the label.
7. Each sample was placed in an ice chest containing crushed ice or Blue Ice for cooling the samples in the field.
8. Immediately before relinquishing samples to the shipping company (FEDEX), the old Blue Ice (or crushed ice) was removed and new frozen Blue Ice was added. The sample bottles were cushioned by wrapping in plastic bubble wrap, placing on Blue Ice, and the ice chest was sealed for shipment.
9. A chain of custody form was completed and placed in a sealable bag inside the cooler. A custody seal was placed across the opening of the cooler and signed and dated. The container was shipped over night for delivery by 10:00 a.m. to:

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

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

<u>Date</u>	<u>Location</u>	<u>Start Time</u>	<u>End Time</u>	<u>Recovery (inches)</u>	<u>Comments</u>
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#### **4.3.5.4.2 Surface Water Sampling at Site C**

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

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

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

1. Water was collected from the drainage ditch by dipping a large plastic bucket into the standing water in the ditch.
2. A water sample of at least 200 mL in volume was poured from the collection device into the sample container.

3. Care was taken to ensure that no soil or other solid or liquid contaminant was introduced into the sample or sample bottle. However, if such contamination had occurred, the contaminated sample would have been discarded and another sample obtained.
4. The sample was not filtered, acidified, or altered in any way from the natural state.
5. Rinse blanks were collected in similar fashion.
6. The sample was labeled as to the following:
  - a) Site C
  - b) Sample location
  - c) Date
  - d) Time
  - e) Depth at which sample was collected
  - f) Physical appearance of sample, i.e., clear, turbid, etc.
  - g) Name of person collecting the sample
7. The sample bottle label was covered with plastic tape so that moisture would not obliterate the label.
8. The sample was placed in the same ice chest containing the groundwater samples and packed in Blue Ice and shipped to TVA along with the groundwater samples.

For the surface water sampling - May 4, 2000:

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

#### **4.3.5.5 Sampling Team Structure and Qualifications**

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

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

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

#### **4.3.5.6 Site Health and Safety Procedures**

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

#### **4.3.5.7 Sample Labeling**

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

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

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

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

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

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

#### **4.3.5.8 Sample Documentation**

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

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

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

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

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

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

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

#### **4.4 Analytical Procedures**

##### **4.4.1 Laboratory Procedures**

Standard analytical procedures for data collected in the laboratory are provided in Appendices D-1 through D-19. For EDTA, analytical results are based on comparison with Na<sub>2</sub>EDTA standards and are calculated as mg/kg or mg/L Na<sub>2</sub>EDTA. Earlier reports on this project reported EDTA results calculated as Na<sub>2</sub>EDTA without note. This Results Report shows the data calculated as Na<sub>2</sub>EDTA and as EDTA. The conversion factor is:  $(292.24\text{g/mol EDTA})/(336.21\text{g/mol Na}_2\text{EDTA}) = 0.8692$ .

##### **4.4.2 Analytical Equipment**

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

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

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

- Contaminated soil, water, and plant samples sent to TVA, as well as related laboratory wastes, were disposed of through TVA's existing hazardous waste disposal contracts. (TVA activity)
- Contaminated soils collected during the process of decontaminating personnel and equipment decontamination were returned to the demonstration plots. (TVA and ATK activity)
- Contaminated rinse water collected during the process of decontaminating personnel and/or equipment was poured onto the demonstration plots. (TVA and ATK activity)

Contaminated soils, plastic tarps or pads, articles of clothing (Tyvek<sup>®</sup> 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**

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

(1) NA = Not Applicable.