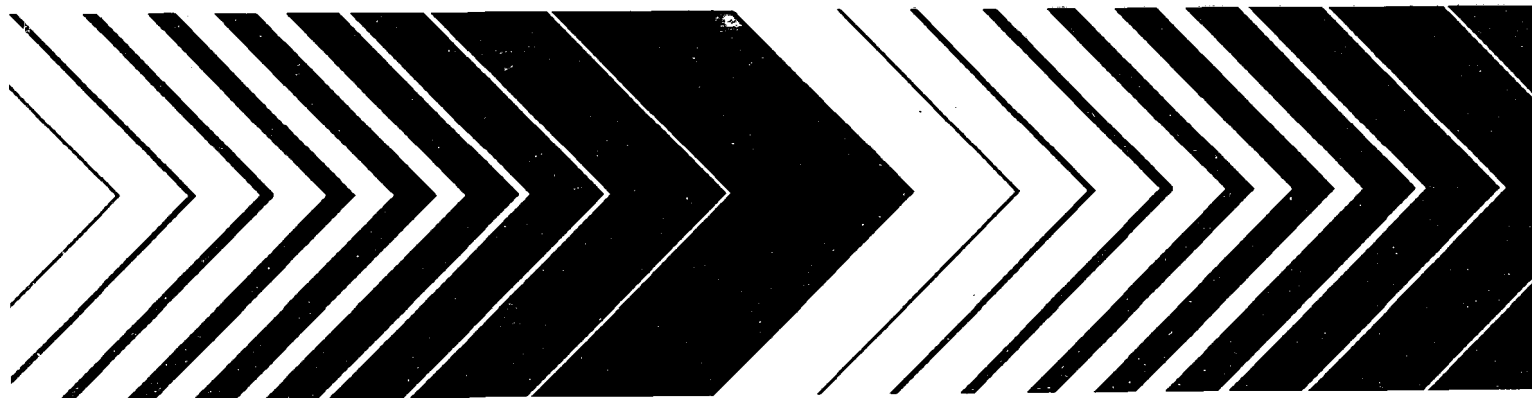




# Technology Evaluation Report

## Electroanalytical Measurement Techniques for Metals- Contaminated Soil Characterization

Battelle Pacific Northwest Laboratory,  
New Mexico State University, and  
Environmental Technologies Group,  
Inc.



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Battelle Pacific Northwest Laboratory, New  
Mexico State University, and Environmental  
Technologies Group, Inc.

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## **Notice**

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## **Executive Summary**

### **Consortium for Site Characterization Technology**

The U.S. Environmental Protection Agency (EPA), through the Environmental Technology Verification Program, is working to accelerate the acceptance and use of innovative technologies that improve the way the nation manages its environmental problems. As part of this program, the Consortium for Site Characterization Technology was established as a pilot program to test and verify field monitoring and site characterization technologies. The Consortium is a partnership involving the U.S. Environmental Protection Agency, the Department of Defense, and the Department of Energy.

This report describes the results of a field demonstration conducted at contaminated sites near Butte, Montana, in which developers of soil characterization technologies were invited to participate. The report presents soil sample analysis results from anodic stripping voltammetry systems operated by Battelle Pacific Northwest National Laboratory. This electroanalytical technique was one of four technologies that were used to analyze soil samples for target elements. Other technologies that were tested include a mobile atomic absorption spectrometer operated by Pace Environmental Laboratories, Inc., and two laser-induced breakdown spectrometers from MelΔok Instruments, Inc., and Los Alamos National Laboratory. The results from these technology demonstrations are published as separate reports.

### **Technology Classification**

The Consortium classifies each candidate technology into one of three development levels on the basis of the maturity of the technology and its expected time to commercialization. Level 1 designates the least developed and Level 3 the most developed technologies. The electrode stripping analysis technologies operated by Battelle Pacific Northwest National Laboratory were classified as Level 1. Although many of the system components used to make the field measurements are commercially available, this test was the first full-scale field trial of these technologies for the analysis of metals-contaminated soil.

The Consortium has further determined that an exhaustive verification of the relatively new and developing Level 1 technologies could not be performed. The field demonstration data sets from the stripping analysis technologies are compiled, organized, and presented in this report along with a validated data set from analytical laboratories using conventional analytical methods. The degree of comparative analysis of the data is purposely limited. The results are intended for distribution to the technology developers in order to assist them in further instrument development and refinement.

## **Demonstration Design**

A demonstration of selected Department of Energy-funded technologies was being planned by MSE-HKM, Inc., under contract to the Department of Energy. The Consortium chose to augment the planned demonstration by bringing in additional technologies and enhancing the laboratory analysis component of the project. Two sites contaminated with heavy metals were identified in the Butte, Montana, area for the demonstration. The first site, Butte/Silver Bow Creek, was contaminated by heavy metals deposited as mill tailings. The second site, Anaconda Smelter/Mill Creek, was contaminated by dry aerosol deposition of smelter stack emissions. The surface soils at both sites contained varying concentrations of heavy metals. Soil conditions at each site were judged to be representative of typical field conditions under which the technology would be expected to operate.

Sixty samples were collected and processed using a preestablished sampling protocol. The soil samples were dried, homogenized, and split ten ways for distribution and analysis by three analytical laboratories and four technologies.

The demonstration plan incorporated the use of reference laboratories to analyze metals in the soil samples using standard EPA laboratory protocols. Laboratory data produced by inductively coupled plasma atomic emission spectroscopy and direct-aspiration, flame atomic absorption spectroscopy (AAS) methods were validated to produce a reference set of target metal concentrations in the field soil samples. The reference data set was used for comparison with analytical results from the demonstration technologies. Quality control samples were also incorporated into the sample analysis plan to obtain additional performance measures for the laboratory and field tests.

## **Demonstration Results**

Anodic stripping voltammetry and potentiometric stripping analysis are related electroanalytical techniques that are used to measure metals in solution. The target metal is first preconcentrated onto a working electrode by placing a voltage potential on the electrode so that a portion of the metal in solution migrates to and is deposited on the electrode surface. In anodic stripping voltammetry, the accumulated metal species is released from the electrode by applying an increasing voltage to the working electrode. During the stripping phase of the analysis, the release of the target metal is measured as peak current and is proportional to the concentration of the metal in the test solution. Potentiometric stripping analysis employs a variation of anodic stripping voltammetry in the stripping stage. In this procedure, either a chemical oxidant is added to the test solution or a constant current is used to strip the target elements from the electrode. The elements are sequentially stripped in order of their oxidation potential. The length of time required to strip the element at a particular electrode potential is used as a measure of the concentration of the element in solution.

The electrochemical stripping analysis techniques were demonstrated alongside three other participating technologies in this study. All participants set up and operated their instruments during a 1-week period in the Butte, Montana, area in September 1995. The incorporation of conventional laboratory analysis into the demonstration provided a validated data set that could be used by developers to evaluate the performance of the technology.

A comparison of the field soil sample results from the reference laboratories showed very close agreement. This observation suggests that the soil samples distributed to the demonstration participants were homogeneous in terms of their chemical composition. A high degree of homogeneity facilitates comparison of the soil analysis results from the demonstrated technologies with those from the laboratories. Data from the reference laboratory and from Battelle Pacific Northwest National Laboratory, New Mexico State University, and Environmental Technologies Group, Inc., are presented in a variety of formats to assist in comparing the data sets produced during the demonstration.

The performance of the stripping analysis methods was examined in three ways: by evaluation of quality control sample analysis results, by evaluation of duplicate sample analysis results, and by comparison of stripping analysis results from field soil sample analysis with conventional laboratory results. The time required to complete stripping analysis limited the analysis to four of the nine target analytes: cadmium, chromium, copper, and lead.

These stripping analysis techniques fall into Level 1 in terms of technology maturity. Consequently, a formal assessment of the systems' performance was not within the scope of this report.

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## Acronyms and Abbreviations

AAS	atomic absorption spectroscopy
AdSV	adsorptive stripping voltammetry
ASV	anodic stripping voltammetry
CAS	Columbia Analytical Services
CCV	continuing calibration verification
CLP	Contract Laboratory Program
cm	centimeter
°C	degrees centigrade
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
ETG	Environmental Technologies Group, Inc.
g	gram
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectroscopy
kg	kilogram
LANL	Los Alamos National Laboratory
LCL	Lower 95 percent confidence limit
LIBS	Laser-induced breakdown spectrometer
MCHD	Mill Creek-high demonstration
MCLD	Mill Creek-low demonstration
MCMD	Mill Creek-medium demonstration
MPD	mean percent difference
NERL	National Exposure Research Laboratory
NIST	National Institute of Standards and Technology
NMSU	New Mexico State University
PAR	Princeton Applied Research
PE	performance evaluation
PNNL	Pacific Northwest National Laboratory
PSA	potentiometric stripping analysis
RPD	relative percent difference
SBHD	Silver Bow-high demonstration
SBLD	Silver Bow-low demonstration
SBMD	Silver Bow-medium demonstration
SNL	Sandia National Laboratories
UCL	upper 95 percent confidence limit

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## **Chapter 1**

### **Introduction**

#### **Site Characterization Technology Challenge**

Rapid, reliable, and cost-effective field analysis and screening technologies are needed to assist in the complex task of characterizing and monitoring hazardous and chemical waste sites. Environmental regulators and site managers often are reluctant to use new technologies that have not been validated in an objective U.S. Environmental Protection Agency (EPA)-sanctioned testing program or through a similar process that facilitates acceptance. Until the performance of field characterization technologies can be verified through objective evaluations, users will remain skeptical of innovative technologies, despite the promise of better, less expensive, and faster environmental analyses.

The Consortium for Site Characterization Technology was established as a pilot program under the Environmental Technology Innovation, Commercialization and Enhancement Program, as outlined in 1993 by President Clinton's Environmental Technology Initiative, to specifically address many of these concerns. The Consortium is a partnership among the EPA, the Department of Energy (DOE), and the Department of Defense (DoD). The mission of the Consortium is to identify, demonstrate, and assess innovative field instruments. It also disseminates information about technology performance to developers, environmental remediation site managers, consulting engineers, and regulators. As a partnership, the Consortium offers valuable expertise to support the demonstration of new and emerging technologies. Through its organizational structure, it provides a formal mechanism for independent assessment, evaluation, and verification of emerging field analytical site characterization technologies.

#### **Technology Demonstration Process**

The Consortium provides technology developers a clearly defined performance assessment, evaluation, and verification pathway for EPA acceptance. The pathway is outlined in the four components of the Consortium's evaluation and verification process:

- Technology identification and selection
- Demonstration planning and implementation
- Performance assessment, evaluation, and verification
- Information distribution

Each component is discussed in detail in the following paragraphs.

### ***Technology Identification and Selection***

The first step of the process is a determination of technology needs. Because a wide range of field characterization and monitoring needs exists, the Consortium must prioritize a technology's suitability for demonstration. Priority is based on the environmental and fiscal impact of the technology and on the likelihood that its acceptance and use will provide cost-effective and efficient environmental solutions. Surveys of EPA, DOE, DoD, state, local, and tribal agencies and industry are carried out to identify candidate technologies that could meet the needs of the environmental characterization community.

Beyond the initial identification, a critical aspect of technology selection is an assessment of the technology's field deployment readiness. Commercialized instruments, or those ready for production, that have a history of successful laboratory or field operation are prime candidates for the demonstration process. Early evolving technology's prototypes, or laboratory instruments requiring extensive testing and modification prior to field deployment are less desirable as demonstration candidates. The candidate technology must meet criteria for one of three levels of maturing:

**Level 1** Demonstrated in a laboratory environment and ready for initial field trials

**Level 2** - Demonstrated in a laboratory environment and in limited field trials

**Level 3** - Demonstrated extensively in the laboratory and in field trials and commercially available

Assessment of the readiness of candidate technologies for field demonstration is based on the following criteria:

- Field portability or transportability
- Applicability to numerous environmentally affected sites
- Potential for solving problems inherent in current analytical methods
- Per sample cost factors
- Potential improvements in data quality, sample preparation, or analysis time
- Ease of use

### ***Demonstration Planning and Implementation***

A technology demonstration plan is prepared according to guidelines provided by the Consortium. This plan includes a technology description, an experimental design, a sampling and analysis plan, a quality assurance project plan, and a health and safety plan. These plans are designed to enable an objective test of technology performance. The demonstration plan also calls for the generation of a validated reference laboratory data set with which the field technology can be compared. Following approval by the EPA and acceptance by the technology developers, the demonstration plan is implemented at appropriate field locations. The Consortium provides technical support to the technology developer during plan preparation and execution and also audits the data collection process.

### ***Performance Assessment, Evaluation, and Verification***

In this component of the demonstration process, the technology analytical results are compared with a reference laboratory data set. The principal product of this phase of the project is a technology report, prepared by an independent party known as the verification organization. The report documents demonstration results and provides an assessment of the technology's performance. The degree of data analysis in the report is determined

by the level of maturity of the technology under evaluation; the more mature technologies receive more detailed analysis.

Level 1 demonstrations are intended to provide the technology developer with access to a controlled field demonstration in which the system can be tested. A detailed evaluation of system performance is left to the developer using the validated reference data set obtained during the demonstration. Level 2 technology performance is evaluated by the Consortium on a limited basis. The most extensive evaluation is done for Level 3 technologies. In this case, the capabilities of the technology are evaluated by the Consortium, and a formal verification statement documenting the technology's performance is issued by the EPA.

### ***Information Distribution***

Innovative technology evaluation reports from these demonstrations are peer reviewed and approved for distribution by the EPA. The Consortium has developed an information distribution strategy to ensure that these documents are readily available to interested parties. This strategy includes access to information via the World Wide Web through a program supported by the Superfund Technology Innovation Office.

### **The Soil-Metals Characterization Demonstration**

The objectives of the metals-contaminated soil characterization technology demonstration were twofold:

1. provide an opportunity for technology developers to analyze soil samples under a documented and scientifically sound experimental plan and
2. provide a validated soil analysis data set from conventional analytical laboratories using prescribed EPA laboratory analysis methods with which technology developers could compare their results

The process used for technology selection involved the publication of a notice of intent to conduct a technology demonstration, which was accompanied by solicitation of applications from interested parties. Usually, the Consortium selects applicants based on the readiness of the technology for field demonstration and on its applicability at environmentally affected sites as determined by the level of regional and national interest in the specific technology.

For this demonstration, the Consortium joined a project funded by the Department of Energy in which several technologies had already been selected for demonstration. The Consortium formalized the demonstration plan development, brought additional technologies to the demonstration, and enhanced the analytical laboratory component of the project.

Contractual arrangements were established with several chemistry laboratories to conduct soil analyses by conventional methodologies. Included in these arrangements was a plan to carry out a preliminary site assessment that involved limited sampling and analysis of soils from the area selected for the demonstrations. These preliminary data were used to further develop the site sampling and analysis plan, prior to the actual demonstration.

The following chapters of this report present the details of the demonstration project. Chapter 2 describes the stripping technologies demonstrated by Battelle Pacific Northwest National Laboratory (PNNL). Chapter 3 describes the site selection, soil sampling, laboratory selection, and analysis methodology. The technical approach taken in evaluation and validation of laboratory data is also outlined in Chapter 3. Chapter 4 gives a detailed analysis of the laboratory data validation process and describes how a reference laboratory data set was



determined. Chapter 5 gives results and an analysis of the performance of the PNNL technologies. Chapter 6 contains developer's comments regarding the demonstration.

## Chapter 2

### Technology Description

#### General Description

Anodic stripping voltammetry (ASV)<sup>1</sup> and potentiometric stripping analysis (PSA) are related electroanalytical techniques that are used to measure metals in solution. The target metal is first preconcentrated onto a working electrode by placing a voltage potential on the electrode so that a portion of the metal in solution migrates to and is deposited on the electrode. In ASV, the accumulated metal species is then stripped from the electrode by applying an increasing voltage to the working electrode. The accumulated metal is released from the electrode when the voltage potential on the electrode is equivalent to the oxidation potential of the target metal. During the stripping phase, electrode current is measured as a function of electrode potential and produces a voltammogram. The release of the target metal from the electrode is measured as peak current and is proportional to the concentration of the metal in the test solution. Potentiometric stripping analysis employs a variation from the ASV method in the stripping stage. Following the metal accumulation stage, the addition of a chemical oxidant or a constant current is used to strip the target elements from the electrode. The elements are sequentially stripped from the electrode in order of their oxidation potential. The length of time required to strip the element at a particular electrode potential is used as a measure of the concentration of the element in solution. Further descriptions of ASV and PSA technologies can be found in the literature (Jagner et al., 1982; Olsen et al., 1994; Wang; 1982, 1985).

Three electrochemical systems were deployed in this demonstration. The ASV system, operated by individuals from Pacific Northwest National Laboratory and New Mexico State University (NMSU), consisted of an EG&G/Princeton Applied Research (PAR) Model 264A voltammetric analyzer, a PAR Model 303A static mercury drop electrode, and a PAR Model 0073 X-Y recorder. A PSA system was also operated by PNNL/NMSU personnel. The system was a TraceLab™ Trace Element Laboratory, consisting of a PSU 20 potentiometric stripping unit (Radiometer A/S, Copenhagen, Denmark). A SAM 20-sample station accessory was used that included a glassy carbon disk as the working electrode in the system. System operation and control were via a personal computer with appropriate software. The third demonstration unit was the Metalyzer™ 3000, another PSA system from Environmental Technologies Group, Inc. (ETG) of Baltimore, Maryland. The Metalyzer is a hand-held, battery-operated system with disposable electrodes. The instrument is commercially available and is typically used for water analysis. Technology developers from ETG were interested in assessing their system's performance in the measurement of metals from soil and from residue extracts.

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<sup>1</sup> Anodic stripping voltammetry is also referred to as adsorptive stripping voltammetry (AdSV), and the two terms are used interchangeably in this report.

## Technology Advantages

According to the technology developers, the ASV and PSA techniques offer several features consistent with, and in some cases, better than, conventional atomic emission or absorption spectroscopic methods. The most important features of these electroanalytical techniques include the following:

- High sensitivity
- High precision
- Ability to speciate metals
- Portable, compact apparatus
- Low power consumption
- Low acquisition cost

## Technology Limitations

The developers indicate several features of the systems that may be viewed as system limitations.

- Like conventional laboratory techniques, the metal to be analyzed must be in solution achieved through an acid digestion preliminary step.
- Some wet chemistry is required in processing the samples.
- Not all elements can be analyzed by electrochemical techniques.
- The presence of some metal pairs in solution can result in the formation of intermetallic compounds, requiring additional chemical additives in the analysis.
- Metals present in solution that have similar oxidation potentials can result in peak overlap, causing difficulty in quantitative analysis.

## Physical Characteristics

Physical attributes and electrical requirements of the two instruments as provided by the developers are given in Table 2-1.

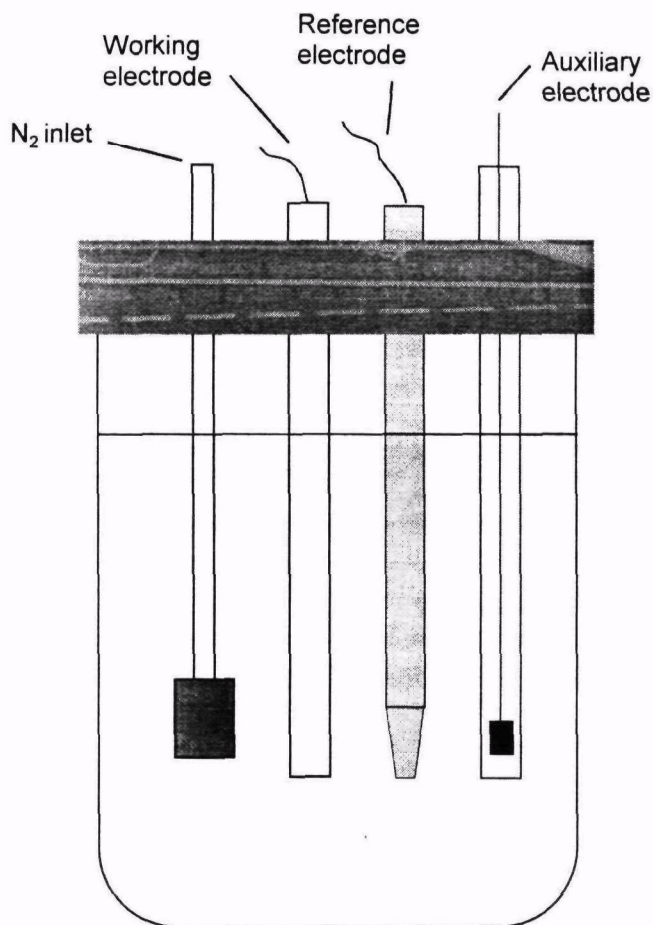
**Table 2-1. Physical Characteristics and Electrical Requirements Associated with the ASV and PSA Systems**

Instrument Parameter	ASV EG&G	PSA TraceLab	PSA Metalyzer
Weight, pounds	25	50	3
Electrical requirements	115 V/3 A	115 V/5 A	Battery powered
Volume (cubic feet)	6	9	1

Ancillary equipment for all systems includes a microwave digestion unit, a top-load balance, laboratory glassware and hardware, and a personal computer and printer. Sample preparation and instrument operation are relatively simple; however, samples must be digested in order to get the elements of interest into solution. One person with technical skills and training is capable of operating the instrument under normal conditions.

## Schematic Diagram

A simple schematic diagram of a typical ASV analysis cell is shown in Figure 2-1. The cell consists of three electrodes: a working electrode (single-drop mercury electrode or glassy carbon disk), a reference electrode, and an auxiliary electrode. The cell also has a nitrogen gas inlet that is used to purge oxygen from the system. The configuration of a PSA system is fundamentally the same with minor variations. The system component that varies most between ASV and PSA systems is the configuration of the working electrode.



**Figure 2-1. Schematic diagram of a typical ASV analysis cell.**

## Operational Features

Sample preparation, sample analysis, and calibration features, as summarized by the instrument developers, are given below.

### *Sample Preparation*

The ASV and PSA systems both require that the target elements be in solution. Consequently, acid leaching and/or digestion of the sample was carried out in a preanalysis sample preparation step. A microwave digestion method similar to those prescribed by the EPA in Method SW-846 (EPA, 1996) was used in this demonstration prior to electrode analysis. Hydrochloric acid was used in place of nitric acid, which is specified in SW-846.

The change was made to ensure compatibility with the electrode analysis systems. The 100-g soil samples were placed in 100-ml beakers and dried in a microwave oven. A 1-g aliquot of the dried soil sample was used in follow-on microwave-assisted acid digestion.

### ***Sample Analysis***

EG&G AdSV analysis procedures for chromium were as follows:

1. The 9.9 ml of supporting electrolyte solution was pipetted into the sample cell and purged with nitrogen for 4 minutes.
2. An accumulation potential of  $-0.8$  V was applied to a fresh mercury drop electrode as the solution was stirred for 10 to 30 seconds.
3. Stirring was stopped and a voltammogram was recorded by applying a negative-going differential pulse potential scan terminating at 1.65 V.
4. A known volume of soil leachate and 10  $\mu$ l of 0.1 M  $\text{KMnO}_4$  were added and steps 2 and 3 were repeated for the analysis of Cr.
5. Quantification of the Cr in solution was achieved by the method of additions using National Institute of Standards and Technology (NIST)-traceable Cr standards.

TraceLab PSA analysis procedures were as follows:

1. The soil leachate was diluted tenfold in a nonaerated HCl solution.
2. An accumulation potential of  $-1.1$  V was applied to a preplate mercury film electrode as the solution was stirred for 2 minutes.
3. The metals were then chemically stripped from the electrode in a quiescent (nonmixed) solution.
4. Quantification was achieved through the method of additions using Cd, Cu, and Pb standard solutions.

ETG Metalyzer 3000 analysis procedures for copper, cadmium, and lead were as follows:

1. The disposable analysis cell was uncapped and filled with extract solution to the indicated level on the cell.
2. The cell cap was closed with the twist cap, forcing the sample into the electrode chamber.
3. The sensor was flexed at the center, breaking a glass ampoule containing chemical reagents which then mixed with the sample.
4. The disposable cell was inserted into the meter, automatically starting the approximate 3-minute analysis cycle.
5. The metal concentrations were read from the digital display.

### ***Calibration***

Calibration of the ASV and TraceLab PSA instruments was carried out using the method of standard additions. Analysis of an unspiked test solution was followed by spiking known amounts of target metals into the solution and repeating the analysis. Alternatively, calibration curves can be prepared and used to determine metal content in the test solutions. The Metalyzer was equipped with a plug-in electronic chip that contained calibration information for the particular lot of disposable analysis cells used in this demonstration.

## Technology Maturity

The ASV and PSA systems operated by PNNL/NMSU personnel have undergone considerable methods development in a laboratory setting. The electrochemical techniques have been well established for the analysis of water samples for trace metal content. Use of these systems for metals-contaminated soil or residue analysis is a relatively new application. The Metalyzer 3000 has also been marketed for routine water testing applications, but has not been previously tested for analyzing soil residue.

## Technology Performance Indicators

The analytical capabilities of the three systems, as reported by the developers are presented in Table 2-2. Instrument detection limits and accuracy and precision data are given in the table for four of the nine target elements. As a result of analysis time constraints, only four elements were selected for analysis. These performance data are included for informational purposes only and are not further evaluated or verified as a part of this demonstration.

**Table 2-2. Detection Level and Accuracy Estimates for the ASV and PSA Systems as Reported by PNNL, NMSU, and ETG**

Element	ASV (EG&G)		PSA (TraceLab)		PSA (Metalyzer)	
	Detection Level (mg/kg)	Accuracy/Precision (%)	Detection Level (mg/kg)	Accuracy/Precision (%)	Detection Level (mg/kg)	Accuracy/Precision (%)
Chromium (Cr)	5	$\pm 33 / \pm 40$	NR	NR	NR	
Cadmium (Cd)	NR	NR	1	$\pm 20 / \pm 40$	1	$\pm 20 / \pm 40$
Copper (Cu)	NR	NR	5	$\pm 20 / \pm 40$	5	$\pm 20 / \pm 40$
Lead (Pb)	NR	NR	5	$\pm 20 / \pm 40$	5	$\pm 20 / \pm 40$

Notes: Accuracy levels are given relative to conventional laboratory analysis using EPA standard methods.  
NR = Not reported.

## Chapter 3

### Demonstration Design and Description

#### Technology Demonstration Objectives

The primary objective of this demonstration was to prepare and execute a scientifically sound test protocol for the collection and analysis of data from metals-contaminated soil samples as determined by candidate technologies. To assist the technology developers in evaluating the data collected from their instruments, the Consortium conducted a parallel analysis of replicate soil samples by conventional laboratory methods. Table 3-1 lists the demonstration participants and their accompanying technologies.

**Table 3-1. Demonstration Participants**

Participant	Technology/Reference Laboratory
Los Alamos National Laboratory	Laser-induced breakdown spectrometer (LIBS) (technology)
MelΔok Instruments, Inc.	Laser-induced breakdown spectrometer (technology)
Pace Environmental Laboratories, Inc. <sup>a</sup>	Flame atomic absorption spectroscopy (technology)
Battelle Pacific Northwest National Laboratory	Anodic stripping voltammetry (technology)
MSE-HKM, Inc.	Inductively coupled plasma atomic emission spectroscopy (reference laboratory)
Sandia National Laboratories Environmental Restoration Program Laboratory	Inductively coupled plasma atomic emission spectroscopy (reference laboratory)
Columbia Analytical Services, Inc.	Inductively coupled plasma emission spectroscopy and flame atomic absorption spectroscopy (reference laboratory)

<sup>a</sup>Point of contact: Khris Olsen (509) 376-4114.

The technologies demonstrated, with one exception, were at the low end of the maturity curve. Consequently, a rigorous technology assessment was not performed on these systems. The soil analysis data from the analytical laboratories were validated and provided to the developers along with their own data for use in further development and refinement of their instruments.

#### Site Selection and Description

To properly assess a field screening technology, a suitable site with soil contaminated by metals was required. Early in the project, a demonstration plan was developed that presented the following criteria to assist in site selection.

- The site soils must contain a wide concentration range of the heavy metals arsenic, cadmium, chromium, copper, iron, manganese, lead, silver, and zinc.

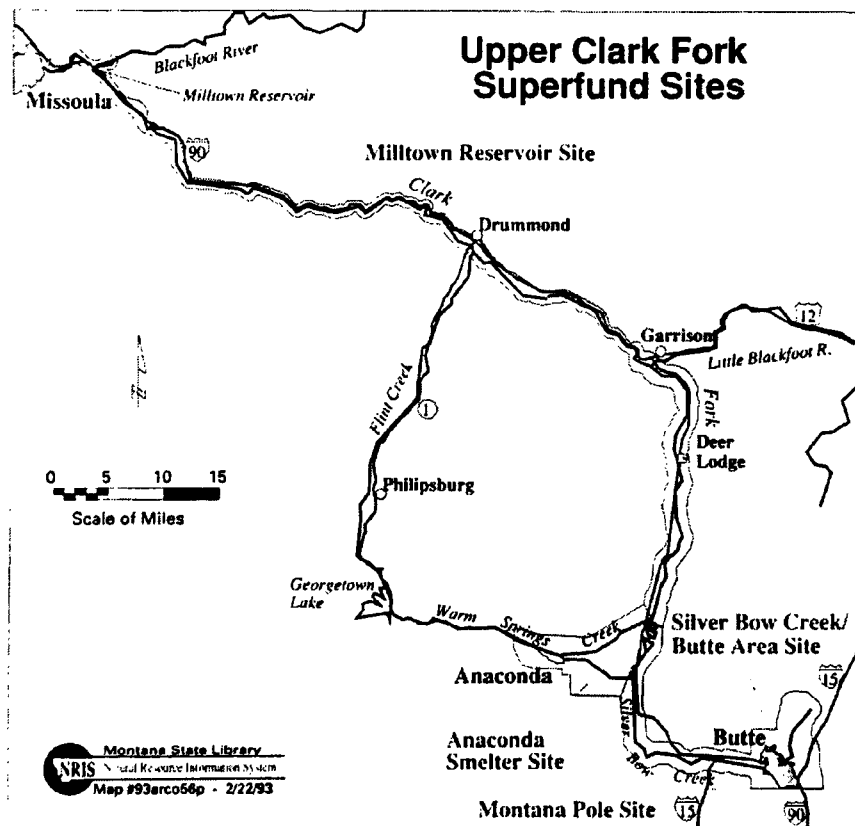
- The site must have at least two sample collection areas with significantly different soil types.
- The heavy metal concentration levels in the soil must be reasonably well characterized and documented.
- The site must be readily accessible for conducting technology demonstrations.

The DOE Characterization Monitoring and Sensor Technology Cross-Cut Program had funded a demonstration project through the Western Environmental Technology Office in Butte, Montana, at a metals-contaminated soil site. The project had been awarded to MSE-HKM, Inc., an on-site contractor (hereafter referred to as MSE). Consortium members, including the EPA Environmental Sciences Division of the National Exposure Research Laboratory (NERL) and Sandia National Laboratories (SNL), chose to augment this demonstration by soliciting additional technologies for demonstration and by providing additional laboratory analysis of the soil samples used in the demonstration. During the preparation of the demonstration plan, two sites, Butte/Silver Bow Creek and Anaconda Smelter/Mill Creek, were selected for the study. Figure 3-1 shows the general location of the sites.

### ***Site 1 Butte/Silver Bow Creek***

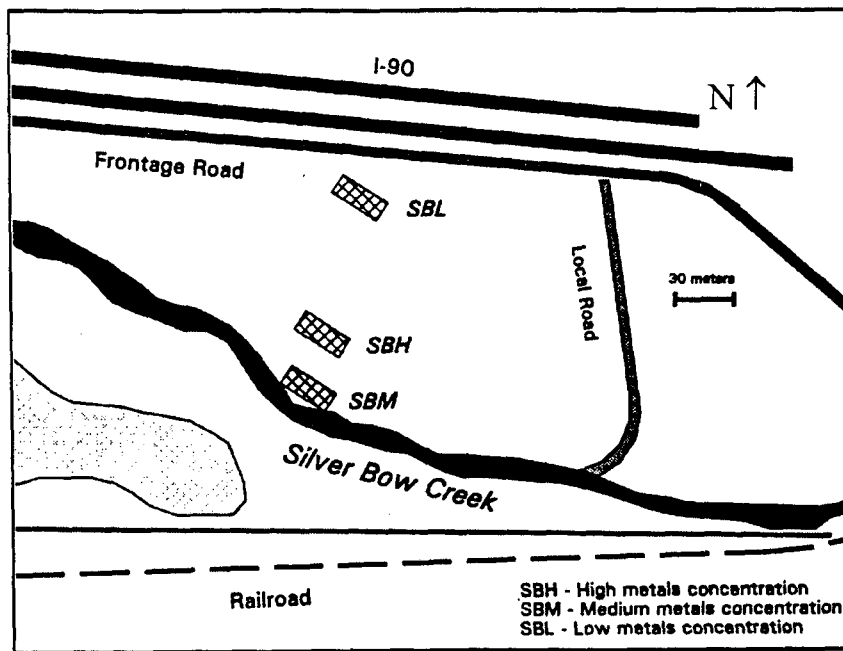
#### **Location**

The Butte/Silver Bow Creek site extends from the west side of Butte, Montana, along Silver Bow Creek to the confluence of Sand Creek and Silver Bow Creek. The site is contaminated by heavy metals from historic and modern mining and mill tailings deposits. Figure 3-2 shows the Butte/Silver Bow Creek collection site.



**Figure 3-1. Montana regional map showing the Silver Bow and Mill Creek (Anaconda) sampling sites.**





**Figure 3-2. Local map of the Silver Bow sampling site.**

### **History**

Mining activities in the Butte area started with a group of small gold, silver, and copper mining operations. Butte became an important mining district in the late 1800s as the size and number of mines grew. With the growth of ore extraction activities came the need for easy access to ore processing facilities. Consequently, many mills and smelters were constructed in the region to concentrate and purify ores from the underground mines. Waste materials from the mineral extraction process, known as tailings, were impounded in ponds and were eventually discharged into Silver Bow Creek.

Approximately 230 km of stream and riparian habitat have been affected by these local operations. The region of contamination begins in Butte and extends westward along Silver Bow Creek to the Milltown Reservoir. Significant mill tailings deposits are found along the creek as well as dispersed over the Silver Bow Creek flood plain, resulting in a large area of contaminated soil.

During the 1960s and 1970s, mining activities gradually shifted from underground to open-pit mining. In 1982, the Anaconda Minerals Company discontinued underground mining in Butte. In the same year, the EPA started site contamination investigations in the area. By the early 1990s, mining operations had ceased and remediation efforts were implemented.

### **Characteristics**

The Butte/Silver Bow Creek sample area encompasses approximately 5.5 km of Silver Bow Creek. The principal groundwater-bearing structure is a shallow alluvial aquifer composed of coarse-grained fan and floodplain deposits. Bedrock formations are found at approximately 1 to 10 m below the surface. The deposits are moderately permeable and are hydraulically connected to the perennial Silver Bow Creek surface stream. Because the Silver Bow Creek is an eroding bedrock valley, the erosion slopes are narrow and near the stream.

A relatively high surface stream gradient of 3.2 mm/m produces a high-energy stream characterized by a straight stream channel and narrow floodplain.

Mill tailings deposits at the Butte/Silver Bow Creek site have produced widespread soil contamination. The contaminated areas are continuous and confined to the narrow floodplain surrounding Silver Bow Creek. Preliminary characterization efforts, conducted during the site selection process, revealed that heavy metals deposits are most concentrated in the top 15 to 50 cm of the soil to a maximum depth of 1.2 m (MSE, 1996). A soil analysis to assess the degree of mill tailings contamination of the local soils was carried out by MSE. Surface soil analysis results for three sampling locations showing the range of contaminant metal concentrations are summarized in Table 3-2.

**Table 3-2. Typical Heavy Metal Soil Contamination at the Butte/Silver Bow Creek Site**

Metal	Soil Concentration (mg/kg)		
	Sample 1	Sample 2	Sample 3
Aluminum (Al)	6,780	2,990	9,480
Arsenic (As)	1,200	297	174
Cadmium (Cd)	41.1	11	0.46
Chromium (Cr)	7.23	6.25	13.5
Copper (Cu)	2,150	1,350	315
Iron (Fe)	31,800	16,500	12,200
Lead (Pb)	2,110	681	182
Manganese (Mn)	2,490	1,160	2,170
Silver (Ag)	90.4	15.9	231
Zinc (Zn)	12,300	2,710	321

Note: Data from a preliminary soil assessment by MSE-HKM, Inc. See MSE, 1996.

### Sampling Location Details

The first of three sample areas was selected at a location approximately 45 m north of the Silver Bow Creek bed in the creek floodplain. The predemonstration samples from this area generally showed the highest concentrations of contaminant metals of all predemonstration samples. Consequently, this site was designated “SBHD” (Silver Bow-high demonstration).<sup>1</sup> A 27-m, northwest-to-southeast transect of the SBHD sample area was divided into ten 400-cm<sup>2</sup> sample plots equally spaced at 3-m intervals along the transect. Each plot was designated with the SBHD identifier followed by a plot number ranging from 1 to 10, with the number increasing from northwest to southeast.

A second sample area was located stream-side, within the Silver Bow Creek bed, and was designated area “SBMD” (Silver Bow-medium demonstration). A 27-m, northwest-to-southeast transect running along the streamside of the SBMD sample area was divided into ten 400-cm<sup>2</sup> sample plots, equally spaced at 3-m intervals. Each plot was designated with the SBMD identifier followed by a plot number ranging from 1 to 10, with the number increasing from northwest to southeast.

A third sample area was located on a hilltop overlooking the SBHD and SBMD sites approximately 120 m from the stream side and was designated area “SBLD” (Silver Bow-low demonstration). A 27-m, northwest-to-

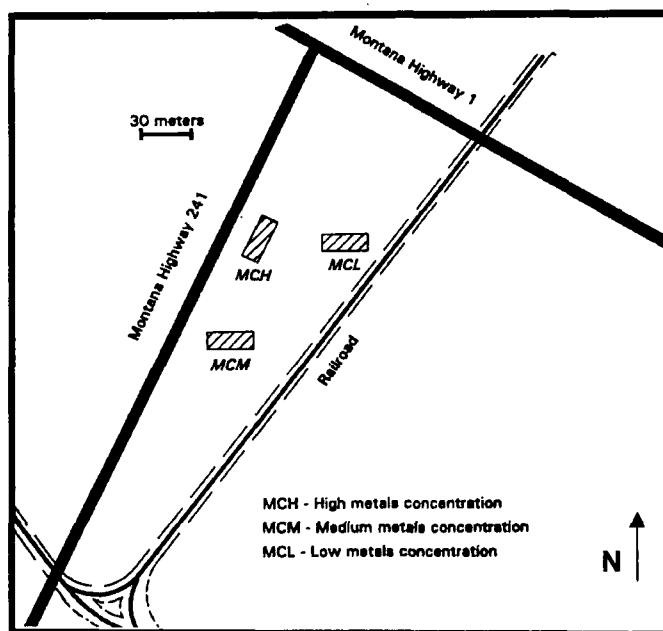
<sup>1</sup> The naming convention uses high, mid, and low as a matter of convenience. These designations do not always correspond to the metal concentrations encountered in the samples.

southeast transect running along the hill top of the SBLD sample area was divided into ten 400-cm<sup>2</sup> sample plots, equally spaced at 3-m intervals. Each plot was designated with the SBLD identifier followed by a plot number ranging from 1 to 10, with the plot number increasing from northwest to southeast.

## ***Site 2 Anaconda Smelter/Mill Creek***

### **Location**

The Anaconda Smelter/Mill Creek sample area, as shown in Figure 3-3, covers approximately 16 km<sup>2</sup> between Anaconda and Opportunity, Montana. The site is located approximately 40 km west of Butte and near the Anaconda smelter. It is bounded by state highway 1 to the north and state highway 241 to the west. Flue dust produced by 100 years of smelter operation has contaminated the site with heavy metals by the process of aerosol deposition.



**Figure 3-3. Local map of the Mill Creek sampling site.**

### **History**

The first copper smelting facilities to process ore from Butte area mining operations were in the Anaconda Smelter/Mill Creek area. The site consists of two facilities, the Upper Works, started in 1884, and the Lower Works, started in 1888. A silver ore refinery was also located between the copper smelting complexes. Smelter flue dust containing high levels of metals such as copper, arsenic, cadmium, and lead was produced as a by-product of the Anaconda smelting activities. Until 1976, flue dust generated by reverberatory furnaces was reprocessed for arsenic recovery. After 1976, the reverberatory furnaces were replaced by an electric furnace, and flue dust was collected by a pollution control system.

From 1976 through 1992, nine dust piles with a total volume of approximately 350,000 m<sup>3</sup> were deposited on the hills around the smelter. From 1985 through 1992, wind scouring of the dust piles was controlled by surfactant

application. Since 1992, however, considerable amounts of the flue dust have been resuspended and deposited downwind from the smelter stack and dust piles.

### Characteristics

The Anaconda Smelter/Mill Creek sample area is immediately adjacent to the Anaconda Smelter site. The area consists of a thick layer of moderately permeable, coarse-grained, floodplain deposits over bedrock. Mill Creek and the sample collection area lie in a structurally broad valley with an accompanying wide floodplain. Mill Creek is also a tributary of Silver Bow Creek.

Deposition of smelter flue dust at the Anaconda Smelter/Mill Creek site has produced widespread soil contamination with metals across the entire floodplain. Arsenic, cadmium, and lead are most concentrated in the top 15 cm of the soil. Cadmium and lead concentrations decrease more rapidly with depth than does arsenic concentration. Typical analysis results from three surface soil samples taken in the Mill Creek area are presented in Table 3-3, as measured during the predemonstration site assessment carried out by MSE.

**Table 3-3. Typical Heavy Metal Soil Contamination at the Anaconda Smelter/Mill Creek Site**

Element	Concentration (mg/kg)		
	Sample 1	Sample 2	Sample 3
Al	5,150	3,450	3,640
As	1,170	887	617
Cd	7.9	4.66	2.92
Cr	10.3	6.71	6.52
Cu	1,320	573	506
Fe	17,400	13,800	16,300
Pb	515	400	277
Mn	305	146	106
Ag	10.3	5.03	4.63
Zn	689	577	414

Note: Data from a preliminary soil assessment by MSE Inc.. See MSE, 1996.

### Sampling Location Details

The first Mill Creek sampling location was approximately 115 m southwest of the highway 1 and highway 241 intersection, and was designated area “MCHD” (Mill Creek-high demonstration).<sup>2</sup> A 27-m, southwest-to-northeast transect of the MCHD sample area was divided into ten 400-cm<sup>2</sup> sample plots, equally spaced at 3-m intervals along the transect. Each plot was designated with the MCHD identifier followed by a plot number ranging from 1 to 10, with the plot number increasing from southwest to northeast.

A second sample area was located approximately 180 m southwest of the intersection of highway 1 and highway 241, and was designated area “MCMD” (Mill Creek-medium demonstration). A 27-m, west-to-east transect of the MCMD sample area was divided into ten 400-cm<sup>2</sup> sample plots, equally spaced at 3-m intervals. Each plot was designated using the MCMD identifier followed by a plot number ranging from 1 to 10, with the plot number increasing from west to east.

<sup>2</sup> The naming convention uses high, mid, and low as a matter of convenience. These designations do not always correspond to the metal concentrations encountered in the samples.

The third Mill Creek sample area was located approximately 115 m south of the intersection of highway 1 and highway 241 and was designated area "MCLD" (Mill Creek-low demonstration). A 27-m, west-to-east transect of the MCLD sample area was divided into ten 400-cm<sup>2</sup> sample plots equally spaced at 3-m intervals. Each plot was designated using the MCLD identifier followed by a plot number ranging from 1 to 10, with the number increasing from west to east.

### ***Sample Collection, Handling, and Distribution***

#### **Sampling Methods**

Ten samples were taken from each of three locations at two sites for a total sample size of 60. The soil in each 400-cm<sup>2</sup> sample plot was removed with a clean stainless steel hand trowel to a depth of 2.5 cm, passed through a No. 10 mesh sieve, homogenized by five passes through a 14-channel riffle splitter, and placed in 1,000-cm<sup>3</sup> labeled glass containers. Each 1,000-cm<sup>3</sup> sample contained approximately 2.5 kg of soil. Sample collection proceeded from levels of low metals concentration to high concentration. All sampling equipment was decontaminated by a detergent wash and double rinse with deionized water between use at each sampling location.

#### **Sample Handling**

All soil samples were taken to MSE, Inc., where they were dried for 12 hours at 105 °C in an oven. After drying, each soil sample was split ten ways. Each split contained an estimated 150 g of soil and was placed in a labeled container. Splits were distributed to analytical laboratories, various technology demonstrators, and archives. Soil sample collection, homogenization, drying, and splitting were carried out during the week of September 18, 1995, by SNL and MSE laboratory personnel prior to the technology demonstration. Samples were stored in locked coolers at room temperature until distribution.

#### **Sample Distribution**

The distribution of the ten sample splits is shown in Table 3-4. The sample numbering convention was in the format: AABB-NN-nnn, where

AA = Site (SB or MC)  
BB = Transect (HD, MD or LD)  
NN = Plot No. (01-10)  
nnn = Split No. (001-010)

With the exception of Columbia Analytical Services (CAS) and Los Alamos National Laboratory (LANL), each analytical laboratory and technology demonstrator received a total of 64 samples (60 field soil samples plus 2 blank and 2 control samples). LANL received two sets of splits for a total of 124 samples and CAS received a total of 32 samples (the 30 field samples plus 1 blank and 1 control sample), because only half of the field soil samples were selected for analysis at this laboratory.

In addition to soil from the site, each laboratory and technology demonstrator received several quality control samples. Included in this set were two blank soil samples and two control soil samples prepared and analyzed by Environmental Resource Associates, Arvada, Colorado, a soils analysis quality control laboratory. These blank and control samples consisted of topsoil that was dried, ground, sieved, and spiked with various metals (in the case of the control sample). The soil was then thoroughly homogenized and split into samples that were

**Table 3-4. Distribution of Field Soil Sample Splits**

Soil Sample Split No.	Recipient Technology/Reference Laboratory
01	Los Alamos National Laboratory LIBS (technology)
02	Los Alamos National Laboratory LIBS (technology) <sup>a</sup>
03	MelΔok Instruments, Inc. LIBS (technology)
04	Battelle Pacific Northwest National Laboratory-anodicstripping voltammetry (technology)
05	Pace Environmental Laboratories, Inc.-flame atomic absorption spectroscopy (technology)
06	MSE-HKM, Inc. (reference laboratory)
07	Sandia National Laboratories (reference laboratory)
08	Columbia Analytical Services, Inc. (reference laboratory)
09	Sandia National Laboratories - archive
10	Sandia National Laboratories - archive

<sup>a</sup> Originally, two similar laser-induced breakdown spectroscopy systems were to be fielded by Los Alamos researchers, with each requiring a sample split. As a result of logistical difficulties, only one system was actually brought to the site and used in the demonstration.

subjected to a round-robin analysis at qualified laboratories. The results from 20 or more analyses of the soil batch were used to define a mean value for each element along with a 95 percent confidence interval (mean value  $\pm 2 \times$  standard deviation).

Each laboratory and developer of a demonstration technology was also instructed to produce matrix duplicates of at least two of the field soil samples so that a measure of analytical precision could be obtained. In the interest of having a diverse but manageable list of target elements, nine metals were selected for analysis by all participants: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), silver (Ag), and zinc (Zn).

## **Laboratory Selection and Analysis Methodology**

### ***Columbia Analytical Services***

Analysis of soil samples was carried out at Columbia Analytical Services, Inc., in Kelso, Washington, along with analysis of several quality control samples. Analysis was carried out at this EPA Contract Laboratory Program (CLP) laboratory to provide a soil analysis data set that could be used as a cross check with the more comprehensive soil sample analysis carried out at the MSE laboratory. As a result of program cost constraints, analysis at the CAS laboratory was limited to half (30) of the 60 field soil samples collected during the demonstration.

Soil samples were digested using EPA SW-846 Method 3050A: *Acid Digestion of Sediments, Sludges, and Soils*. Columbia Analytical Services analyzed all 32 control and field soil samples by inductively coupled plasma atomic emission spectroscopy using the EPA SW-846 Method 6010A.

The laboratory also generated its own duplicates of the 32 soil, control, and blank soil sample digestates and conducted a second analysis by atomic absorption spectroscopy (AAS) using EPA SW-846 Method 7000A. The specific methods employed in the analysis included flame aspiration and graphite furnace. They are listed below for each of the target elements.

Ag (silver)	Method 7760A: silver (atomic absorption, direct aspiration)
As (arsenic)	Method 7060A: arsenic (atomic absorption, furnace technique)
Cd (cadmium)	Method 7131A: cadmium (atomic absorption, furnace technique)
Cr (chromium)	Method 7190: chromium (atomic absorption, direct aspiration)
Cu (copper)	Method 7210: copper (atomic absorption, direct aspiration)
Fe (iron)	Method 7380: iron (atomic absorption, direct aspiration)
Mn (manganese)	Method 7460: manganese (atomic absorption, direct aspiration)
Pb (lead)	Method 7420: lead (atomic absorption, direct aspiration)
Zn (zinc)	Method 7950: zinc (atomic absorption, direct aspiration)

A matrix duplicate sample was also made of original sample number MCLD-1-008. This duplicate was digested and analyzed by ICP and AAS methods to give a measure of overall laboratory analytical precision on matrix samples.

### ***MSE Laboratory***

The MSE laboratory, located near the sampling site in Butte, Montana, did the preassessment soil sampling and analysis. It also performed, in collaboration with SNL, the actual demonstration soil sampling, processing, and distribution. The MSE laboratory carried out a complete analysis of all demonstration soil and quality control samples. Although MSE is not a CLP laboratory, it used standard EPA SW-846 methodology in its analyses. The laboratory adheres to quality control procedures specified in the standard EPA analysis protocols used for soils analysis and operates under a written quality assurance plan.

Sixty soil samples plus 2 control soil samples and 2 blank soil samples were digested using EPA SW-846 Method 3050A: *Acid Digestion of Sediments, Sludges, and Soils*. All 64 samples were analyzed by ICP using EPA protocol SW-846 Method 6010A. Matrix duplicates were also made of 4 samples. These underwent digestion and analysis by ICP so that a measure of method precision could be obtained for this particular soil matrix.

### ***SNL Environmental Restoration Program Laboratory***

The SNL Environmental Restoration Laboratory was selected as an additional reference laboratory. This laboratory primarily provides rapid screening data which are used in conjunction with conventional CLP-type analysis for the Sandia internal environmental restoration program. A laboratory quality assurance/control plan was under development during this study. Data from this laboratory were obtained with a mobile inductively coupled atomic emission spectroscopy system. The unit is a conventional benchtop ICP system that has been adapted for field use. The instrument exhibits higher detection limits and more calibration drift than benchtop units normally used in the laboratory.

Soil samples were digested at the SNL laboratory in a slightly different manner than that used at the other two laboratories. This laboratory used a microwave-assisted acid digestion method formally designated SW-846 Method 3051: *Microwave Assisted Acid Digestion of Sediment, Sludges, Soils, and Oils*. The SNL laboratory analyzed all 64 soil and quality control samples by ICP using EPA protocol SW-846 Method 6010A.

### **Demonstration Narrative**

Predemonstration soil samples were collected during the week of August 21, 1995. These samples were used by the participants in instrument setup and calibration. The actual demonstration soil samples were collected

September 18–22, about 1 week prior to the technology demonstration. Sample processing and packaging was completed on September 24. Participants in the demonstration were on the site during the week of September 24–29. A complete set of 60 soil samples plus quality control samples were given to each of the participants at the beginning of the week.

Because access to the actual soil sampling sites was limited and the local media were invited to observe activities on selected days during the demonstration, the demonstration area was set up on an easily accessible, paved parking lot about one-half mile from the Silver Bow sampling site. Several vans, tents and generators were installed at the site to support the various systems. Temperatures ranged from freezing in the morning to the mid-sixties during the day. Space heaters were used in some of the tents and vehicles during the cold morning hours. The actual demonstration lasted 6 days; about 2 days were used for instrument setup, checkout, and disassembly and 4 days for soil analysis. Participants worked at their own pace. A typical day during the demonstration period began at 9 a.m. and ended at 7 p.m.

### **Deviations from the Demonstration Plan**

A comparison of the demonstration plan prepared prior to the study and the actual conduct of the study as recorded in the various field and data logbooks reveals a number of discrepancies, which are discussed below.

- The initial soil sampling effort at Silver Bow Creek had to be repeated because a temperature control circuit failed during sample drying. Soil temperatures were determined to be well in excess of the 105 °C specified in the demonstration plan. The samples were discarded and additional samples were collected and processed.
- All soil samples were dried at an oven temperature of 175 °C instead of the 105 °C specified in the demonstration plan. As noted in the previous paragraph, the primary oven failed and a backup oven had a minimum temperature control level of 175 °C. In the interest of maintaining the project schedule, the 175 °C drying temperature was used.
- Some of the soil sampling was carried out during inclement, rainy weather. Problems were encountered when sieving moist soil with a No. 10 screen. Larger (No. 6 and No. 8) sieve sizes were used to facilitate soil processing of the SBLD samples in the field. These and all other samples were homogenized following sieving so demonstrators and laboratories received comparable samples. Intercomparison of SBLD, SBMD, and SBHD samples was not done in this study, so sieve size differences among sample sets does not appear to be significant.
- The certificates of analysis that accompanied the soil control samples were distributed to participants after all analytical results were submitted to SNL. Access to control soil sample results during the demonstration was not specified in the demonstration plan, however. This procedure did not compromise the demonstration design since final analytical data were submitted prior to access to control sample results.
- Analysis of the data from the CAS laboratory revealed beyond a reasonable doubt that two blocks of five samples were mislabeled. The specific blocks in question were from the Mill Creek sampling site, series MCHD and MCMD. The switch could have occurred either as a result of mislabeling of sample containers in the field or during receipt and logging of the samples at the CAS laboratory. An investigation to determine the source of the error was carried out; however, the source could not be determined from the available chain-of-custody documentation. Despite the fact that a clear incidence of mislabeling could not be determined, the data were corrected since the switch was unmistakable in the data analysis phase of the project.



## **Chapter 4**

### **Laboratory Data Results and Evaluation**

#### **Laboratory Data Validation Methodology**

One of the objectives of this study was to provide the technology developers with a validated set of soil analysis results from reference laboratory methods for comparison with field results. Both qualitative and quantitative laboratory data quality indicators were used in the data validation process for all participating laboratories. These are described more fully in the following sections.

#### ***Qualitative Factors***

Qualitative factors included degree of experience of the laboratory staff, experience in soils analysis, level of certification, if any, and past performance on laboratory audits. These factors were used along with additional quantitative factors in assessing laboratory data quality.

#### ***Quantitative Factors***

Five specific quantitative factors were also evaluated in the soil analysis data set provided by each laboratory to assist in the data validation process. These factors were blank sample analysis, control sample analysis, analytical precision, instrument stability, and spike recovery. Each factor is described more fully in the following paragraphs.

#### **Soil Blank Analysis**

The results from the blind blank soil analyses were directly compared with the information given on the certificate of analysis accompanying the samples, which were provided by Environmental Resource Associates. These analysis data were used as a semiquantitative check on the methods used by the laboratories to detect contaminant levels, because the soil contained either low or nondetectable levels of many of the target elements.

#### **Control Soil Sample Analysis**

The results from the blind control soil sample analysis from each reference laboratory were directly compared with the certified heavy metal concentrations in the soil, as determined by interlaboratory analyses of the same lot of soil. Environmental Resource Associates prepared the soil and coordinated the interlaboratory study. An analysis certificate shipped with the control sample included a certified value and a “performance acceptance limit”<sup>1</sup> for each element in the sample. The results from the control samples from each of the laboratories were

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<sup>1</sup> The certificate from Environmental Resource Associates indicates that the performance acceptance limits for each element “closely approximate the 95% confidence interval about the certified value.”

an important indicator of laboratory performance levels. Analysis results that fell within the 95 percent confidence interval were judged to indicate an acceptable level of performance.

### **Duplicate Analysis Precision**

Laboratory analytical precision was estimated by calculating the relative percent difference (RPD) between two analyses of predigestion duplicate soil samples prepared by each laboratory. The following equation was used.

$$RPD = \frac{|Y_a - Y_b|}{\frac{(Y_a + Y_b)}{2}} (100)$$

where

$RPD$  = relative percent difference

$Y_a$  = sample result

$Y_b$  = duplicate sample result

Relative differences in excess of 20 percent, as specified in EPA Methods 6010A (ICP) and 7000A (AAS), are taken to indicate questionable laboratory analytical process control.

### **Instrument Stability**

The analytical laboratories also carried out continuing calibration procedures during their sample analyses. In this procedure, a calibration solution for each of the target elements was analyzed at the onset of the analysis. The same solutions were periodically analyzed throughout the course of the analysis, typically after every tenth sample analysis. The results of each check were reported as a percent recovery of the starting calibration value. The data give an indication of calibration drift encountered over the course of an extended analysis interval. The control limits, prescribed in EPA Methods 6010A and 7000A, are  $\pm 10$  percent of the initial calibration value. Calibration checks falling outside these limits indicate inadequate analytical process control.

### **Matrix Spike Recoveries**

Some of the laboratories also conducted spiked sample recovery measurements on one or more soil samples. In this procedure, a measured quantity of each of the target elements was added to a laboratory replicate of a soil sample. Digestion and analysis of unspiked and spiked samples were carried out. The difference between the spiked and unspiked sample was compared with the known spiked amount and expressed as a percent sample recovery. Sample recoveries falling outside the range of 75 to 125 percent, as prescribed in EPA Methods 6010A and 7000A, are indicative of questionable analytical process control.

### **Laboratory-to-Laboratory Data Comparison**

Summary statistical parameters and data presentation formats were used to provide a quantitative measure of the degree of comparability among the data sets from the participating laboratories. These are more fully described below.

### Method Difference

The method difference or bias is a summary statistic of the difference observed for a particular method relative to a reference method. The mean percent difference (MPD) of one data set versus another reference data set was calculated using the following equation:

$$MPD = \frac{1}{n} \sum_{i=1}^n \left[ \left( \frac{y_i - x_i}{x_i} \right) (100) \right]$$

where,

- $MPD$  = mean percent difference
- $n$  = number of measurement values
- $x_i$  = designated reference value
- $y_i$  = paired value from other method

### Scatter Plots

Scatter plots and associated statistical parameters were also used to compare data from one laboratory with that from another. These plots enable a quick visual comparison. Related statistics include a least-squares method linear regression giving the best straight line through the data. The regression line has the following equation:

$$Y = AX + B$$

where  $A$  is the slope of the line and  $B$  is the  $y$ -intercept value.

The Pearson product-moment correlation coefficient ( $r$ ) was also computed. This is a measure of the degree of linearity between the two data sets (Havlicek and Crain, 1988). A correlation coefficient of 1 suggests perfect correlation while a correlation of 0 indicates no correlation between two data sets.

### Statistical Tests

The statistical equivalence of the analytical laboratory data sets was further evaluated with the Wilcoxon matched pair test. In essence, this nonparametric statistical test allows assessment of whether a statistically significant bias exists between two methods on a set of paired samples. The test produces a test statistic through an arithmetic scheme that ranks the differences encountered in sample pair results. The test statistic is essentially a measure of the ratio of *observed differences* in the two data sets to expected *random differences* in the same two data sets. Knowledge of the test statistic and the sample size allows one to determine whether the differences encountered in the paired data values can be attributed to the random variation that would be expected to occur between equivalent methods, or to bias in the methods or data sets. The quantitative aspect of the test is related to the  $p$ -value, which is associated with the test statistic and the number of paired samples used in the test. By convention, a  $p$ -value of 0.05 is often used as the decision point as to whether a statistically significant bias exists. For example, the determination of a test statistic with an associated  $p$ -value of 0.05 indicates that the observed differences between two methods carry a 5 percent chance of being attributable to random variation alone. Additional information on the use of this nonparametric test for paired-sample analysis can be found in Conover (1980).

The statistical test results are used in conjunction with linear regression parameters such as slope and intercept to further compare the two data sets. The statistical test provides an indication as to whether one method is

consistently biased relative to another. A second determination is made regarding the extent of that bias, if it exists. For example, consider the case where the statistical test indicates a significant bias between two sets of laboratory data. Examination of the linear regression data may reveal that the methods differ by only 5 percent. In consideration of the overall uncertainties encountered in the sampling and analytical processes, a 5 percent method bias is tolerable and is not a reason for rejecting one data set over another. This two-phase evaluation of the data is discussed further in the section dealing with laboratory-to-laboratory data comparison.

### **Columbia Analytical Services Data**

Half of the total number of soil samples generated in this demonstration project were analyzed by CAS. A more detailed qualitative and quantitative assessment of the laboratory's performance follows.

#### ***General Indicators of CAS Data Quality***

As noted earlier, CAS is a CLP laboratory and follows standard EPA analysis protocols and procedures in its soil analysis work. Since it is a part of the CLP program, the laboratory also undergoes periodic system audits and analytical process audits through the use of blind control sample analyses. The laboratory provided a quality assurance document along with the analysis results for the sample set submitted. Laboratory performance indicators, such as matrix spike recovery data, duplicate sample summary data, laboratory internal control sample analysis, and periodic instrument blank and calibration data collected throughout the analysis interval were included in the report. CAS also provided copies of sample chain-of-custody forms and all raw data generated in the analysis. No warning flags or out-of-limits quality control indicators were noted in the cover letter provided with the quality control data package. Personnel from MSE audited the CAS laboratory. The audit confirmed that CAS operations were in accordance with the standard procedures used in these analyses.

#### ***Quantitative Indicators of CAS Data Quality***

The analytical results and an accompanying quality control data package were sent by CAS to the Sandia project leader. The data package contained concentration levels or nondetects reported for all nine target elements in all 32 samples. Specific quantitative data quality factors are discussed in the following paragraphs.

### **Blank Soil Sample Results**

Analytical results from the soil blank analysis are given for CAS ICP and AAS methods as well as for other participating laboratories in Table 4-1. The "true" metal levels in the soil, as determined by round-robin analysis of the blank soil lot number at qualified laboratories, are given in the final column of the table.

The CAS analysis results on the blank soil sample track the certified levels reasonably well. Detection levels for the CAS ICP are slightly higher for As and Pb than for the other target elements. Iron, manganese, chromium, and zinc are all reported at levels very close to the certified levels. During the course of the analysis, a blank solution was periodically analyzed with the ICP instrument to check for contamination or excessive calibration drift. The results from these periodic checks showed consistent instrument detection levels in the expected concentration range for all target elements.

### **Control Soil Sample Results**

The analytical results for the control soil samples are shown in Figure 4-1 as a percent difference from the certified value for each element. The analysis certificate supplied with the control soil sample also gives a 95

**Table 4-1. Reference Laboratory Blank Soil Sample Results**

Element	Metal Concentration Level (mg/kg)				
	CAS ICP	CAS AAS	MSE ICP	SNL ICP	Certified Level
As	<40	1	2.1	<98	<2
Cd	<1	<0.5	0.4	<8	<1
Cr	5	<10	6.7	<19	7
Cu	8	6	5.6	<76	<5
Fe	6,760	7,210	7,740	6,350	8,180
Pb	<20	<10	9.3	<13	9
Mn	159	167	172	<38	159
Ag	<2	<2	0.4	<6	<2
Zn	27	28	24.4	76	24

Notes: A "less than" (<) symbol indicates not detected. The number following the symbol gives the detection limit. MSE and SNL data shown are the average of two analyses.

percent confidence interval about the average value as determined by a round-robin study of the soil batch by a number of qualified analytical laboratories. The upper 95 percent confidence limit (UCL) and lower 95 percent confidence limit (LCL) are also plotted in Figure 4-1. The CAS results show that the results for all of the target elements fall within these limits. Most fall within  $\pm 10$  percent of the certified value for both ICP and AAS analysis. These data indicate acceptable laboratory performance.

### Duplicate Sample Analysis Results

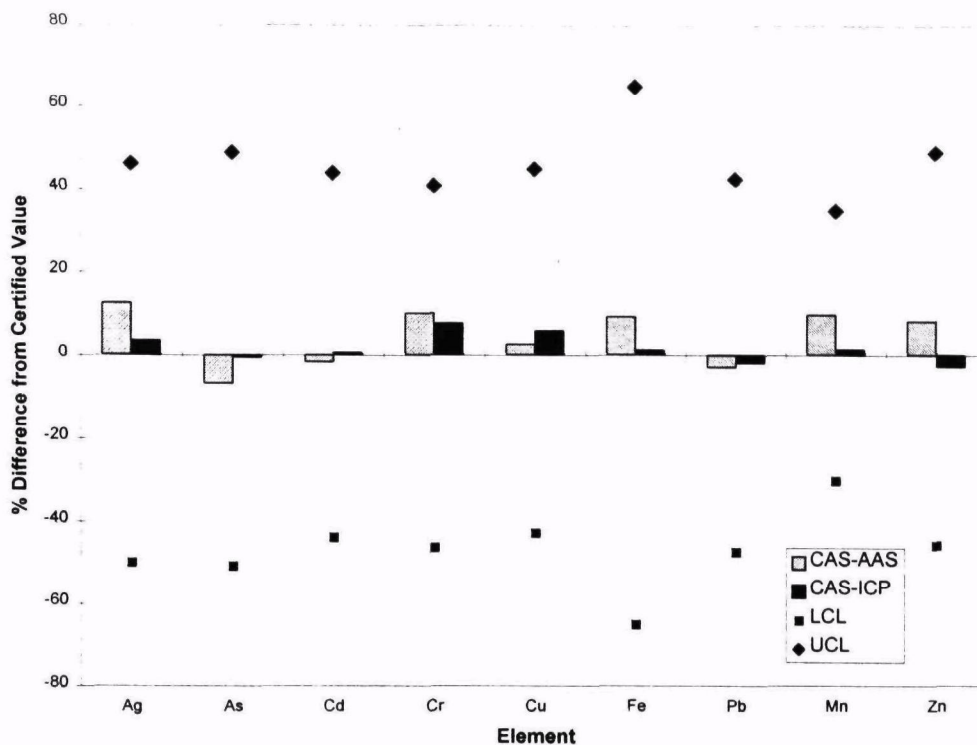
Duplicate results from two soil samples analyzed by both ICP and AAS are given in Figure 4-2. The relative percent difference between duplicate samples, as described earlier in this section, is plotted for each of the runs. Plotted RPD values of unity indicate a value of less than or equal to 1. With two exceptions, all RPDs fall within 20 percent. The two exceptions are Cr by AAS and Cd by ICP. No explanation is given as to why these duplicates showed poor agreement. In general, however, the data reveal acceptable analytical process control. No precision data are shown for Cr analysis by AAS on sample SBLD-1-008 since a no-detect was reported for at least one of the determinations.

### Instrument Stability

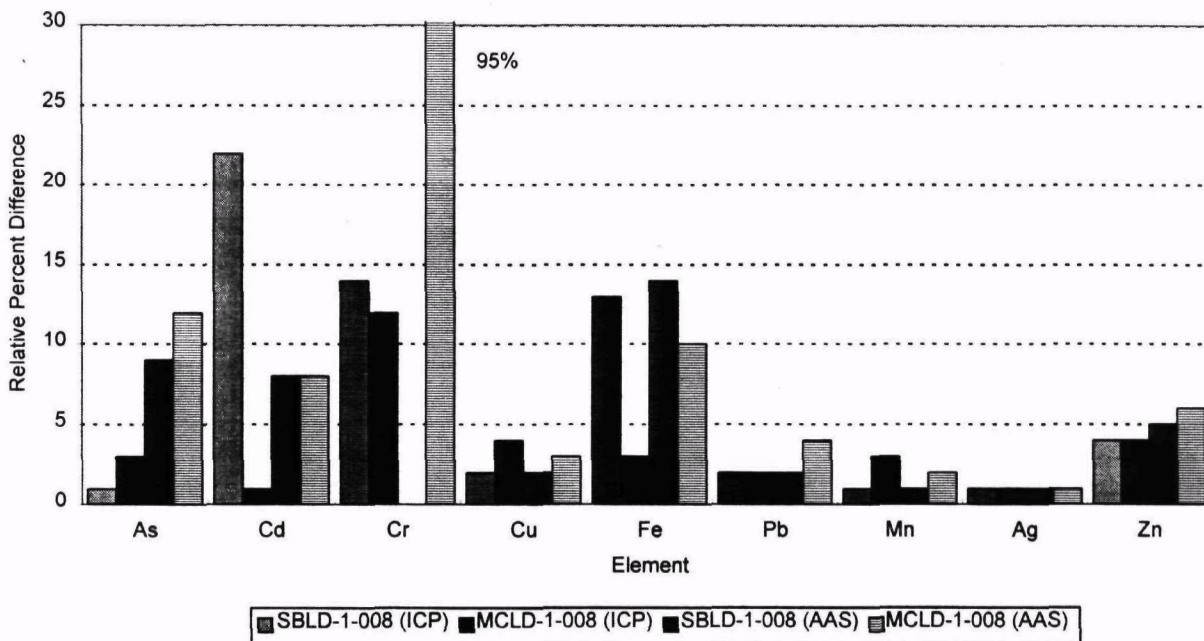
An indication of instrument stability throughout the course of the analysis is given by continuing calibration verification (CCV) analysis. A known standard is repeatedly run, typically following every 10 analyses on the ICP or AAS instrument, in order to check instrument calibration drift. The time interval between successive calibration checks is on the order of 1 hour. Typical CCV results for CAS ICP analysis of four elements are given in Figure 4-3. The results are plotted in a control chart format with percent recovery relative to the starting value of the calibration solution on the y-axis and the calibration number on the x-axis. All CCV data for all target elements from both ICP and AAS analysis indicated recoveries between 90 and 110 percent, which is within the quality control criteria specified in the method.

### Spike Recoveries

Spike recovery data from the CAS analyses are shown in Figure 4-4. Here the deviations from 100 percent recovery are shown for four spiked soil samples, two of which were analyzed by ICP and two by AAS methods. In accordance with the standard method, the laboratory did not report recoveries for spiked elements when the



**Figure 4-1. Control soil sample analysis results from CAS. The upper and lower 95 percent confidence limits with respect to the certified values are also shown.**



**Figure 4-2. Duplicate soil sample analysis results from CAS.**

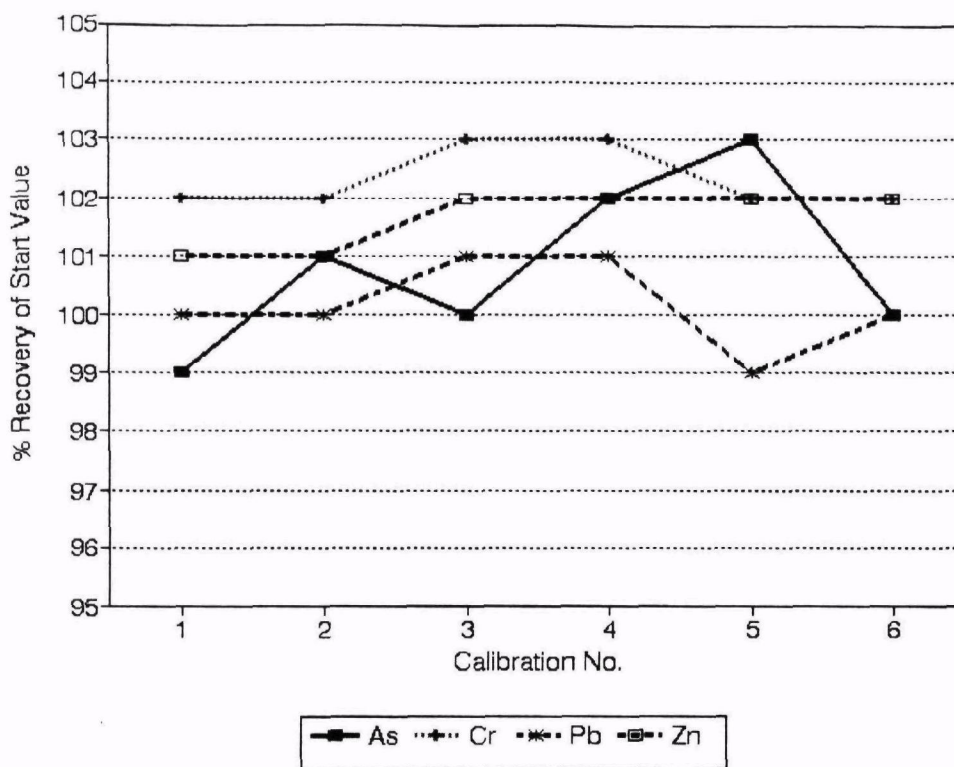


Figure 4-3. Continuing calibration verification results from CAS.

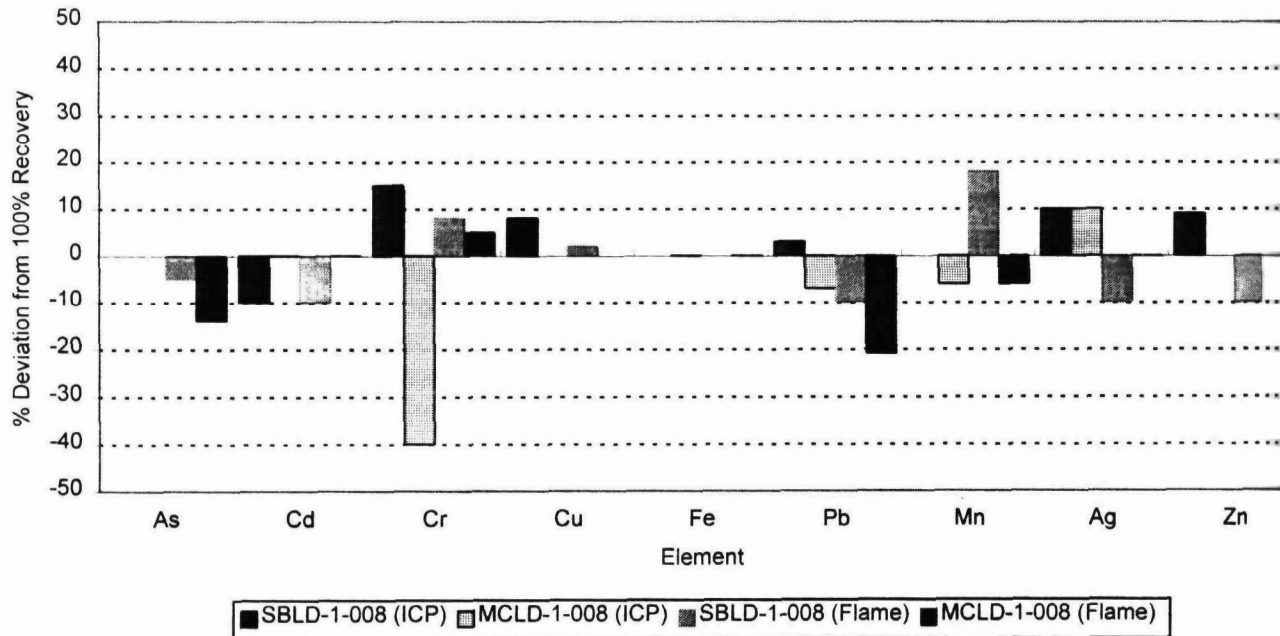


Figure 4-4. Spiked soil sample recovery results from CAS. See text for explanation of missing data.

spike amount added was less than 25 percent of the unspiked metal content of the sample. Hence, no data are seen for iron, which was present at high concentration levels in the unspiked soil samples. Spike levels were too low for As, Cu, Mn, and Zn in selected samples as well, as reflected by no data entries in the accompanying graph. Standard ICP Method 6010A specifies lower and upper recovery limits at 75 and 125 percent, respectively (corresponding to  $\pm 25$  percent difference as plotted in Figure 4-4). The data show that with the exception of Cr, none of the valid spike recovery levels fall outside this range.

### ***CAS Performance***

The foregoing quantitative and qualitative indicators reveal that overall performance of the CAS laboratory was acceptable. In particular, analysis of blank soil and control soil samples by ICP and AAS reveals acceptable performance. Spiked sample analysis using the soil matrix generated in the study also gave acceptable recoveries in all cases, except Cr, in which an adequate spike of each target element was introduced into the original soil sample. Instrument stability, as evidenced by periodic calibration checks, was also within control limit guidelines. Together, the quality control parameters suggest a high level of confidence in the accompanying field soil sample data.

### **MSE-HKM Data**

This DOE contract laboratory has not been part of the EPA CLP program; however, in practice, the laboratory follows CLP guidelines and standard EPA analysis protocols. A more detailed qualitative and quantitative assessment of the laboratory's performance follows.

### ***General Indicators of MSE Data Quality***

MSE has a complete quality assurance/control plan, which was sent to the SNL project leader as a part of the analysis results package. A member of the SNL project team also conducted an audit of the MSE laboratory prior to the demonstration to determine compliance with standard EPA methods used in this analysis. The audit report indicated acceptable laboratory procedures and conformance with standard methods used in these analyses.

MSE included quality control sample documentation in its package. Laboratory performance indicators such as matrix spike recovery data, duplicate sample summary data, results from an in-house control sample analysis, periodic instrument calibration data throughout the analysis interval, and periodic blank analysis data throughout the analysis interval were included. Several out-of-limits conditions were noted in the cover letter associated with the data package. These anomalies are discussed in detail in later sections of the data presentation.

### ***Quantitative Indicators of MSE Data Quality***

#### **Blank Soil Sample Results**

Data from the quality control blank soil sample are given in Table 4-1, along with similar data from other participating laboratories. Detectable amounts of all target elements were reported by MSE, and the agreement between MSE values and the certified blank soil levels was the best of all three laboratories. The MSE laboratory detection levels for most of the target elements were the lowest reported of all the participating laboratories. During the course of the analysis, a blank solution was periodically analyzed with the ICP instrument to check for contamination or excessive calibration drift. Results from these periodic checks showed consistent instrument detection levels in the expected concentration range for all target elements.



### **Control Soil Sample Results**

The analytical results for control soil samples are shown in Figure 4-5 as a percent difference from the certified value for each element. The analysis certificate supplied with the control soil sample also gives a 95 percent confidence interval about the average value as determined by a round-robin study of the soil batch by qualified analytical laboratories. The upper 95 percent confidence limit and lower 95 percent confidence limit are also plotted in Figure 4-5. The MSE results, like those from CAS, fall within  $\pm 10$  percent of the certified value for nearly all of the target elements. Larger differences on the order of  $-30$  percent are noted for Ag; however, the reported results still fall within the 95 percent confidence interval about the mean certified level. These data indicate acceptable laboratory performance.

### **Duplicate Analysis Results**

The relative percent differences are plotted in Figure 4-6 for each laboratory analyses of the duplicate field soil sample. All RPDs, with two exceptions, fall within the 20 percent criteria. The exceptions are an Mn measurement with an RPD slightly in excess of 35 percent and a Cd measurement with an RPD of about 28 percent. Three other Mn and Cd precision determinations were within the 20 percent criteria specified in standard Method 6010A. The laboratory uses an RPD limit of 20 percent as the acceptable range of variability in duplicate analysis. Consequently, these results reveal an acceptable degree of analytical process control.

### **Instrument Stability**

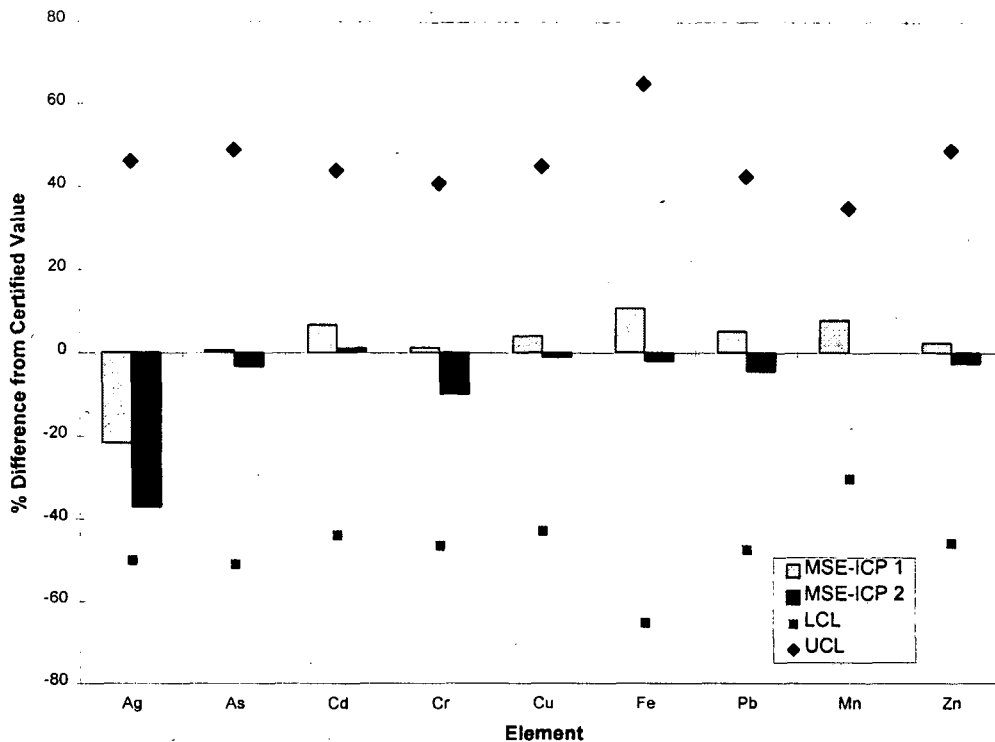
A plot of continuing calibration verification data for MSE analysis runs is given in a control chart format in Figure 4-7. The results for only four elements are given for one of the four batch analyses conducted by the laboratory. All CCV data for all analyses showed acceptable ( $\pm 10$  percent of original value) recoveries, indicating acceptable instrument stability over the course of the analyses.

### **Spike Recoveries**

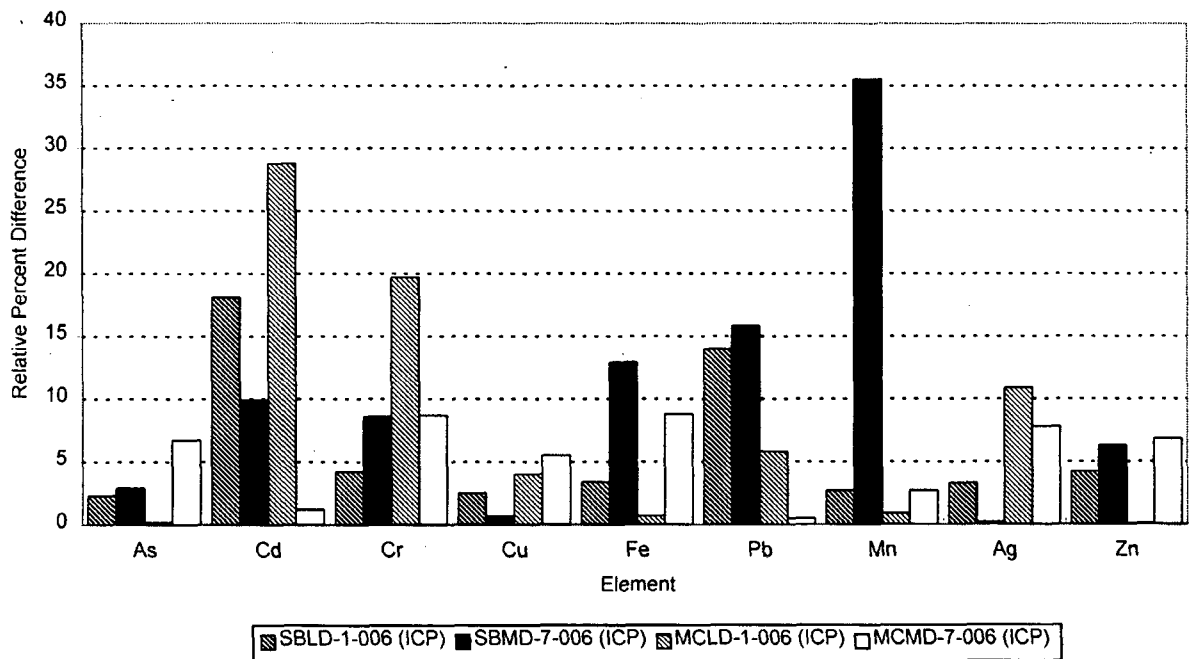
Spike recovery data from the MSE analyses are shown in Figure 4-8. Element recovery values are shown for samples that were spiked prior to digestion and analysis of the sample on the ICP instrument. The laboratory reported recoveries for spiked elements even when the spike amount was less than 25 percent of the unspiked metal content of the sample. For comparability of the MSE data with CAS data, however, the same spike validation criteria specified in EPA Method 6010A were applied to the MSE data as well. If the spiked amount was less than 25 percent of the total elemental content of the sample before the spike, the spike was judged invalid and no data were reported. Consequently, no data are shown for Fe, Cu, and other elements in selected instances. The valid set of spike recovery data revealed that only Pb fell outside laboratory acceptance limits of 75 to 125 percent in one of the four batch analyses.

### **Additional Quantitative Laboratory Data Quality Measures**

The MSE quality control data package also revealed several out-of-limits conditions for a serial dilution test that was carried out on selected field samples. In this test, the concentrations of target elements were measured by ICP in a dilution of the sample digestate. A fivefold or greater serial dilution was then made of this original sample and also analyzed by ICP. The measured amount in the diluted sample, taking dilution factors into account, is expected to agree to within  $\pm 10$  percent of the original sample amount. Large deviations suggest sample matrix effects, which may affect quantitative results. The sample matrix may introduce either positive or negative interferences for a particular element when the sample is analyzed in a relatively concentrated form. The data from these serial dilution tests are given in Table 4-2. The data show that the  $\pm 10$  percent limit of these



**Figure 4-5. Control soil sample results from MSE. The upper and lower 95 percent confidence limits with respect to the certified values are also shown in the graph.**



**Figure 4-6. Duplicate soil sample results from MSE.**

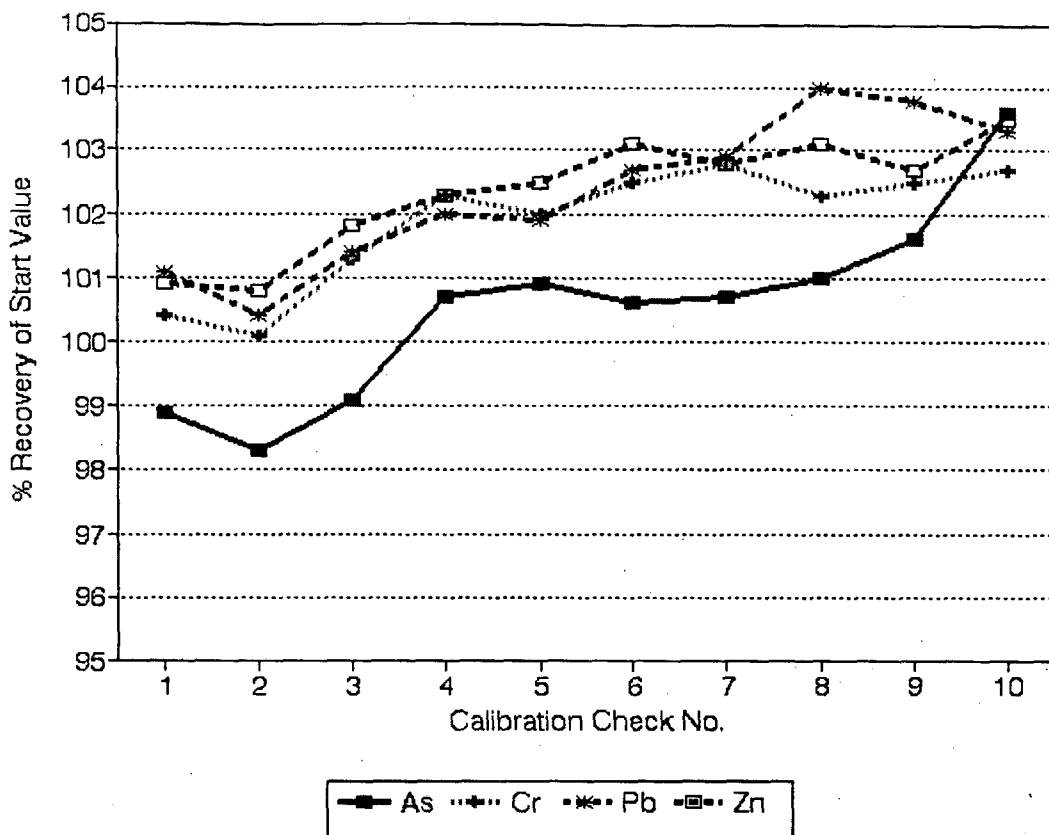


Figure 4-7. Continuing calibration verification results from MSE.

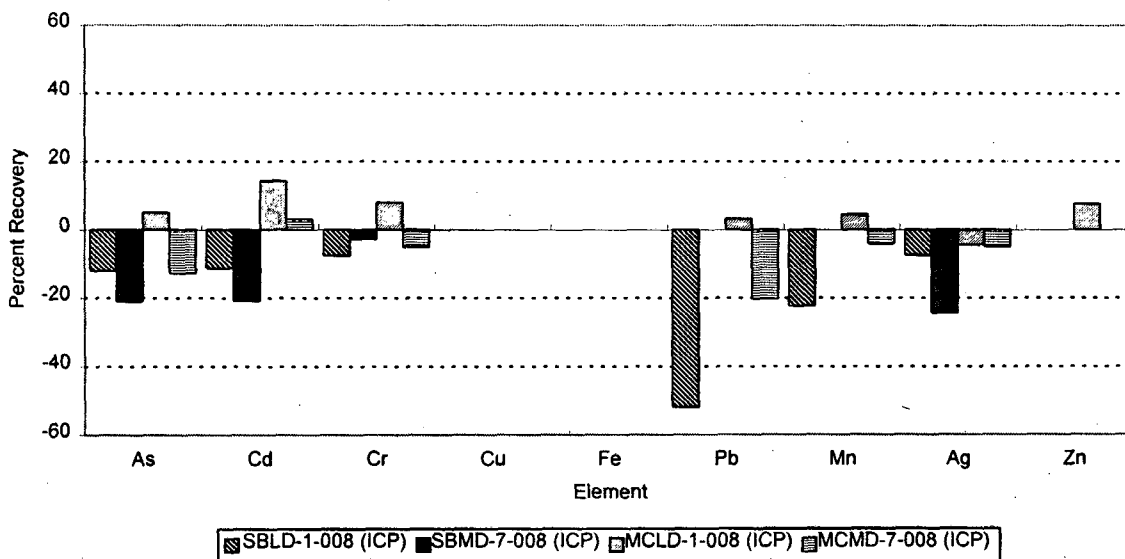


Figure 4-8. Spiked soil sample recovery results from MSE. See text for explanation of missing data.

**Table 4-2. Serial Dilution Results from MSE**

Element	Percent difference between measurements at two dilution levels			
	Sample No. SBLD-1	Sample No. SBMD-7	Sample No. MCLD-1	Sample No. MCMD-7
Ag	<b>62</b>	2.7	4.2	<b>100</b>
As	<b>24</b>	0.9	4.1	6.8
Cd	<b>48</b>	8.3	<b>64</b>	<b>39</b>
Cr	<b>17</b>	<b>71</b>	7.0	<b>11</b>
Cu	2.7	2.6	2.6	5.7
Fe	1.9	0.1	1.7	5.8
Mn	1.7	1.4	0.1	4.7
Pb	1.4	3.6	4.7	<b>13</b>
Zn	0.2	0.2	0.2	4.8

Note: Those values in excess of 10 percent are shown in bold type.

measurements was exceeded for Ag, As, Cd, Cr, and Pb in selected dilution tests. Although these results are not cause for exclusion of the data, they do reveal that, for at least some of the samples, sample matrix effects contribute to overall uncertainty in the analytical results.

### ***MSE Performance***

The MSE laboratory analysis results on blank and control soil samples, instrument precision and stability, and spike recovery, in general, reveal acceptable laboratory process control. Several out-of-limits warnings were encountered in the quality control reports; however, their presence does not warrant rejection of the data set. Serial dilution recoveries outside the  $\pm 10$  percent range indicate that sample matrix effects were influential in the overall quantitative recovery of the field soil samples.

### **Sandia National Laboratories Environmental Restoration Program Laboratory Data**

The SNL Environmental Restoration Laboratory was selected as an additional laboratory. This laboratory primarily serves to provide rapid screening data which are used in conjunction with CLP-type analyses for Sandia's internal environmental restoration program.

A quality assurance/control plan was under development during this study. In this analysis the SNL laboratory followed formal laboratory procedures for soil analyses. Data from this laboratory were obtained with a mobile laboratory ICP-AES system (shortened to ICP in this report). The unit is a conventional benchtop unit that has been adapted for field use. Consequently, it exhibits higher detection limits and more calibration drift than the ICP systems commonly used in the laboratory. A more detailed qualitative and quantitative assessment of the laboratory's performance follows.

### ***General Indicators of SNL Laboratory Data Quality***

The SNL laboratory followed the SW-846 analysis protocols in the soil analysis. The demonstration project leader did not receive a copy of the laboratory quality assurance plan because the plan was under development at the time of the demonstration. The SNL laboratory did provide some quality control data such as CCV and method blank results.

## ***Quantitative Indicators of SNL Laboratory Data Quality***

### **Blank Soil Sample Results**

Blank soil data for SNL are presented in Table 4-1, along with similar data from the other participating laboratories. Nondetectable amounts of all except two target elements were reported by SNL. Detection limits, in general, were higher for SNL than for the other laboratories owing to the characteristics of the mobile ICP instrument used in this analysis. Some of the elements, such as Cr and Pb, that were known to exist in the blank were not detected in the SNL blank analysis as a result of these high detection levels.

### **Control Soil Sample Results**

The analytical results for control soil samples are plotted in Figure 4-9 as percent difference from certified values. The results show that, with the exception of Ag, all of the target element results fall within the lower and upper bounds of the 95 percent confidence interval established by the quality control laboratory that developed and tested the control sample. In general, the results for the target elements fall within  $\pm 30$  percent of the certified value. Silver results fall outside the lower confidence limit by a margin of nearly 20 percent. Discussions with laboratory personnel indicated that these results were most likely a result of the poor solubility of silver in the microwave digestion technique used in this analysis. The microwave method relies solely on nitric acid rather than on a mixture of nitric and hydrochloric acids used in the conventional digestion technique. With the exception of the silver analysis, the results reveal acceptable laboratory performance.

### **Duplicate Analysis Results**

No duplicate sample analyses were conducted by the SNL Environmental Restoration Program laboratory.

### **Instrument Stability**

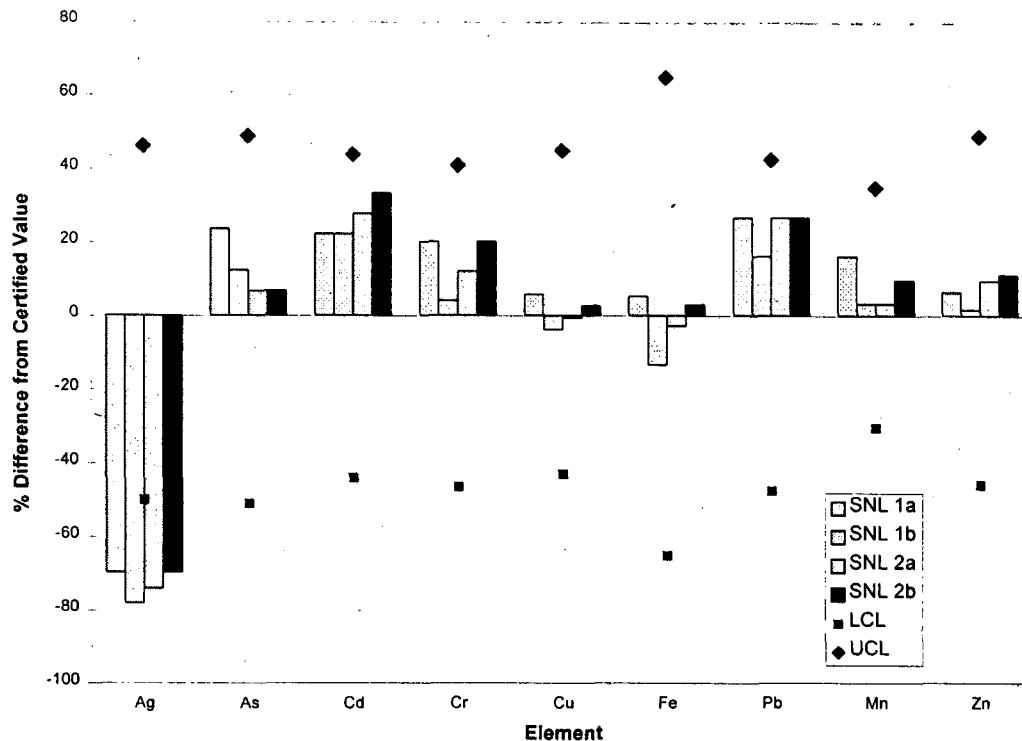
A plot of CCV data for four elements in the SNL runs is given in control chart format in Figure 4-10. Calibration recoveries fell outside the  $\pm 10$  percent limits for the following elements: Cd, Cr, Cu, Pb, and Zn. Recovery data outside the normal control limits revealed stability problems attributable to the mobile ICP system.

### **Spike Recoveries**

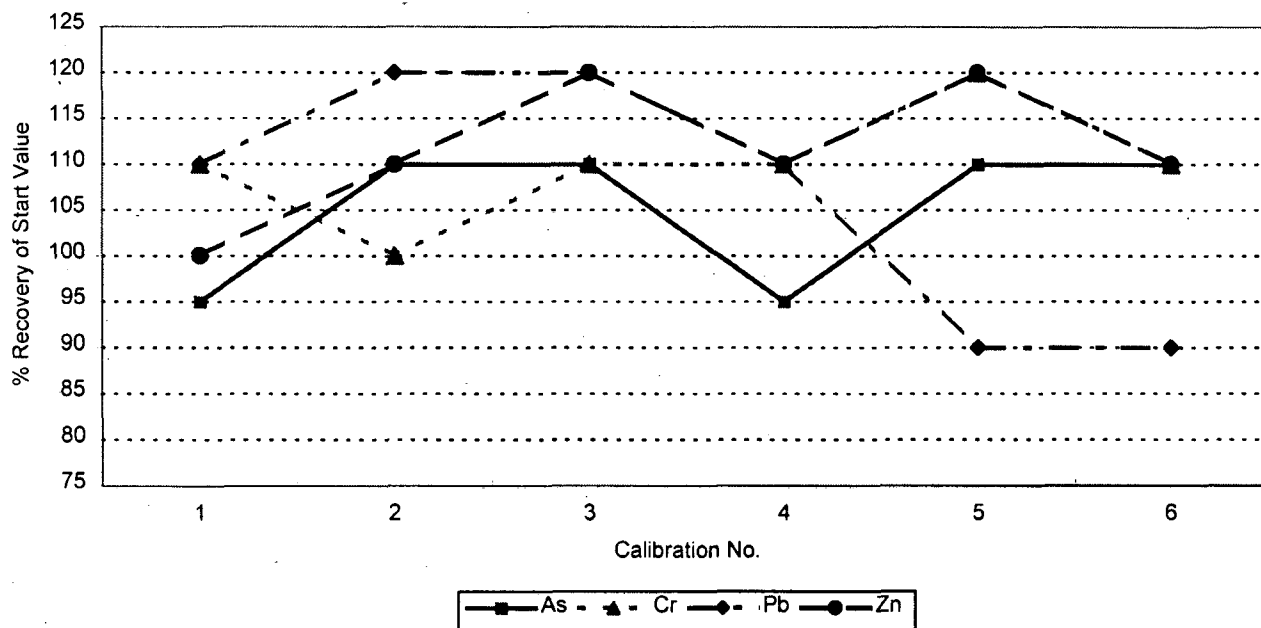
No spike recovery analysis was done by the SNL Environmental Restoration Program Laboratory.

### ***SNL Laboratory Performance***

Laboratory results for the control soil samples fell within the 95 percent confidence interval of the certified soil concentration value of the standard for all elements except Ag. The CCV data were outside the normal tolerance limits of  $\pm 10$  percent by as much as a factor of two for some of the target elements. Duplicate analyses were not run on any of the field samples. Consequently, no measure of instrument precision on the actual field soil sample matrix was available. Matrix spike recovery analysis also was not carried out. In light of the limited extent of laboratory quality control data, and the fact that a less stable mobile ICP system was used, the judgment was made to regard these data as informational and not include them in the validated data set from the other reference laboratories.



**Figure 4-9. Control soil sample results from SNL. The upper and lower 95 percent confidence limits with respect to the certified values are also shown in the graph.**



**Figure 4-10. Continuing calibration verification results from SNL.**

## Laboratory-to-Laboratory Data Comparison

The results of several quantitative comparisons of MSE and CAS laboratory data are given in the following paragraphs. Included are the results and discussion of mean percent difference computations, scatter diagrams, statistical test results, and a semiquantitative analysis of overall sample variability.

### Mean Percent Difference

An estimate of MPD for the soil samples collected at the two sites is given for each target element in Table 4-3. In this computation, CAS ICP is the designated reference data set on the basis of the laboratory's experience and acceptable performance on the quality control samples. Thirty sample pairs from each laboratory were used for comparison because CAS analyzed only half of the total number of soil samples collected. These percent difference estimates provide a measure of the overall comparability of the three data sets from the two laboratories. Low difference values reveal agreement between the analyses. The standard deviation is also given in the table and is a measure of the degree of variability encountered in the computed MPD for each element. With only a few exceptions, mean differences for nearly all elements are less than  $\pm 10$  percent in the comparisons of the CAS ICP reference data set with the CAS AAS and MSE ICP data sets. The comparison of Ag and Cd between CAS ICP and CAS AAS data sets showed differences on the order of 15 percent. Chromium by CAS AAS does not compare well at all; however, the comparison with MSE ICP Cr data is quite good. The poor figures for the CAS AAS Cr data may be attributable to the fact that most of the soil samples had Cr levels near the lower limit of detection of the AAS method.

**Table 4-3. Mean Percent Differences from MSE ICP and CAS AAS Data**

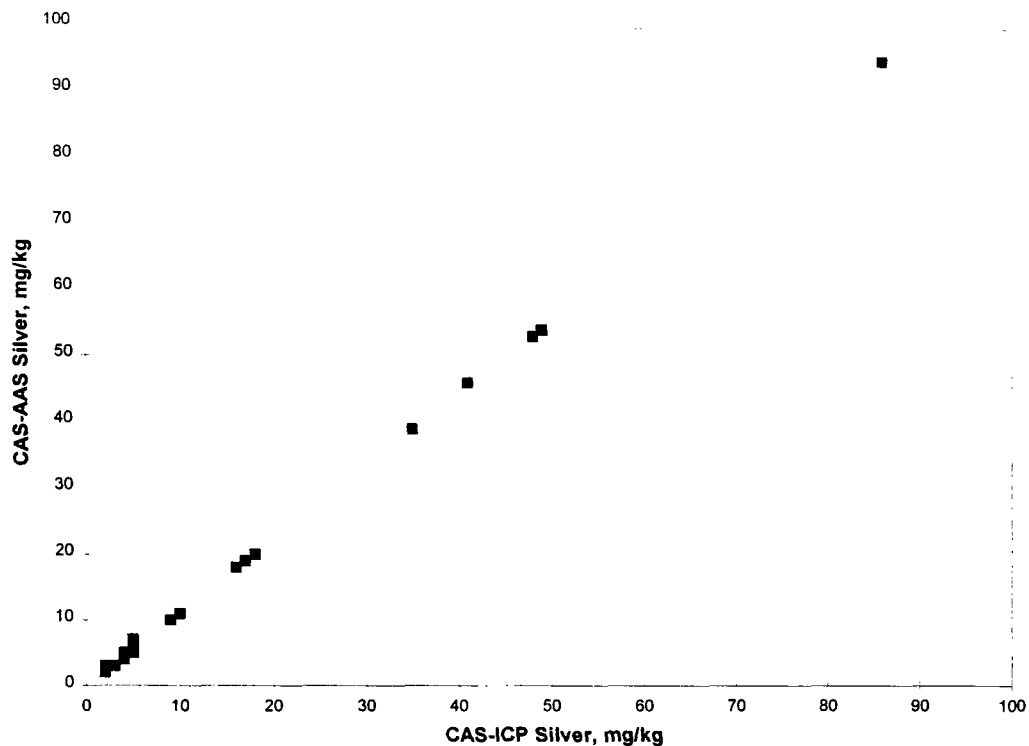
Element	Mean Percent Difference (ref: CAS ICP Data Set)	
	MSE Laboratory (ICP)	CAS Laboratory (AAS)
Ag	$1.3 \pm 12.8$	$15.7 \pm 13.6$
As	$0.6 \pm 21.3$	$-10.9 \pm 7.8$
Cd	$10.8 \pm 25.9$	$-16.6 \pm 22.9$
Cr	$7.1 \pm 31.4$	$105.1 \pm 109.6$
Cu	$0.2 \pm 13.6$	$4.0 \pm 3.6$
Fe	$6.1 \pm 20.4$	$10.5 \pm 3.2$
Mn	$0.1 \pm 19.7$	$4.3 \pm 5.2$
Pb	$-2.1 \pm 15.3$	$5.4 \pm 1.9$
Zn	$-4.7 \pm 14.4$	$4.2 \pm 22.4$

Notes: The mean value is followed by the standard deviation. The CAS laboratory ICP AES data set was used as the reference in this analysis.

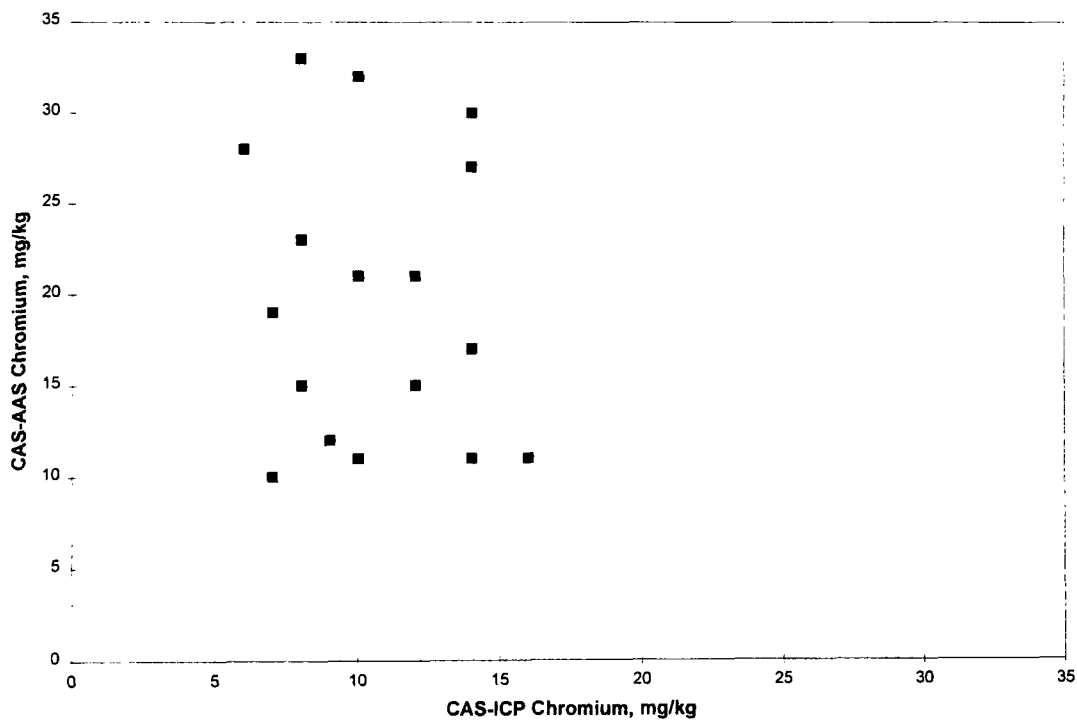
### Scatter Plots

Scatter plots showing intercomparisons of the CAS AAS and MSE ICP field soil sample data with the corresponding CAS ICP analysis data are presented in Figures 4-11 through 4-16 for selected elements to illustrate the various degrees of comparability encountered in the data. The CAS ICP data are plotted on the x-axis with either the CAS AAS or the MSE ICP data plotted on the y-axis. The comparison of the CAS AAS data with the CAS ICP data was very good with the exception of Cr data, shown in Figure 4-12, corroborating the high mean percent difference value noted for Cr in the previous section.

The MSE data show as good or better correlation with the CAS ICP data. This very close agreement is observed despite the fact that the CAS ICP and CAS AAS samples were laboratory duplicates from the same field soil

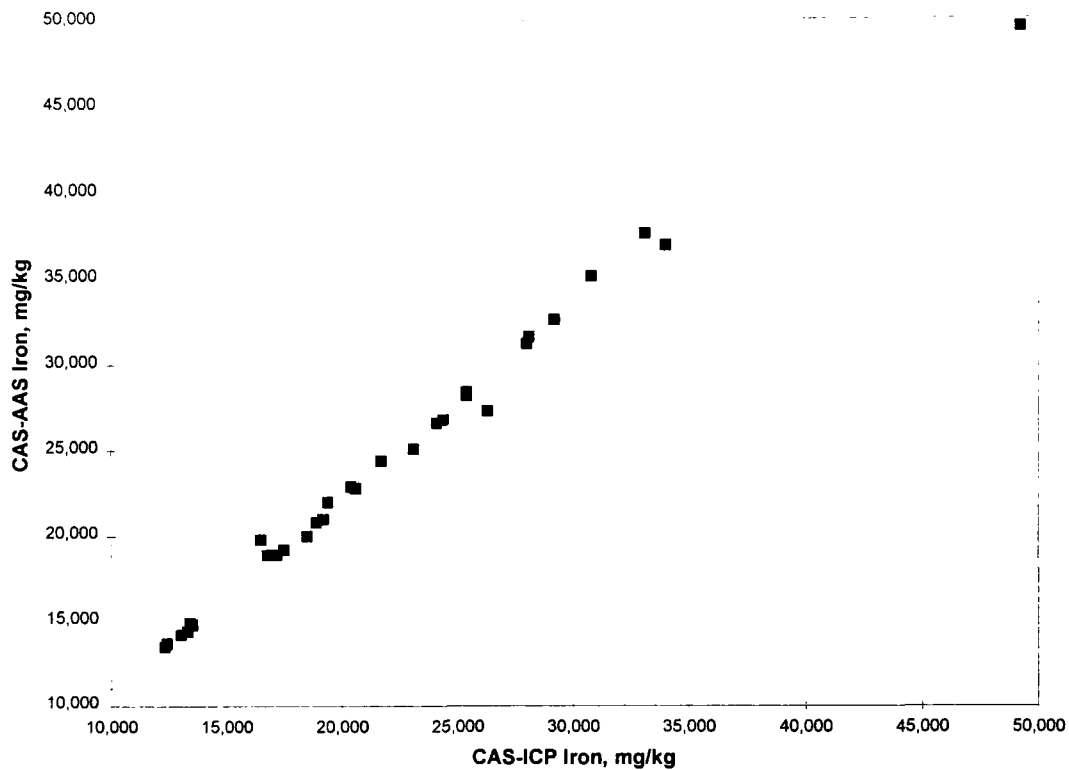


**Figure 4-11. CAS AAS vs. CAS ICP silver measurements on field replicate soil samples.**

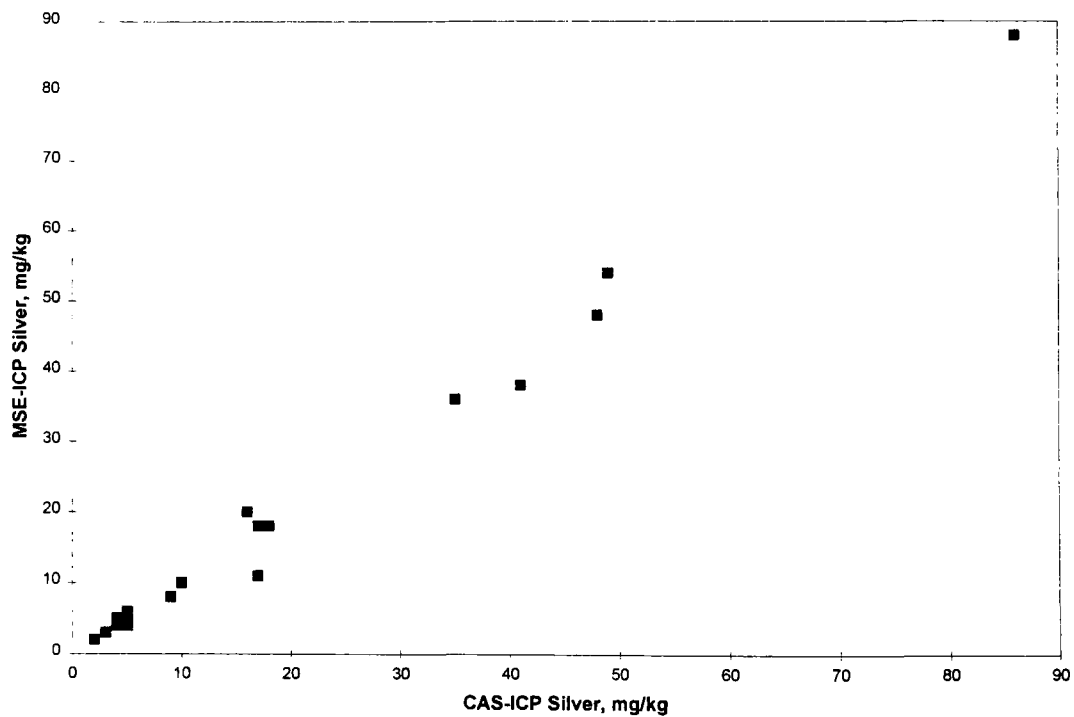


**Figure 4-12. CAS AAS vs. CAS ICP chromium measurements on field replicate soil samples. Nondetectable results are not shown in the plot.**

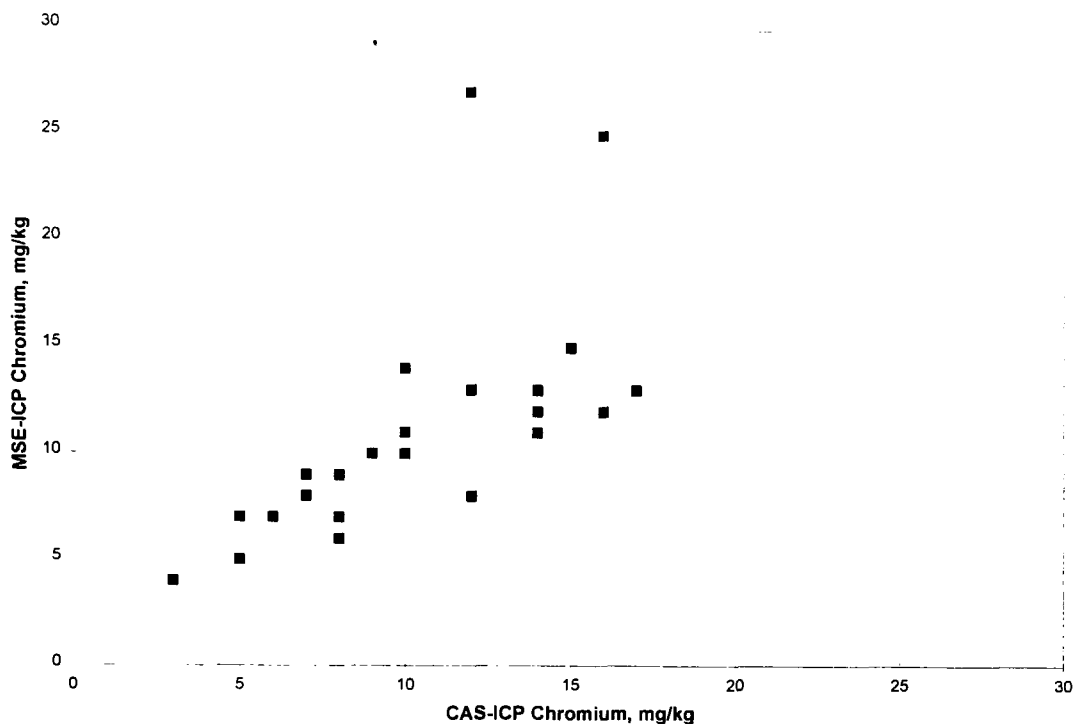




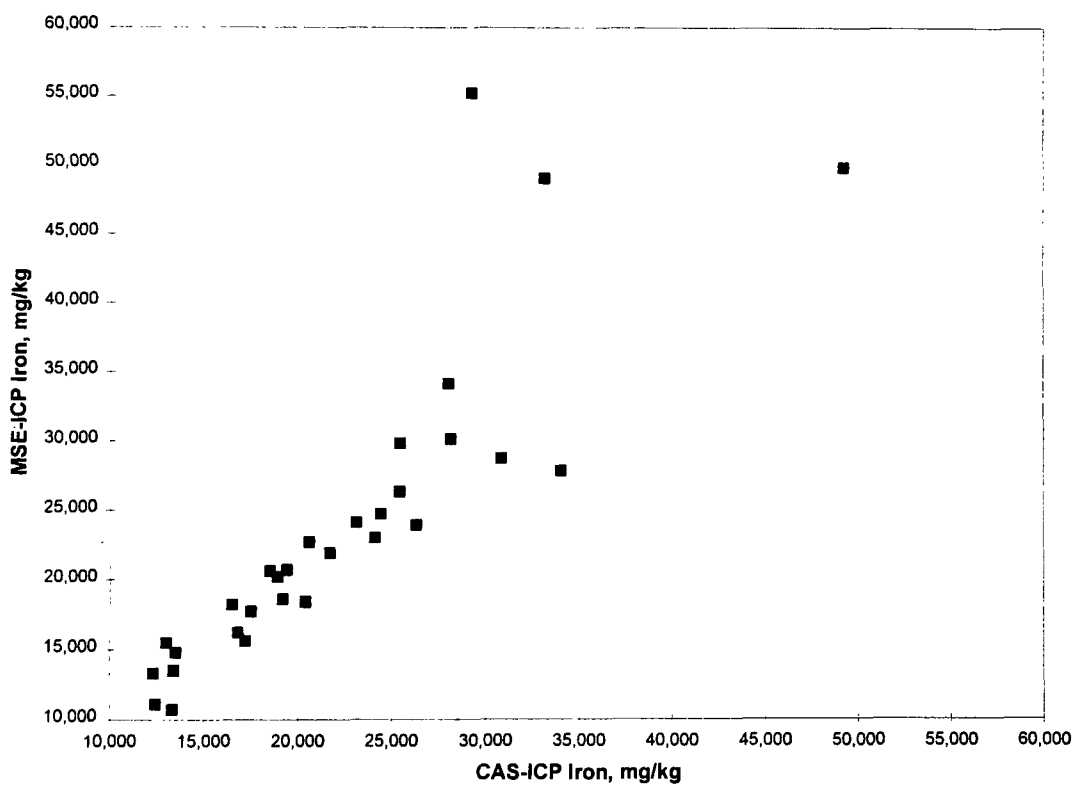
**Figure 4-13. CAS AAS vs. CAS ICP iron measurements on field replicate soil samples.**



**Figure 4-14. MSE ICP vs. CAS ICP silver measurements on field replicate soil samples.**



**Figure 4-15. MSE ICP vs. CAS ICP chromium measurements on field replicate soil samples.**



**Figure 4-16. MSE ICP vs. CAS ICP iron measurements on field replicate soil samples.**

sample digestate whereas the MSE samples were from a different field sample split. A good comparison between MSE ICP and CAS ICP data reveals that soil sample splits were chemically similar and that soil processing and mixing produced relatively homogeneous samples.

The slope and intercept of the best straight line through the data and the correlation coefficient,  $r$ , which is a quantitative measure of the degree of linearity in the data pairs, is given in Table 4-4 for CAS AAS and MSE ICP data set comparisons with the CAS ICP data set. Coefficients greater than about 0.8 indicate a reasonably strong linear relationship between the two data sets. Correlation coefficients less than 0.8 are encountered for Cr in both data sets. The CAS AAS Cr data were plotted against the MSE ICP Cr data and a scatter plot much like that shown in Figure 4-12 was obtained. This result further suggests that the CAS AAS Cr data may be suspect. The MSE ICP Cr data show slightly better correlation when plotted against the CAS ICP data, as shown in Figure 4-15. The slope parameters shown in Table 4-4 are a measure of the bias of one method with respect to another. With a few exceptions the regression line slopes are in the range of 0.9 to 1.10, which corresponds to a bias in the range of  $\pm 10$  percent. Exceptions are encountered for Cd and Cr in the CAS AAS data set as well as for Cr and Fe in the MSE data set.

**Table 4-4. Reference Laboratory Linear Regression Results**

Element	CAS AAS Data Set			MSE ICP Data Set		
	Corr. Coeff.	Slope	Intercept	Corr. Coeff.	Slope	Intercept
Ag	1.00	1.10	0.26	1.00	1.02	-0.1
As	0.99	0.96	-29	0.99	1.04	-16
Cd	0.85	0.49	2.2	0.98	0.90	1.1
Cr	-0.13	0.34	23	0.66	0.83	2.2
Cu	1.00	1.07	-16	0.99	0.99	13
Fe	0.99	1.04	1,350	0.86	1.16	-1,980
Mn	1.00	1.08	-10	0.95	0.93	36
Pb	1.00	1.06	-3.8	0.92	0.95	3.1
Zn	1.00	1.09	-28	0.99	0.91	72

Notes: The CAS ICP data set was used as the reference data set (x variable) in these regression analyses. The y variable was either the CAS AAS or MSE ICP data set. The slope and intercept values correspond to the values  $A$  and  $B$  in the linear equation  $y = Ax + B$ .

### ***Statistical Bias Testing***

The Wilcoxon matched pair test was used to compare the CAS AAS and MSE ICP data sets with the CAS ICP data set. The SNL laboratory data were not included in this test because they did not meet the data validation criteria. The Wilcoxon test is a nonparametric test which enables a decision to be made as to whether a statistically significant bias exists between two methods. The term “nonparametric” refers to the fact that the observations (in this case the reported metal concentrations in the soil samples) need not conform to a particular statistical distribution. The Wilcoxon test provides a quantitative measure of the likelihood or probability that observed differences between two methods are attributable to random variation only. Application of the test produces a test statistic and an accompanying p-value. The p-value represents the probability of observing a test statistic value greater than or equal to that obtained in the test from the null or “no difference” distribution—the distribution of test statistic values that would be encountered if in fact no bias is present between the two methods in question.

A p-value of 0.05 is often chosen as the boundary point in deciding whether two methods are statistically different. A test statistic with an accompanying p-value of 0.05 or less indicates that the two methods being

compared are statistically different and that the decision to call them different carries a 95 percent chance of being correct. Alternatively, it can be stated that the decision to call the methods different has a 5 percent chance of being incorrect.

The results of the statistical test as applied to the CAS AAS and MSE ICP laboratory data sets are summarized in Table 4-5. The test results between CAS ICP and CAS AAS data sets indicate that significant differences were observed between the two methods for all elements. The p-values associated with the test statistics for all elements are less than 0.01, indicating that a clearly distinguishable bias exists between the ICP and AAS analysis. This observation is corroborated by the scatter plots shown in Figures 4-11 through 4-13. Nearly all the plotted points fall above a diagonal line extending from the lower left to the upper right corner of the figures. This line is the zero bias line. Points falling above the diagonal line reveal a positive bias of the AAS method relative to the ICP method and those falling below the line reveal a negative bias.

**Table 4-5. Wilcoxon Matched Pair Statistical Test Results**

Element	Statistically Significant Bias Between Two Methods?	
	CAS (AAS) vs. CAS (ICP)	MSE (ICP) vs. CAS (ICP)
Ag	Yes (<0.01)	No (0.67)
As	Yes (<0.01)	No (0.91)
Cd	Yes (<0.01)	No (0.39)
Cr	Yes (<0.01)	No (0.94)
Cu	Yes (<0.01)	No (0.68)
Fe	Yes (<0.01)	No (0.31)
Mn	Yes (<0.01)	No (0.99)
Pb	Yes (<0.01)	No (0.98)
Zn	Yes (<0.01)	No (0.68)

Note: The p-value associated with the test statistic is given in parentheses.

A statistical comparison of the MSE ICP data with the CAS ICP data reveals that the two data sets are statistically equivalent; thus no statistically significant method bias exists in one data set with respect to the other. In this case all p-values associated with the computed test statistic are significantly greater than 0.05. For example, the p-value associated with the test statistic for Cu was 0.68. This indicates that the observed differences between the MSE ICP data and the CAS ICP data carry a 68 percent likelihood of being attributable to random variation between two equivalent methods. These results are corroborated by the scatter plots shown in Figures 4-14 through 4-16. The plotted points fall above and below the diagonal “zero bias” line with approximately equal frequency, indicating no consistent bias in the results.

### ***Intra- and Interlaboratory Variability***

Each laboratory conducted a duplicate analysis of a digestate from a soil sample split made from a homogenized bulk field soil sample. The intralaboratory ICP instrument variability was estimated by computing the RPD for each target element from the duplicate analysis results of sample number MCLD-1 from the CAS and MSE laboratories. The average of these RPD values is shown in column 2 of Table 4-6 for each target element. The interlaboratory variability was estimated by computing four RPD values between the four measurement results from both laboratories and averaging the results. These data are shown in column 3 of Table 4-6. A comparison of the two columns of data (intra- and interlaboratory RPDs) suggests that in most cases instrument variability is

**Table 4-6. Estimates of Intra- and Interlaboratory Sample Variation**

Element	Average Intralab RPD	Average Interlab RPD
Ag	5.1	5.1
As	1.5	8.1
Cd	14.3	14.3
Cr	15.6	9.8
Cu	3.9	7.4
Fe	1.9	1.7
Mn	2.1	2.9
Pb	3.9	4.6
Zn	2.2	4.7

of the same order of magnitude as the variability arising from heterogeneity in the sample splits going to the different laboratories and technologies.

### **Reference Laboratory Data Set**

Based on the foregoing analyses, a reference data set was compiled by averaging the MSE ICP, CAS ICP, and CAS AAS data sets. This reference data set was then further used for comparison with the soil analysis data sets provided for the various demonstration technologies. A summary of the reasons for including or excluding the laboratory data sets in the reference data set is given below.

- The CAS ICP data are judged to be valid, based on the laboratory's acceptable performance on the various control, duplicate, and soil recovery analyses. The 30-sample CAS ICP data set is used as one component in the reference data set.
- The 30-sample CAS AAS data set is also included in the reference data set despite the fact that the data set was shown to be biased with respect to the CAS ICP data set. The decision to include these data in the reference set was founded upon the linear regression results. Linear regression and correlation analysis show a high degree of correlation and small bias between the CAS ICP and CAS AAS data. The CAS AAS biases relative to the CAS ICP method are typically less than 10 percent for most target elements. A bias of  $\pm 10$  percent is relatively small and acceptable in light of the  $\pm 20$  percent tolerance in laboratory precision that was deemed acceptable in the laboratory data validation process. The AAS Cr data, although not well correlated with the ICP data, were also included in the reference data set. No substantive reasons to exclude one set of measurements over another were apparent in this particular case. Consequently, both were included.
- The MSE data are similarly accepted as valid in light of their very good correlation with the CAS ICP data for all elements and their demonstrated statistical equivalence with the CAS ICP data set.
- The SNL laboratory data are not used in the reference data set. The data package could not be validated because some key quality control parameters were not provided in the analysis results package. Furthermore, a less sensitive, lower precision, mobile ICP instrument was used, which contributed to greater uncertainty in this data set.

In summary, the reference data set is made up of an average of the MSE ICP, CAS ICP, and CAS AAS data sets for the 30 field soil samples that were analyzed by all three methods. Single values from the MSE ICP data set are used for the other 30 field samples not analyzed by CAS.

The interlaboratory comparisons revealed that all validated data had either a tolerable bias or were statistically equivalent. Consequently, no elements were excluded in compilation of the reference data set. Although all of the target elements were included in this set, it should be noted that interlaboratory comparisons revealed that the results from some elements should be regarded with a lower level of confidence than others. In particular, Cr results were variable among all three methods and should be treated with appropriate caution when they are used for comparison with field technology results.

## **Chapter 5**

### **Demonstration Results**

#### **Technology–Laboratory Data Comparison Methods**

For Level 1 technologies such as the stripping analysis techniques, a formal comparison of field technology and laboratory results is left to the instrument developer. To assist the developer in the interpretation of the data, several data formats and simple comparative analyses are included with the raw data. The stripping analysis results from the quality control samples (blank soil, control soil, and duplicates) are presented in the same manner as described earlier for the laboratory data, but with little interpretation or assessment. In addition, the field soil sample analysis data are presented in tabular format in Appendix A. The validated results from each laboratory are shown alongside the stripping analysis results for each target element. This chapter contains scatter plots in which the stripping analysis data are plotted against the reference laboratory data set. To further assist the technology developer in understanding the data, possible analytical approaches are suggested for comparing the technology data and reference laboratory data.

#### **Field Observations**

Periodically during the demonstration, an observer checked in with the electrochemical analysis teams to monitor progress. No instrument breakdowns were noted and, in general, the soil analysis went smoothly. Personnel from PNNL, NMSU, and ETG began their soil analysis on Monday, September 25, and completed their work on Thursday, September 28, averaging about 15 soil samples per 10-hour work day. Field observers noted that the electrochemical analyses appeared to be quite labor intensive, involving considerable wet chemistry in the sample workup. Although the weather during the demonstration was occasionally rainy, windy, and cold, it did not appear to adversely affect the performance of the electrochemical systems.

#### **General Description of Electrochemical Analysis Results**

A total of 60 field soil samples plus 2 control and 2 blank soil samples were submitted for various electrochemical analyses using anodic stripping voltammetry and potentiometric stripping analysis. The EG&G ASV system was used only for Cr analysis. The two PSA systems (TraceLab and Metalyzer) were used for analysis of Cd, Cu, and Pb. As a result of time constraints, analysis was not carried out for the other 5 target elements. For the elements analyzed (Cd, Cr, Cu, and Pb), a nearly complete analysis report was submitted. For several samples, neither a detected amount nor an indication of no detect was given. No details or explanations were given in the analysis report for these few cases of no reported data. Soil performance evaluation and soil blank samples were analyzed by the PNNL/NMSU ASV and PSA systems only. Duplicate analyses were carried out on three field soil samples as well. No performance evaluation (PE), blank, or duplicate sample analyses were done with the Metalyzer PSA system.

## Quality Control Sample Results

Results from a stripping analysis of quality control samples are presented in the following sections. The field technology results are presented in a format that facilitates comparison of the technologies and laboratory data. In light of the relatively new application of these electroanalytical techniques to soil residue analysis, only a limited discussion of the results is presented. Further evaluation of the data and an overall assessment of the systems' performance are left to the technology developer.

### *Blank Soil Sample Analysis*

Blank soil sample analysis results from the PNNL/NMSU ASV and PSA systems are given in Table 5-1, along with certified sample contamination levels. The MSE laboratory results are also shown because these results tracked the certified values most closely among the participating laboratories. The ASV system was used for Cr analysis; the PSA system was used for Cd, Cu, and Pb analysis. No blank sample analysis data were available from the ETG Metalyzer system.

**Table 5-1. Blank Soil Analysis Results for PNNL/NMSU ASV and PSA, MSE Laboratory and Accompanying Certified Levels**

Element	Metal Concentration Level (mg/kg)		
	ASV/PSA	MSE by ICP	Certified Level
Ag	NA	0.4	<2
As	NA	2.1	<2
Cd	<1 (PSA)	0.4	<1
Cr	21 (ASV)	6.7	7
Cu	0.7 (PSA)	5.6	<5
Fe	NA	7,740	8,180
Pb	9 (PSA)	9.3	9
Mn	NA	172	159
Zn	NA	24.4	24

Notes: NA = no analysis. A "less than" (<) symbol indicates not detected. The number following is the reported instrument detection level.

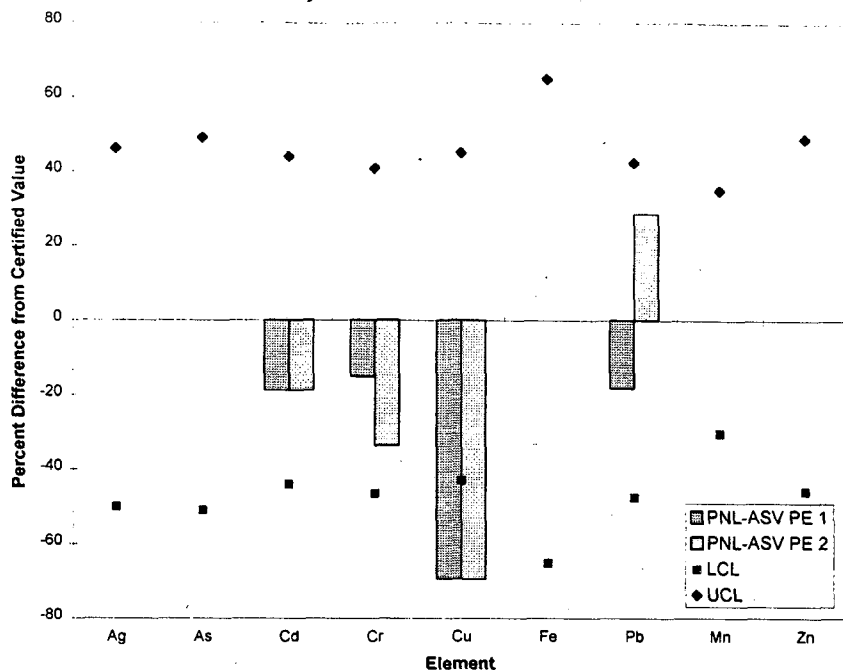
### *Control Soil Sample Analysis*

Control soil samples, with well-characterized target element concentrations, were analyzed with the PNNL/NMSU ASV and PSA stripping analysis systems. The ETG personnel did not analyze PE samples during the demonstration. The results for each control sample analysis from the PNNL/NMSU ASV and PSA systems for Cd, Cr, Cu, and Pb are shown in Figure 5-1. The results are expressed in terms of a percentage deviation from a certified concentration level of each element in this particular soil lot determined through a multilaboratory, round-robin study as described in Chapter 4. The plotted data reveal that ASV/PSA analysis results were within the 95 percent upper and lower confidence limits about the mean certified value for Cr, Cd, and Pb. Copper results fall below the lower 95 percent confidence interval of the PE sample.

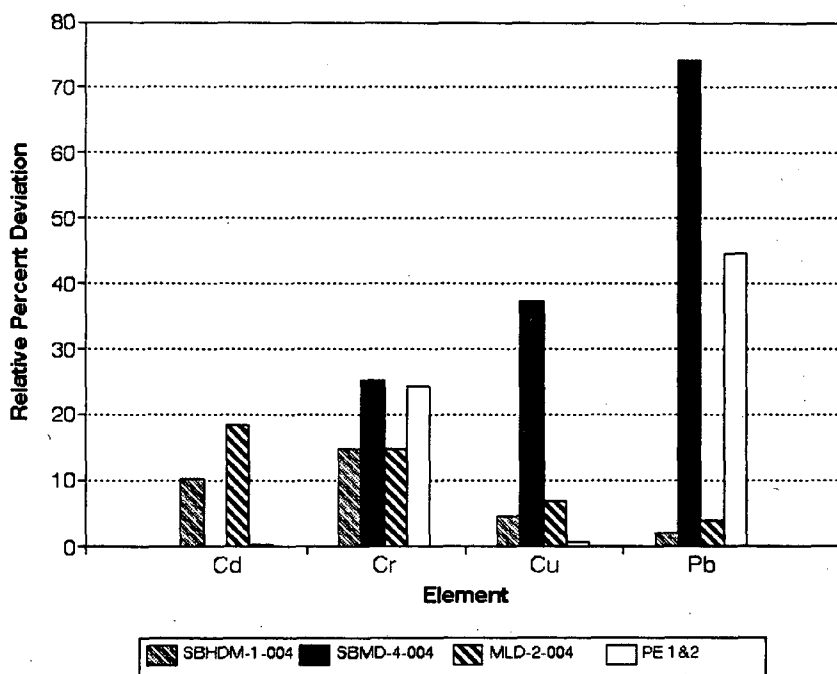
### *Duplicate Sample Analysis*

Duplicate sample analysis results are shown as RPD values in Figure 5-2. Relative percent deviations were computed for 4 duplicate sample analyses for the PNNL/NMSU ASV and PSA systems. (No duplicate samples





**Figure 5-1. Control soil sample analysis results from the PNNL/NMSU ASV and PSA systems. The upper and lower confidence limits with respect to the certified level are also shown on the graph. The ASV system was used for Cr and the PSA system for Cd, Cu and Pb.**



**Figure 5-2. Duplicate sample analysis results for the EG&G ASV (Cr) and the TraceLab PSA (Cd, Cu, Pb) systems.**

were run with the ETG Metalyzer.) One set of duplicate performance evaluation samples and three sets of field soil samples were included in this data set. Ten of the fifteen RPD determinations were less than 20 percent. Twelve of the 15 RPD determinations were less than or equal to 30 percent.

### ***Recovery Analysis***

None of the soil and control samples analyzed with the various electrochemical analysis systems were spiked prior to analysis. Consequently, there are no recovery data to present.

### **Field Soil Sample Analysis Results**

Analysis results were returned for 53 of 60 field soil samples from the Metalyzer (Cd, Cr, and Pb) analysis, 60 of 60 for the EG&G ASV (Cr) analysis, and 59 of 60 for the TraceLab PSA (Cd, Cu, and Pb) analysis. The results tally reported indications of no detect. The field sample analysis data are presented in graphical and tabular formats to assist the developers in comparing their data against the reference data set from the analytical laboratories. A series of seven scatter plots (Figures 5-3 through 5-9) are presented on the following pages where the data from the three stripping analysis systems are plotted with respect to reference laboratory data. As a part of the laboratory data validation process, laboratory data from the CAS ICP, CAS AAS, and MSE ICP laboratory results were averaged together to yield a reference laboratory value. (See Chapter 4 of this report for a discussion of the makeup of the reference laboratory data set.) All reported data in excess of the instrument detection limit are plotted; however, in many cases, the points on the scatter plots are overlaid and are indistinguishable from each other. The zero bias line extends from the lower left to the upper right of each plot. Points falling on or close to this line are indicative of good comparability of the stripping analysis data with reference laboratory data.

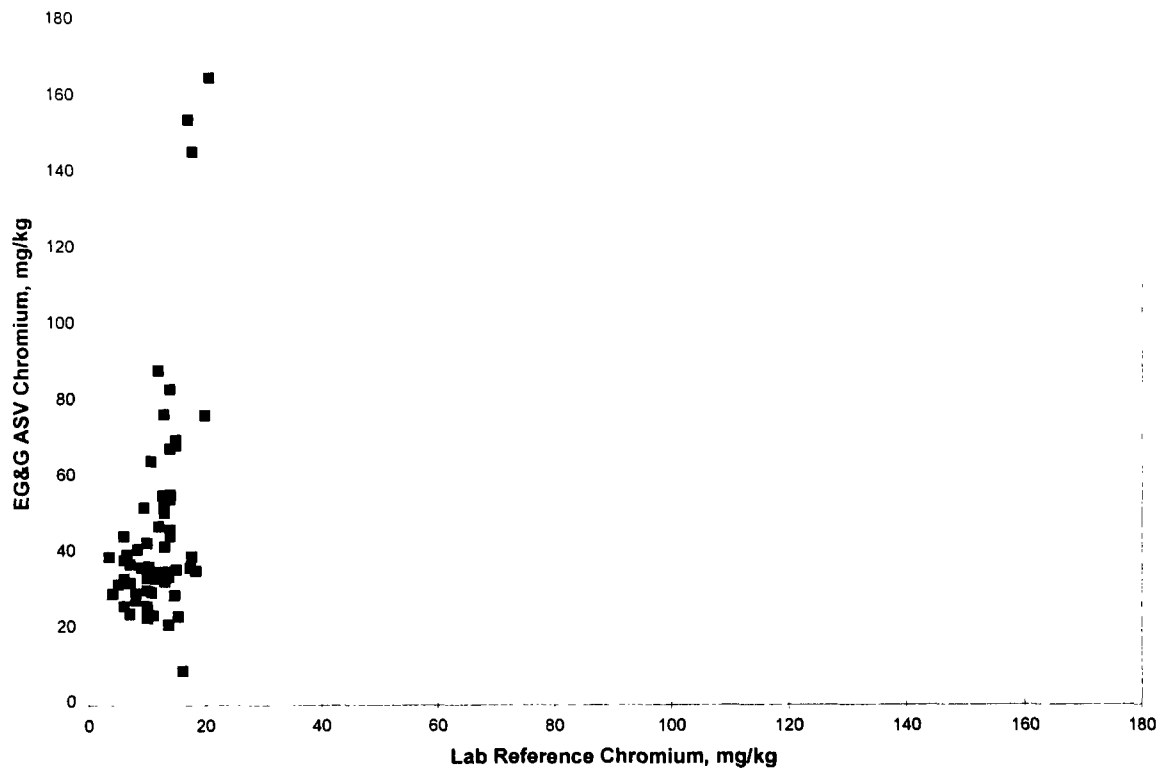
The various electrochemical analysis data are also presented in tabular form in Appendix A to facilitate their comparison with individual reference laboratory results. Tables are presented in which analysis results for each of the 60 soil samples are given for CAS ICP, CAS AAS, MSE ICP, reference laboratory, and each of the three electrochemical analysis systems for the four target elements selected for analysis by the participants.

### **Comparison of Stripping Analysis Results with Reference Laboratory Data**

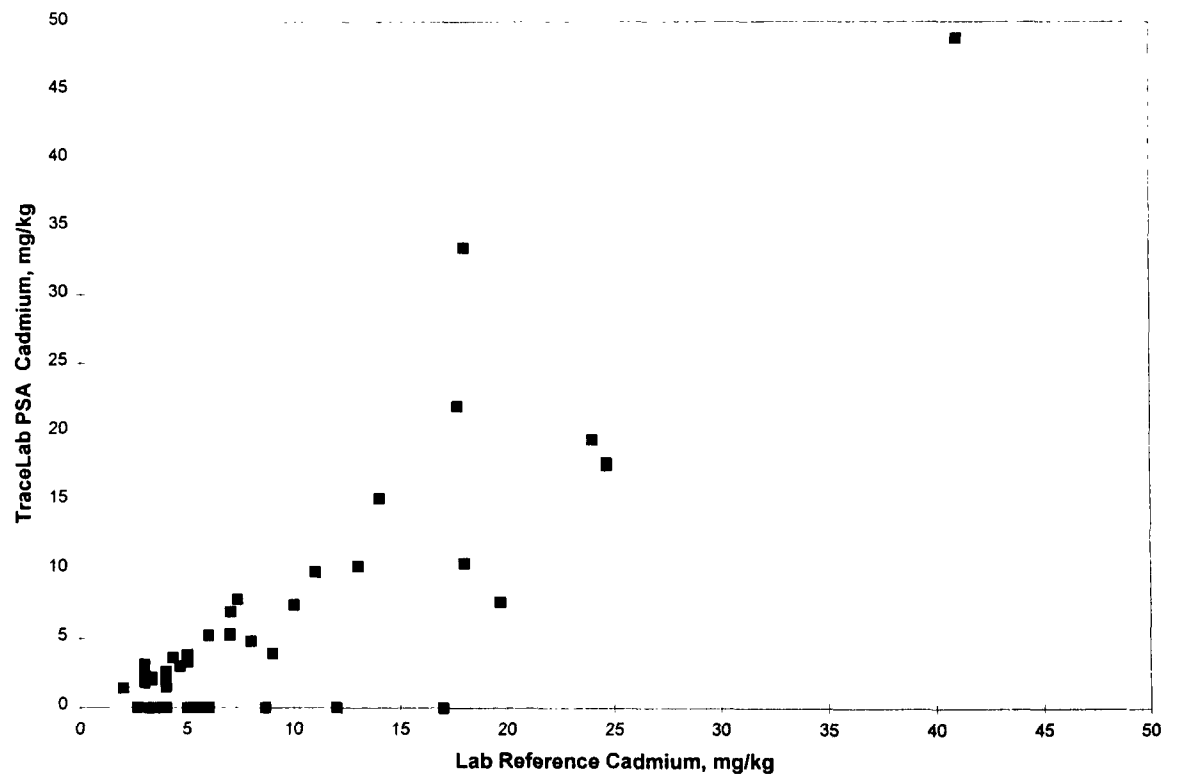
The following analytical approaches are offered as illustrations of how an evaluation of instrument performance relative to a laboratory data set might be carried out.

### ***Mean Percent Difference***

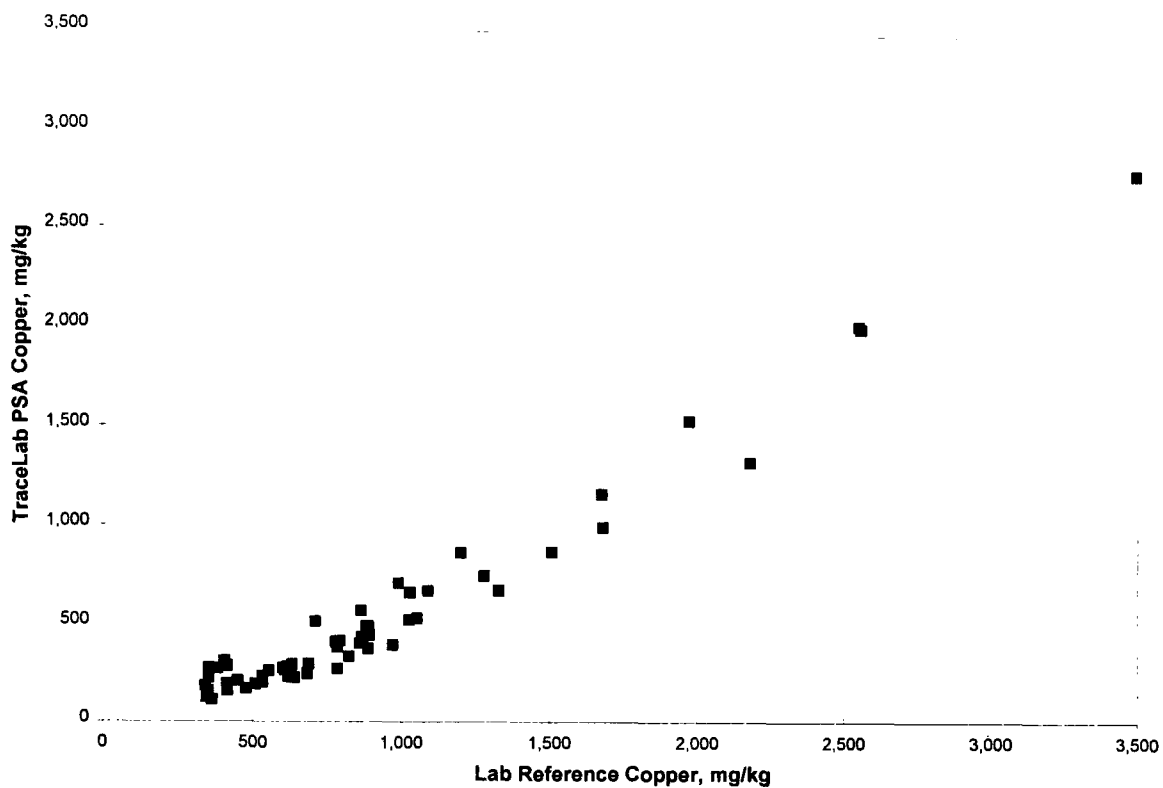
The MPD, as defined in Chapter 4, for the data from the stripping analyses relative to the reference laboratory data set are given in Table 5-2. A low MPD and an accompanying low standard deviation can be taken as an indicator of good comparability between methods. The best MPD is noted for Pb analysis by the TraceLab PSA system. The worst is for Cr by the EG&G ASV technique.



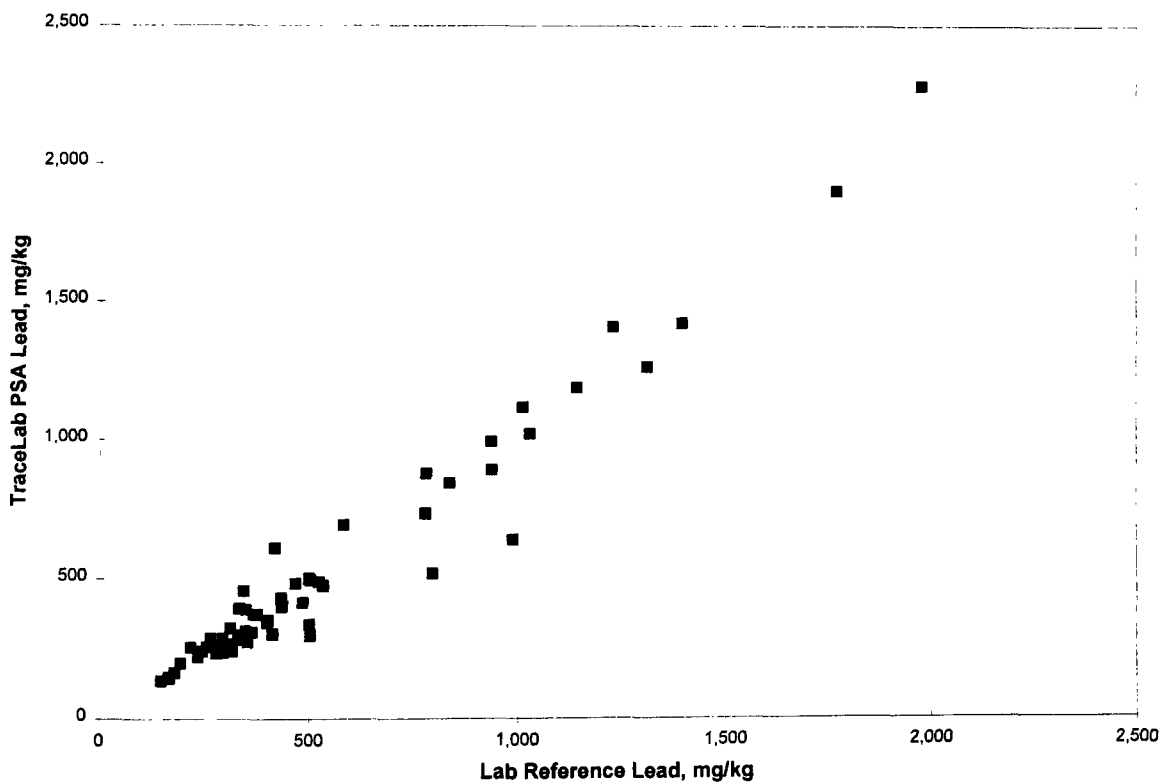
**Figure 5-3. EG&G ASV vs. reference laboratory chromium measurements.**



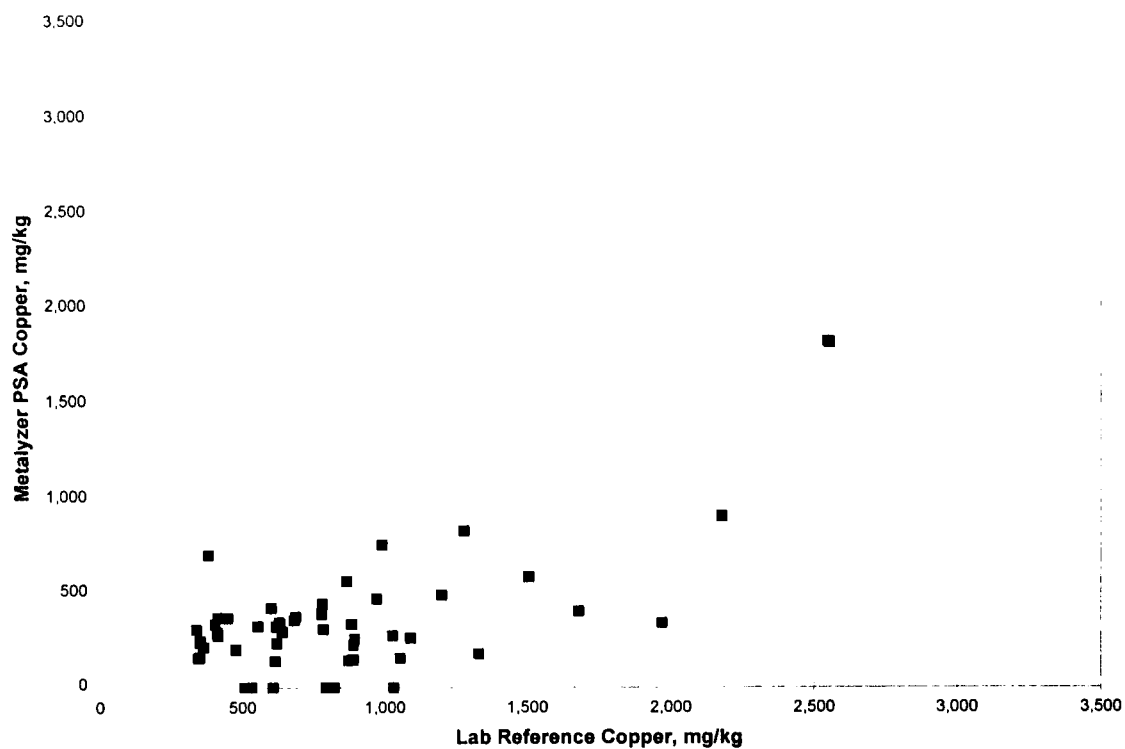
**Figure 5-4. TraceLab PSA vs. reference laboratory cadmium measurements.**



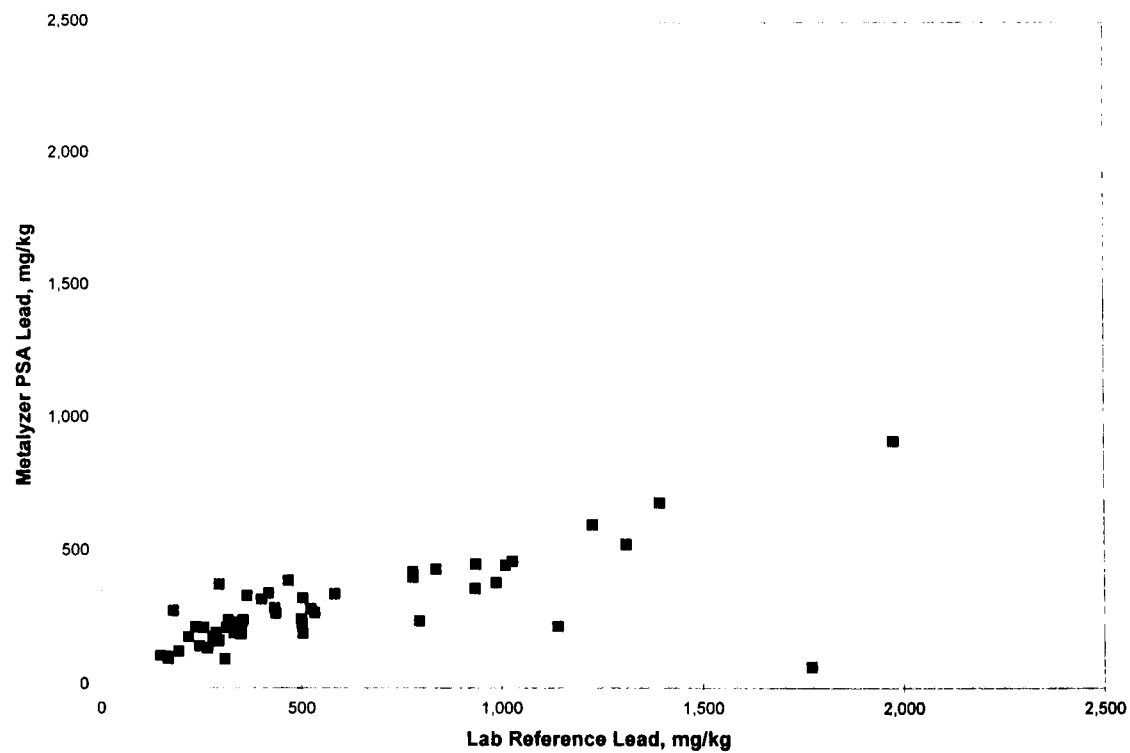
**Figure 5-5. TraceLab PSA vs. reference laboratory copper measurements.**



**Figure 5-6. TraceLab PSA vs. reference laboratory lead measurements.**



**Figure 5-7. Metalyzer PSA vs. reference laboratory copper measurements.**



**Figure 5-8. Metalyzer PSA vs. reference laboratory lead measurements.**

**Table 5-2. Mean Percent Difference for PNNL/NMSU ASV and PSA Analyses Relative to Reference Laboratory Data**

Element	ASV (EG&G) Mean Percent Difference	PSA (TraceLab) Mean Percent Difference	PSA (Metalyzer) Mean Percent Difference
Ag	NA	NA	NA
As	NA	NA	NA
Cd	NA	-22 ± 28	NA
Cr	322 ± 203	NA	NA
Cu	NA	-4 ± 16	-48 ± 28
Fe	NA	NA	NA
Mn	NA	NA	NA
Pb	NA	-4 ± 16	-37 ± 25
Zn	NA	NA	NA

Note: NA = no analysis. Only selected target elements were analyzed in this technology demonstration.

### ***Linear Regression Coefficients***

The linear regression slope, y-intercept, and correlation coefficient for the stripping analysis and reference laboratory data are given in Table 5-3. The slope yields a measure of the linear association between the two data sets. A slope of 2 indicates that a technology reports a value two times that of the reference laboratory, whereas a slope of 0.5 indicates the technology reports a value half the reference laboratory value. A regression analysis will always yield a slope value, even when the data are poorly correlated. The correlation coefficient is an indication of the strength of linear association between two variables. Values near unity suggest good correlation between the data sets. Values near zero suggest no correlation of the data. The correlation coefficients shown in Table 5-3 are best for the TraceLab instrument and poorest for the EG&G ASV instrument. Correlation results for the Metalyzer fall in between.

**Table 5-3. Comparison of Linear Regression Coefficients for the ASV and PSA Systems and Reference Laboratory Data Set**

Element	Slope	Intercept (mg/kg)	Correlation Coefficient
Cr (ASV)	3.75	3	0.50
Cd (TraceLab)	1.02	-2	0.90
Cu (TraceLab)	0.81	-210	0.98
Pb (TraceLab)	1.08	-54	0.98
Cd (Metalyzer)	NA	NA	NA
Cu (Metalyzer)	0.47	-18	0.72
Pb (Metalyzer)	0.27	146	0.71

Notes: NA = no analysis. Nearly all reported results for Cd analysis with the Metalyzer were no detects. Consequently, a regression analysis was not carried out for this element.

### ***Statistical Bias Testing***

A statistical test such as the Wilcoxon matched pair test can be used to investigate whether a statistically significant bias exists between the stripping analysis and the reference laboratory data set. The results from such a test should be used in conjunction with linear regression data, such as the data presented in Table 5-3. Although the statistical test may indicate that a significant bias exists between the two methods, the magnitude of

that bias must also be considered in the overall assessment of method comparability. Because the stripping analysis technologies are designated Level 1, formal statistical testing is left to the discretion of the technology developer.

### **Conclusions**

Since the stripping analysis technologies are developing technologies that have not undergone extensive field testing, a comprehensive assessment of their performance was not undertaken in this demonstration.

Conclusions as to the systems' overall performance are left to the technology developer.

## **Chapter 6**

### **Developer's Comments**

A review draft version of this report was sent to Dr. Khris Olsen of PNNL. Following his review, suggested changes and corrections were submitted in writing to SNL. All of the suggested changes were made. No further developer comments were received from PNNL for inclusion in this section.



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## **Appendix A**

### **Tabular Data for PNNL/NMSU/ETG Stripping Analysis and Reference Laboratory Field Soil Samples**

### **Table Description**

The results are organized by element with two tables for each element. The first table gives results from the Silver Bow site and the second gives results from the Mill Creek site. The data are further described as follows:

Column 1	Sample Number
Column 2	MSE Laboratory ICP AES Results
Column 3	CAS Laboratory ICP AES Results
Column 4	CAS Laboratory Flame AAS Results
Column 5	Reference Laboratory Data Set (Average of Columns 2-4)
Column 6	Field Technology Results

Note that stripping analysis results are reported for only four (Cd, Cr, Cu and Pb) of the nine target elements.

**Table A-1. Cadmium Analysis Results for TraceLab PSA and Reference Laboratories (Part 1, Silver Bow Site)**

<b>Sample No.</b>	<b>MSE_Cd (mg/kg)</b>	<b>C_IC_Cd (mg/kg)</b>	<b>C_AA_Cd (mg/kg)</b>	<b>Ref_Cd (mg/kg)</b>	<b>TraceLab_Cd (mg/kg)</b>
SBHD1	22.6	27	23.7	24.4	17.7
SBHD2	12.5			12.5	10.2
SBHD3	21.6	22	14.9	19.5	7.6
SBHD4	9.9			9.9	7.4
SBHD5	48.5	54	20.1	40.9	48.8
SBHD6	18.3			18.3	10.4
SBHD7	19.0	18	15.7	17.6	21.8
SBHD8	18.0			18.0	33.4
SBHD9	15.5	14	11.5	13.7	15.1
SBHD10	24.3			24.3	19.4
SBMD1	5.8	6	2.7	4.8	3.8
SBMD2	11.8			11.8	
SBMD3	7.8	15	3.4	8.7	<1
SBMD4	16.5			16.5	<1
SBMD5	14.6	11	7.1	10.9	9.8
SBMD6	7.8			7.8	4.8
SBMD7	9.8	7	9.7	8.8	3.9
SBMD8	4.6			4.6	<1
SBMD9	6.6	6	5	5.9	<1
SBMD10	5.7			5.7	5.2
SBLD1	4.9	5	3.7	4.5	3.0
SBLD2	3.5			3.5	2.0
SBLD3	3.8	3	2.8	3.2	2.0
SBLD4	2.7			2.7	2.4
SBLD5	3.1	3	2.7	2.9	2.2
SBLD6	4.9			4.9	3.3
SBLD7	7.3	8	6.6	7.3	7.8
SBLD8	3.1			3.1	3.1
SBLD9	2.4	4	2.6	3.0	1.8
SBLD10	3.7			3.7	2.6

**Table A-2. Cadmium Analysis Results for TraceLab PSA and Reference Laboratories (Part 2, Mill Creek Site)**

<b>Sample No.</b>	<b>MSE_Cd (mg/kg)</b>	<b>C_IC_Cd (mg/kg)</b>	<b>C_AA_Cd (mg/kg)</b>	<b>Ref_Cd (mg/kg)</b>	<b>TraceLab_Cd (mg/kg)</b>
MCHD1	4	3	3	3	<1
MCHD2	4			4	<1
MCHD3	3	3	2	3	<1
MCHD4	4			4	<1
MCHD5	5	4	3	4	<1
MCHD6	3			3	<1
MCHD7	4	3	2	3	<1
MCHD8	6			6	<1
MCHD9	27	25	22	25	17.5
MCHD10	4			4	<1
MCMD1	3	4	3	4	<1
MCMD2	4			4	<1
MCMD3	4	3	3	3	<1
MCMD4	4			4	<1
MCMD5	6	5	5	5	<1
MCMD6	5			5	<1
MCMD7	7	5	5	5	<1
MCMD8	7			7	5.3
MCMD9	8	7	6	7	5.2
MCMD10	6			6	<1
MCLD1	2	2	2	2	1.4
MCLD2	4			4	1.5
MCLD3	4	3	3	3	2.2
MCLD4	4			4	2.5
MCLD5	4	4	3	4	<1
MCLD6	4			4	<1
MCLD7	5	4	4	4	3.6
MCLD8	4			4	<1
MCLD9	5	3	3	4	<1
MCLD10	7			7	6.9

**Table A-3. Cadmium Analysis Results for Metalyzer PSA and Reference Laboratories (Part 1, Silver Bow Site)**

<b>Sample No.</b>	<b>MSE_Cd (mg/kg)</b>	<b>C_IC_Cd (mg/kg)</b>	<b>C_AA_Cd (mg/kg)</b>	<b>Ref_Cd (mg/kg)</b>	<b>Metalyzer PSA_Cd (mg/kg)</b>
SBHD1	22.6	27	23.7	24.4	18
SBHD2	12.5			12.5	<10
SBHD3	21.6	22	14.9	19.5	<10
SBHD4	9.9			9.9	<10
SBHD5	48.5	54	20.1	40.9	26.2
SBHD6	18.3			18.3	<10
SBHD7	19.0	18	15.7	17.6	<10
SBHD8	18.0			18.0	<10
SBHD9	15.5	14	11.5	13.7	21.6
SBHD10	24.3			24.3	<10
SBMD1	5.8	6	2.7	4.8	<10
SBMD2	11.8			11.8	
SBMD3	7.8	15	3.4	8.7	<10
SBMD4	16.5			16.5	<10
SBMD5	14.6	11	7.1	10.9	<10
SBMD6	7.8			7.8	<10
SBMD7	9.8	7	9.7	8.8	<10
SBMD8	4.6			4.6	<10
SBMD9	6.6	6	5	5.9	<10
SBMD10	5.7			5.7	
SBLD1	4.9	5	3.7	4.5	<10
SBLD2	3.5			3.5	<5
SBLD3	3.8	3	2.8	3.2	<5
SBLD4	2.7			2.7	<5
SBLD5	3.1	3	2.7	2.9	<5
SBLD6	4.9			4.9	<5
SBLD7	7.3	8	6.6	7.3	<10
SBLD8	3.1			3.1	<5
SBLD9	2.4	4	2.6	3.0	<5
SBLD10	3.7			3.7	<10

**Table A-4. Cadmium Analysis Results for Metalyzer PSA and Reference Laboratories (Part 2, Mill Creek Site)**

<b>Sample No.</b>	<b>MSE_Cd (mg/kg)</b>	<b>C_IC_Cd (mg/kg)</b>	<b>C_AA_Cd (mg/kg)</b>	<b>Ref_Cd (mg/kg)</b>	<b>Metalyzer PSA_Cd (mg/kg)</b>
MCHD1	4	3	3	3	<10
MCHD2	4			4	<10
MCHD3	3	3	2	3	<10
MCHD4	4			4	<10
MCHD5	5	4	3	4	<10
MCHD6	3			3	
MCHD7	4	3	2	3	
MCHD8	6			6	
MCHD9	27	25	22	25	
MCHD10	4			4	<10
MCMD1	3	4	3	4	<10
MCMD2	4			4	<10
MCMD3	4	3	3	3	<10
MCMD4	4			4	<10
MCMD5	6	5	5	5	<10
MCMD6	5			5	<10
MCMD7	7	5	5	5	<10
MCMD8	7			7	<10
MCMD9	8	7	6	7	<10
MCMD10	6			6	
MCLD1	2	2	2	2	<7.2
MCLD2	4			4	<10
MCLD3	4	3	3	3	<8.8
MCLD4	4			4	<8.8
MCLD5	4	4	3	4	<10
MCLD6	4			4	<10
MCLD7	5	4	4	4	<10
MCLD8	4			4	<10
MCLD9	5	3	3	4	<10
MCLD10	7			7	<10

**Table A-5. Chromium Analysis Results for EG&G ASV and Reference Laboratories (Part 1, Silver Bow Site)**

<b>Sample No.</b>	<b>MSE_Cr (mg/kg)</b>	<b>C_IC_Cr (mg/kg)</b>	<b>C_AA_Cr (mg/kg)</b>	<b>Ref_Cr (mg/kg)</b>	<b>EG&amp;G ASV_Cr (mg/kg)</b>
SBHD1	6	8	<10	6.8	32.3
SBHD2	4			4.4	29.4
SBHD3	5	5	<10	5.0	32.0
SBHD4	6			5.7	26.2
SBHD5	7	8	23	12.7	34.0
SBHD6	7			6.8	37.2
SBHD7	7	5	<10	6.2	38.4
SBHD8	6			5.7	33.4
SBHD9	7	6	<10	6.6	39.8
SBHD10	9			9.2	36.3
SBMD1	13	17	<10	15.0	70.2
SBMD2	20			20.0	76.6
SBMD3	27	12	15	18.1	145.6
SBMD4	21			21.2	165.0
SBMD5	25	16	11	17.3	154.0
SBMD6	14			13.7	83.6
SBMD7	14	10	<10	12.0	88.5
SBMD8	14			13.8	55.8
SBMD9	10	9	<10	9.4	52.3
SBMD10	8			7.8	29.4
SBLD1	15	15	<10	15.2	36.0
SBLD2	14			14.0	46.5
SBLD3	13	14	11	12.5	55.6
SBLD4	13			12.7	76.9
SBLD5	12	14	<10	12.8	51.0
SBLD6	14			13.5	45.2
SBLD7	13	17	<10	14.9	68.8
SBLD8	13			12.6	52.8
SBLD9	12	16	<10	13.9	44.9
SBLD10	14			13.5	67.9



**Table A-6. Chromium Analysis Results for EG&G ASV and Reference Laboratories (Part 2, Mill Creek Site)**

<b>Sample No.</b>	<b>MSE_Cr (mg/kg)</b>	<b>C_IC_Cr (mg/kg)</b>	<b>C_AA_Cr (mg/kg)</b>	<b>Ref_Cr (mg/kg)</b>	<b>EG&amp;G ASV_Cr (mg/kg)</b>
MCHD1	8	7	10	8	41.2
MCHD2	10			10	43.0
MCHD3	4	3		4	39.2
MCHD4	6			6	44.7
MCHD5	11	10	11	11	64.6
MCHD6	10			10	30.4
MCHD7	7	6	28	14	21.4
MCHD8	10			10	33.6
MCHD9	10	9	12	10	36.7
MCHD10	13			13	35.4
MCMD1	11	10	21	14	54.6
MCMD2	10			10	26.2
MCMD3	11	14	30	18	35.5
MCMD4	13			13	32.8
MCMD5	13	14	17	15	29.1
MCMD6	10			10	23.1
MCMD7	13	12	21	15	23.6
MCMD8	12			12	35.2
MCMD9	12	14	27	18	39.4
MCMD10	13			13	42.0
MCLD1	7	8	33	16	9.1
MCLD2	8			8	27.8
MCLD3	9	7	19	12	33.7
MCLD4	12			12	47.4
MCLD5	8	12	21	14	34.0
MCLD6	11			11	34.2
MCLD7	10	10	32	17	36.4
MCLD8	7			7	24.1
MCLD9	9	8	15	11	30.0
MCLD10	11			11	23.9

**Table A-7. Copper Analysis Results for TraceLab PSA and Reference Laboratories (Part 1, Silver Bow Site)**

<b>Sample No.</b>	<b>MSE_Cu (mg/kg)</b>	<b>C_IC_Cu (mg/kg)</b>	<b>C_AA_Cu (mg/kg)</b>	<b>Ref_Cu (mg/kg)</b>	<b>TraceLab PSA_Cu (mg/kg)</b>
SBHD1	1,570	1,670	1,790	1,677	1,164
SBHD2	1,330			1,330	670
SBHD3	2,460	2,510	2,700	2,557	2,006
SBHD4	991			991	708
SBHD5	2,620	2,410	2,620	2,550	2,020
SBHD6	1,680			1,680	994
SBHD7	1,010	1,010	1,060	1,027	520
SBHD8	1,030			1,030	660
SBHD9	1,620	1,400	1,500	1,507	869
SBHD10	1,970			1,970	1,539
SBMD1	281	385	371	346	124
SBMD2	864			864	566
SBMD3	788	512	522	607	264
SBMD4	2,180			2,180	1,328
SBMD5	1,090	1,240	1,270	1,200	862
SBMD6	780			780	408
SBMD7	1,270	1,290	1,280	1,280	745
SBMD8	449			449	208
SBMD9	608	644	635	629	233
SBMD10	710			710	513
SBLD1	394	374	376	381	271
SBLD2	351			351	223
SBLD3	339	357	359	352	273
SBLD4	414			414	284
SBLD5	347	332	338	339	183
SBLD6	404			404	308
SBLD7	566	647	648	620	251
SBLD8	414			414	160
SBLD9	305	376	370	350	156
SBLD10	363			363	112

**Table A-8. Copper Analysis Results for TraceLab PSA and Reference Laboratories (Part 2, Mill Creek Site)**

<b>Sample No.</b>	<b>MSE_Cu (mg/kg)</b>	<b>C_IC_Cu (mg/kg)</b>	<b>C_AA_Cu (mg/kg)</b>	<b>Ref_Cu (mg/kg)</b>	<b>TraceLab PSA_Cu (mg/kg)</b>
MCHD1	682	663	701	682	245
MCHD2	792			792	413
MCHD3	419	400	420	413	194
MCHD4	687			687	296
MCHD5	956	828	880	888	372
MCHD6	533			533	202
MCHD7	589	626	668	628	228
MCHD8	859			859	400
MCHD9	3,340	3,490	3,640	3,490	2,797
MCHD10	889			889	486
MCMD1	631	631	657	640	224
MCMD2	532			532	232
MCMD3	585	621	651	619	230
MCMD4	632			632	292
MCMD5	825	795	845	822	333
MCMD6	893			893	441
MCMD7	890	821	885	865	432
MCMD8	871			871	427
MCMD9	1,020	1,010	1,130	1,053	530
MCMD10	784			784	270
MCLD1	476	513	535	508	191
MCLD2	477			477	167
MCLD3	595	598	610	601	274
MCLD4	554			554	260
MCLD5	721	775	837	778	406
MCLD6	971			971	392
MCLD7	853	878	916	882	488
MCLD8	784			784	381
MCLD9	624	598	622	615	280
MCLD10	1,090			1,090	669

**Table A-9. Copper Analysis Results for Metalyzer PSA and Reference Laboratories (Part 1, Silver Bow Site)**

<b>Sample No.</b>	<b>MSE_Cu (mg/kg)</b>	<b>C_IC_Cu (mg/kg)</b>	<b>C_AA_Cu (mg/kg)</b>	<b>Ref_Cu (mg/kg)</b>	<b>Metalyzer PSA_Cu (mg/kg)</b>
SBHD1	1,570	1,670	1,790	1,677	
SBHD2	1,330			1,330	180
SBHD3	2,460	2,510	2,700	2,557	1,814
SBHD4	991			991	758
SBHD5	2,620	2,410	2,620	2,550	1,820
SBHD6	1,680			1,680	403
SBHD7	1,010	1,010	1,060	1,027	278
SBHD8	1,030			1,030	<132
SBHD9	1,620	1,400	1,500	1,507	587
SBHD10	1,970			1,970	341
SBMD1	281	385	371	346	158
SBMD2	864			864	
SBMD3	788	512	522	607	<192
SBMD4	2,180			2,180	906
SBMD5	1,090	1,240	1,270	1,200	492
SBMD6	780			780	446
SBMD7	1,270	1,290	1,280	1,280	832
SBMD8	449			449	370
SBMD9	608	644	635	629	349
SBMD10	710			710	
SBLD1	394	374	376	381	706
SBLD2	351			351	248
SBLD3	339	357	359	352	240
SBLD4	414			414	373
SBLD5	347	332	338	339	309
SBLD6	404			404	337
SBLD7	566	647	648	620	237
SBLD8	414			414	278
SBLD9	305	376	370	350	163
SBLD10	363			363	215

**Table A-10. Copper Analysis Results for Metalyzer PSA and Reference Laboratories (Part 2, Mill Creek Site)**

<b>Sample No.</b>	<b>MSE_Cu (mg/kg)</b>	<b>C_IC_Cu (mg/kg)</b>	<b>C_AA_Cu (mg/kg)</b>	<b>Ref_Cu (mg/kg)</b>	<b>Metalyzer PSA_Cu (mg/kg)</b>
MCHD1	682	663	701	682	360
MCHD2	792			792	<135
MCHD3	419	400	420	413	292
MCHD4	687			687	378
MCHD5	956	828	880	888	150
MCHD6	533			533	
MCHD7	589	626	668	628	
MCHD8	859			859	
MCHD9	3,340	3,490	3,640	3,490	
MCHD10	889			889	226
MCMD1	631	631	657	640	298
MCMD2	532			532	<140
MCMD3	585	621	651	619	325
MCMD4	632			632	338
MCMD5	825	795	845	822	<143
MCMD6	893			893	259
MCMD7	890	821	885	865	566
MCMD8	871			871	146
MCMD9	1,020	1,010	1,130	1,053	157
MCMD10	784			784	
MCLD1	476	513	535	508	<100
MCLD2	477			477	203
MCLD3	595	598	610	601	424
MCLD4	554			554	328
MCLD5	721	775	837	778	392
MCLD6	971			971	472
MCLD7	853	878	916	882	338
MCLD8	784			784	312
MCLD9	624	598	622	615	143
MCLD10	1,090			1,090	265

**Table A-11. Lead Analysis Results for TraceLab PSA and Reference Laboratories (Part 1, Silver Bow Site)**

<b>Sample No.</b>	<b>MSE_Pb (mg/kg)</b>	<b>C_IC_Pb (mg/kg)</b>	<b>C_AA_Pb (mg/kg)</b>	<b>Ref_Pb (mg/kg)</b>	<b>TraceLab PSA_Pb (mg/kg)</b>
SBHD1	1,170	1,220	1,290	1,227	1,402
SBHD2	1,010			1,010	1,114
SBHD3	946	902	955	934	990
SBHD4	936			936	888
SBHD5	2,080	1,850	2,000	1,977	2,280
SBHD6	1,310			1,310	1,258
SBHD7	1,030	992	1,060	1,027	1,018
SBHD8	1,770			1,770	1,895
SBHD9	1,500	1,310	1,370	1,393	1,416
SBHD10	1,140			1,140	1,184
SBMD1	410	1,260	1,290	987	638
SBMD2	631			631	
SBMD3	456	513	539	503	296
SBMD4	779			779	877
SBMD5	677	823	883	794	517
SBMD6	836			836	842
SBMD7	696	798	840	778	732
SBMD8	466			466	482
SBMD9	537	471	494	501	336
SBMD10	342			342	456
SBLD1	200	166	171	179	165
SBLD2	166			166	148
SBLD3	139	147	154	147	135
SBLD4	245			245	241
SBLD5	173	161	165	166	144
SBLD6	217			217	255
SBLD7	324	374	393	364	310
SBLD8	193			193	198
SBLD9	264	302	315	294	236
SBLD10	294			294	287

**Table A-12. Lead Analysis Results for TraceLab PSA and Reference Laboratories (Part 2, Mill Creek Site)**

<b>Sample No.</b>	<b>MSE_Pb (mg/kg)</b>	<b>C_IC_Pb (mg/kg)</b>	<b>C_AA_Pb (mg/kg)</b>	<b>Ref_Pb (mg/kg)</b>	<b>TraceLab PSA_Pb (mg/kg)</b>
MCHD1	391	391	417	400	343
MCHD2	582			582	692
MCHD3	384	415	452	417	610
MCHD4	312			312	322
MCHD5	520	521	556	532	474
MCHD6	484			484	414
MCHD7	355	361	388	368	372
MCHD8	376			376	372
MCHD9	388	396	423	402	351
MCHD10	332			332	394
MCMD1	229	235	240	235	220
MCMD2	350			350	390
MCMD3	267	283	294	281	253
MCMD4	256			256	256
MCMD5	442	424	441	436	400
MCMD6	265			265	288
MCMD7	362	336	362	353	274
MCMD8	349			349	312
MCMD9	484	495	529	503	494
MCMD10	413			413	302
MCLD1	298	306	319	308	266
MCLD2	316			316	241
MCLD3	291	279	288	286	248
MCLD4	331			331	282
MCLD5	264	275	297	279	234
MCLD6	342			342	284
MCLD7	350	330	340	340	298
MCLD8	432			432	431
MCLD9	540	497	530	522	488
MCLD10	499			499	500

**Table A-13. Lead Analysis Results for Metalyzer PSA and Reference Laboratories (Part 1, Silver Bow Site)**

<b>Sample No.</b>	<b>MSE_Pb (mg/kg)</b>	<b>C_IC_Pb (mg/kg)</b>	<b>C_AA_Pb (mg/kg)</b>	<b>Ref_Pb (mg/kg)</b>	<b>Metalyzer PSA_Pb (mg/kg)</b>
SBHD1	1,170	1,220	1,290	1,227	608
SBHD2	1,010			1,010	456
SBHD3	946	902	955	934	370
SBHD4	936			936	460
SBHD5	2,080	1,850	2,000	1,977	921
SBHD6	1,310			1,310	534
SBHD7	1,030	992	1,060	1,027	472
SBHD8	1,770			1,770	77.4
SBHD9	1,500	1,310	1,370	1,393	690
SBHD10	1,140			1,140	229
SBMD1	410	1,260	1,290	987	392
SBMD2	631			631	
SBMD3	456	513	539	503	203
SBMD4	779			779	412
SBMD5	677	823	883	794	250
SBMD6	836			836	442
SBMD7	696	798	840	778	432
SBMD8	466			466	400
SBMD9	537	471	494	501	240
SBMD10	342			342	
SBLD1	200	166	171	179	287
SBLD2	166			166	116
SBLD3	139	147	154	147	120
SBLD4	245			245	155
SBLD5	173	161	165	166	108
SBLD6	217			217	190
SBLD7	324	374	393	364	343
SBLD8	193			193	136
SBLD9	264	302	315	294	175
SBLD10	294			294	386



**Table A-14. Lead Analysis Results for Metalyzer PSA and Reference Laboratories (Part 2, Mill Creek Site)**

<b>Sample No.</b>	<b>MSE_Pb (mg/kg)</b>	<b>C_IC_Pb (mg/kg)</b>	<b>C_AA_Pb (mg/kg)</b>	<b>Ref_Pb (mg/kg)</b>	<b>Metalyzer PSA_Pb (mg/kg)</b>
MCHD1	391	391	417	400	330
MCHD2	582			582	350
MCHD3	384	415	452	417	353
MCHD4	312			312	224
MCHD5	520	521	556	532	280
MCHD6	484			484	
MCHD7	355	361	388	368	
MCHD8	376			376	
MCHD9	388	396	423	402	
MCHD10	332			332	244
MCMD1	229	235	240	235	226
MCMD2	350			350	220
MCMD3	267	283	294	281	189
MCMD4	256			256	224
MCMD5	442	424	441	436	278
MCMD6	265			265	148
MCMD7	362	336	362	353	252
MCMD8	349			349	200
MCMD9	484	495	529	503	334
MCMD10	413			413	
MCLD1	298	306	319	308	107
MCLD2	316			316	252
MCLD3	291	279	288	286	205
MCLD4	331			331	203
MCLD5	264	275	297	279	190
MCLD6	342			342	228
MCLD7	350	330	340	340	208
MCLD8	432			432	296
MCLD9	540	497	530	522	294
MCLD10	499			499	257