



Technology Evaluation Report

Mobile Atomic Absorption Spectrometer for Metals- Contaminated Soil Characterization

Pace Environmental Laboratories



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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 United States 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 a mobile atomic absorption spectroscopy (AAS) system operated by Pace Environmental Laboratories. This spectroscopic technique was one of four technologies that were used to analyze soil samples for a number of target elements. Other technologies that were tested include a laser-induced breakdown spectrometer operated by MelΔok, Inc.; a second laser-induced breakdown spectrometer from Los Alamos National Laboratory; and anodic stripping voltammetry systems fielded by Battelle Pacific Northwest 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 mobile atomic absorption spectrometer system operated by Pace Environmental Laboratories was classified as a Level 2 technology. The instrumentation system used in the demonstration is commercially available and thus is a Level 3 technology. However, the field operators of the instrument were not the instrument developers, and the technology was originally designed to be operated in a conventional laboratory.

The Consortium has determined that an exhaustive verification of the relatively new and developing Level 1 technologies should not be performed. Level 2 and Level 3 technologies are analyzed in greater detail, with Level 3 technologies getting the most complete data analysis. The results from Level 1 and Level 2 technologies are primarily 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

The mobile atomic absorption spectrometer, fielded in this study by Pace Environmental Laboratories, Inc., is a conventional laboratory benchtop spectrometer that has been installed in a van along with various support hardware so that on-site soil sample processing and analysis can be carried out. The atomic absorption technique is based on the principle that ground-state atoms will absorb light at specific wavelengths for each element. A preanalysis sample digestion step is required to get the elements into solution prior to the absorption analysis step. The sample solution is aspirated into an air-acetylene flame through which a beam of light is directed. The method is quantitative since the degree of light absorption can be directly related to the concentration of atoms in the sample. The direct-aspiration atomic absorption method used in this demonstration is relatively mature since the instrument is commercially available and is used in many laboratories.

The Pace mobile atomic absorption system was successfully 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 plan 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 field 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 reference laboratories. Data from the reference laboratory and Pace technology data are presented in a variety of forms to assist in comparing the data sets produced during the demonstration.

The accuracy of the Pace mobile atomic absorption system was assessed using three methods: (1) Pace results on quality control samples, (2) mean percent difference estimates for each target element in the field soil samples relative to reference laboratory data, and (3) regression analysis against reference laboratory data. The latter gave an overall agreement of ± 20 percent or less for most of the nine target elements. Problems were encountered for selected elements, however. Poor results for arsenic were at least partially attributable to the fact that the mobile AAS system was not optimized for arsenic determinations. Poor results for chromium were also encountered and were at least in part attributable to the fact that the level of chromium in the soil samples was at or near the detection level for the spectroscopic methods employed both by this mobile system and the reference laboratory.

The overall precision of the mobile system was determined to be in an acceptable range of 20 percent or less by duplicate analysis of soil sample splits. A comparison of the Pace mobile atomic absorption data with the reference laboratory data shows generally good agreement between the two data sets. Detailed cost information on the application and use of this on-site technology is not presented. However, overall costs are expected to be similar to those encountered in conventional laboratory analyses since the mobile system is essentially a laboratory system, requiring similar sample processing and operator skills.

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Acronyms and Abbreviations

°C	degrees centigrade
°F	degrees Fahrenheit
AAS	atomic absorption spectroscopy
ac	alternating current
CAS	Columbia Analytical Services
CCV	continuing calibration verification
CLP	Contract Laboratory Program
cm	centimeter
cm ²	square centimeters
cm ³	cubic centimeters
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
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
m	meter
MCHD	Mill Creek-high demonstration
MCLD	Mill Creek-low demonstration
MCMD	Mill Creek-medium demonstration
mg	milligram
mm/m	millimeters per meter
MPD	mean percent difference
NERL	National Exposure Research Laboratory
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
V	volt
W	watt

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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 prototypes, evolving technologies, 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 maturity:

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 Pace atomic absorption spectrometer. 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 Pace system. Chapter 6 contains developer's comments regarding the demonstration.

Chapter 2

Technology Description

General Description

Flame atomic absorption spectroscopy (AAS) is a mature technology that is used to measure elemental species in a variety of sample media. Atomic absorption occurs when an atom in a particular energy state absorbs photons of incident light at a specific wavelength as the atom transitions to a higher energy electronic state. An aerosol nebulizer in the atomic absorption spectrometer is used to atomize a sample fluid containing the element of interest into an air-acetylene flame. The thermal energy in the flame destroys all chemical bonds in the aspirated sample, changing all species to the atomic state. A light beam from a hollow cathode lamp, specific for each element, is directed through the flame, onto a monochromator, and ultimately to a detector. The monochromator/detector measures the degree of light absorption from the beam at a specific wavelength band while the solution is aspirated into the flame. The extent of light absorption is directly related to the concentration of the element of interest in the liquid sample that is aspirated into the flame.

The direct-aspiration flame AAS method is much like inductively coupled plasma atomic emission spectroscopy (ICP AES) in that the sample must be in solution prior to analysis. Standard methods usually specify acid digestion of the sample using a mixture of nitric and hydrochloric acids. Sample digestion can also use nitric acid and a microwave oven. Only those species that are solubilized in the digestion process can be detected by the method. Those species that are strongly bound to insoluble components in the sample may not be reduced to the atomic state in the flame aspiration phase and thus would not be detected by the instrument.

Technology Advantages

According to information provided by Pace Environmental Laboratories, the mobile AAS analytical technique offers several advantages over conventional laboratory-based atomic emission or absorption spectroscopic methods. The most important advantages are given below:

- Laboratory hardware equivalence—Laboratory-proven technology in a mobile environment
- Laboratory analysis method equivalence—EPA SW-846 Method 3050A, *Acid Digestion of Sediments, Sludges, and Soils*, and SW-846 Method 7000A, *Atomic Absorption Methods*
- Analysis costs—Cost per sample in the mobile laboratory compare favorably with those quoted by a conventional laboratory
- Instrument precision and accuracy—Accuracy and precision comparable to conventional laboratory methods
- Response time—Results are available in near real time. Shipping and reporting delays are avoided

Technology Limitations

Several of the more important technology limitations are listed below:

- Analysis time—A throughput time of one soil sample per hour is typical
- Instrument cost—The estimated total capital cost is \$172,000 for the flame absorption spectrometer and accompanying vehicle. Vehicle acquisition and modification costs result in considerably higher costs compared with a conventional laboratory system
- Instrument mobility—Because of the requirement of a relatively large vehicle to house the spectrometer and accompanying facilities, areas with poor or limited access pose a problem for on-site analysis
- Analytical versatility—The system is configured for sample introduction by conventional flame aspiration only and as such is not optimized for low-level arsenic analysis

Physical Characteristics

The Pace Environmental Laboratories mobile AAS system is a Perkin-Elmer Model 3110 atomic absorption spectrometer that was not modified in any way prior to installation in an 8- × 16-foot trailer. The trailer was modified to include an exhaust vent above the spectrometer's flame aspiration unit and a fume hood for acid digestion of soil samples. The overall size of the instrument is 0.7 m (wide) × 0.4 m (high) × 0.6 m (deep). Its weight is 55 kg, and although the instrument is a comparatively small benchtop unit, it is not portable. The instrument requires about 300 W of 115 V ac power to operate. About 3 hours were required for initial instrument setup and about 1 hour setup time each day prior to sample analysis. Operators included two trained technicians and a staff chemist. All three individuals were involved in the analysis process, principally because of the considerable time requirements associated with sample preparation and digestion prior to analysis on the spectrometer.

Ancillary equipment and supplies include an electric generator, gravimetric balance, glassware, fume hood, hot plates, and various chemicals used in sample digestion. Minimal chemical waste is produced during instrument operation; however, acid waste is produced during the sample digestion phase of the analysis. Minimal routine maintenance is required during normal instrument usage. Daily calibrations are performed on the instrument, with accompanying periodic checks on calibration drift during the sample analysis sequence.

Because this mobile AAS is a commercially available instrument, data processing capabilities are well developed and automated. Sample throughput is in the range of one to two samples per hour. This estimate is based on 10 hours per day of operational time, with continuous sample preparation, digestion, and analysis for nine target elements.

System Layout

A diagram of the mobile laboratory layout in the trailer is shown in Figure 2-1.

Technology Maturity

The Pace AAS system is a commercially available laboratory instrument that was mounted in a trailer. Consequently, the technology can be regarded as mature. Under the guidelines of the Consortium, commercially available instruments are normally classed as Level 3 in terms of their performance evaluation. This particular demonstration was given a Level 2 classification because the operators were not affiliated with Perkin-Elmer, the

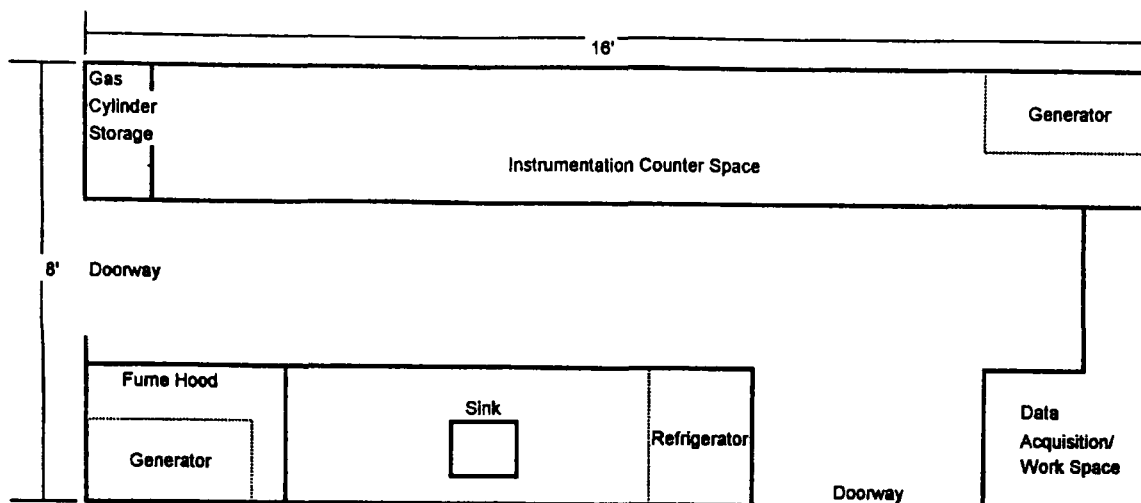


Figure 2-1. Diagram of the mobile laboratory floor plan.

instrument developer, and because the instrument was designed for use in a fixed laboratory. The instrument may be considered field mobile rather than field portable.

Technology Performance

The analytical capabilities of the Pace AAS system as reported by Pace Environmental Laboratories are presented in Table 2-1. Minimum detection levels and accuracy and precision data are given in the table for the target elements in this demonstration.

Table 2-1. AAS System Capabilities as Reported by Pace Environmental Laboratories

Element	Minimum Detection Level (mg/kg)	Upper Conc. Limit (mg/kg)	Accuracy (%)	Precision (%)
Silver (Ag)	0.5	200	± 10	± 20
Arsenic (As)	12.5	5000	± 10	± 20
Cadmium (Cd)	0.25	100	± 10	± 20
Chromium (Cr)	2.5	250	± 10	± 20
Copper (Cu)	1.0	250	± 10	± 20
Iron (Fe)	1.5	300	± 10	± 20
Manganese (Mn)	0.5	100	± 10	± 20
Lead (Pb)	5.0	1000	± 10	± 20
Zinc (Zn)	0.25	50	± 10	± 20

Operational Procedure

All soil samples were digested in accordance with EPA SW-846 Method 3050A, *Acid Digestion of Sediments, Sludges, and Soils*. Atomic absorption measurements were carried out using EPA SW-846 Method 7000A. The specific methods for each of the target elements are given below:

Arsenic	None (A nonstandard direct aspiration method was used)
Cadmium	Method 7130: cadmium (atomic absorption, direct aspiration)
Chromium	Method 7190: chromium (atomic absorption, direct aspiration)
Copper	Method 7210: copper (atomic absorption, direct aspiration)
Lead	Method 7420: lead (atomic absorption, direct aspiration)
Iron	Method 7380: iron (atomic absorption, direct aspiration)
Manganese	Method 7460: manganese (atomic absorption, direct aspiration)
Silver	Method 7760A: silver (atomic absorption, direct aspiration)
Zinc	Method 7950: zinc (atomic absorption, direct aspiration)

Quality Control

The analytical procedure incorporated a number of quality control samples. Initial and continuing calibrations were run in the same manner as that for the reference laboratories (described in Chapter 4). Method blanks were also prepared and periodically run throughout the analysis sequence. One out of every 20 of the soil samples was split and the split spiked with a known amount of each target element. Element recoveries were then determined in the same manner as that for the reference laboratories (described in Chapter 4). Additional information concerning the quality control sample results is given in Chapter 5.

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. ^a	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)

^aPoint of contact: Jim Archer (612) 525-3475.

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.

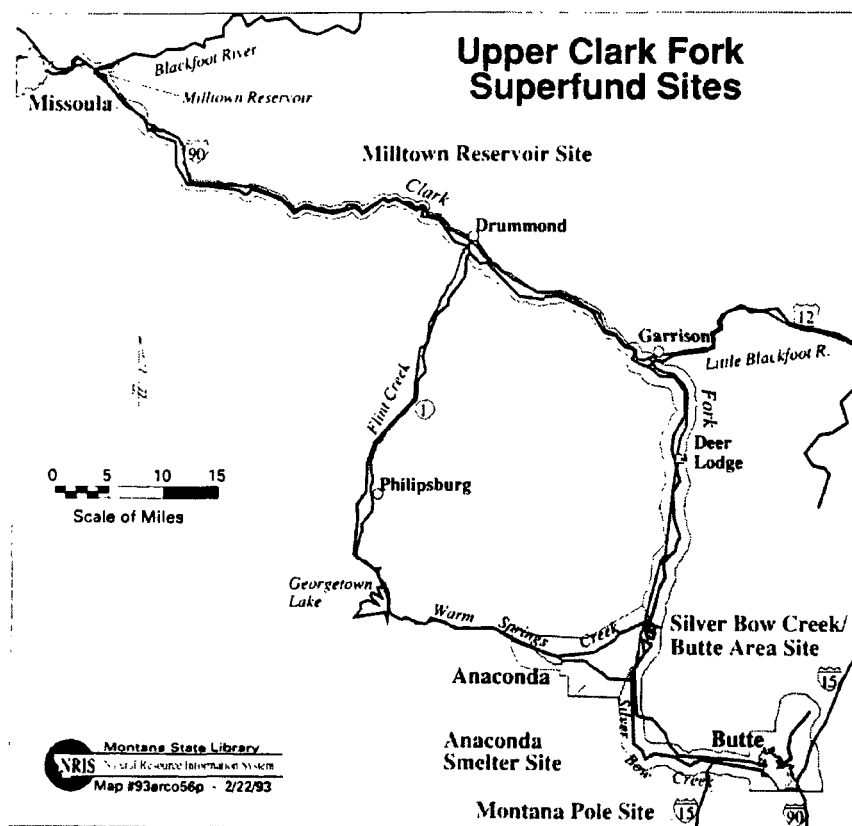


Figure 3-1. Montana regional map showing the Silver Bow and Mill Creek (Anaconda) sampling sites.

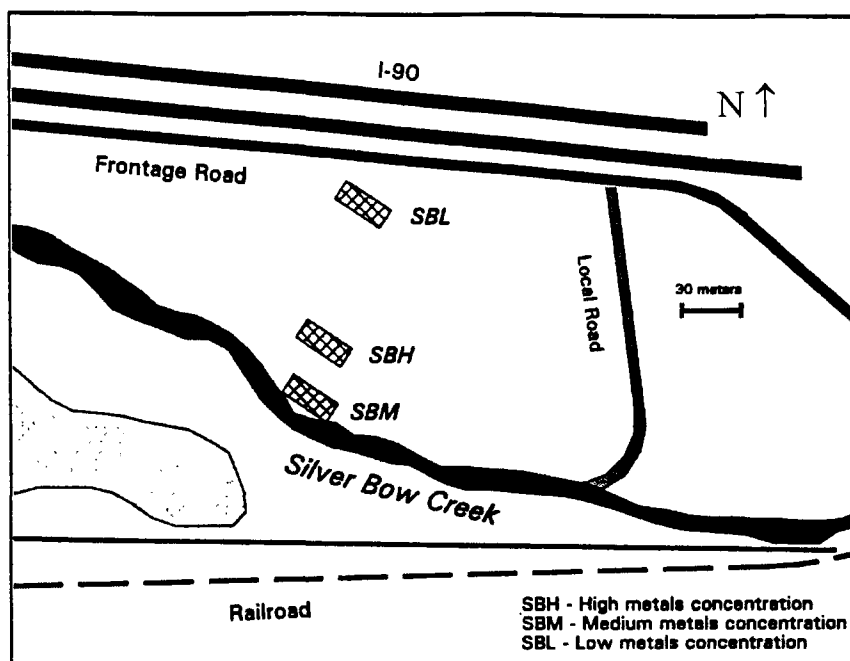


Figure 3-2. Local map of the Silver Bow sampling site.

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).¹ A 27-m, northwest-to-southeast transect of the SBHD sample area was divided into ten 400-cm² 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-cm² 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-

¹ 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-cm² 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 km² 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.

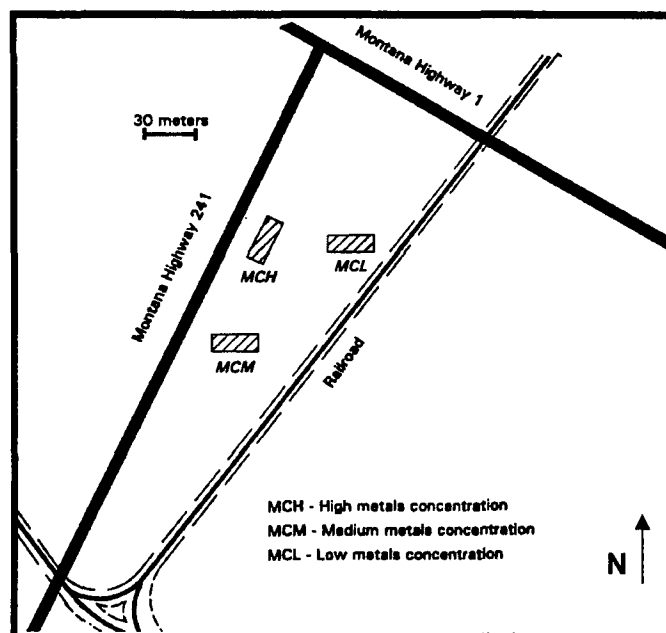


Figure 3-3. Local map of the Mill Creek sampling site.

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 m³ 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).² A 27-m, southwest-to-northeast transect of the MCHD sample area was divided into ten 400-cm² 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-cm² 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.

² 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-cm² 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-cm² 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-cm³ labeled glass containers. Each 1,000-cm³ 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) ^a
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

^a 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 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”¹ for each element in the sample. The results from the control samples from each of the laboratories were

¹ 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 ± 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 ± 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

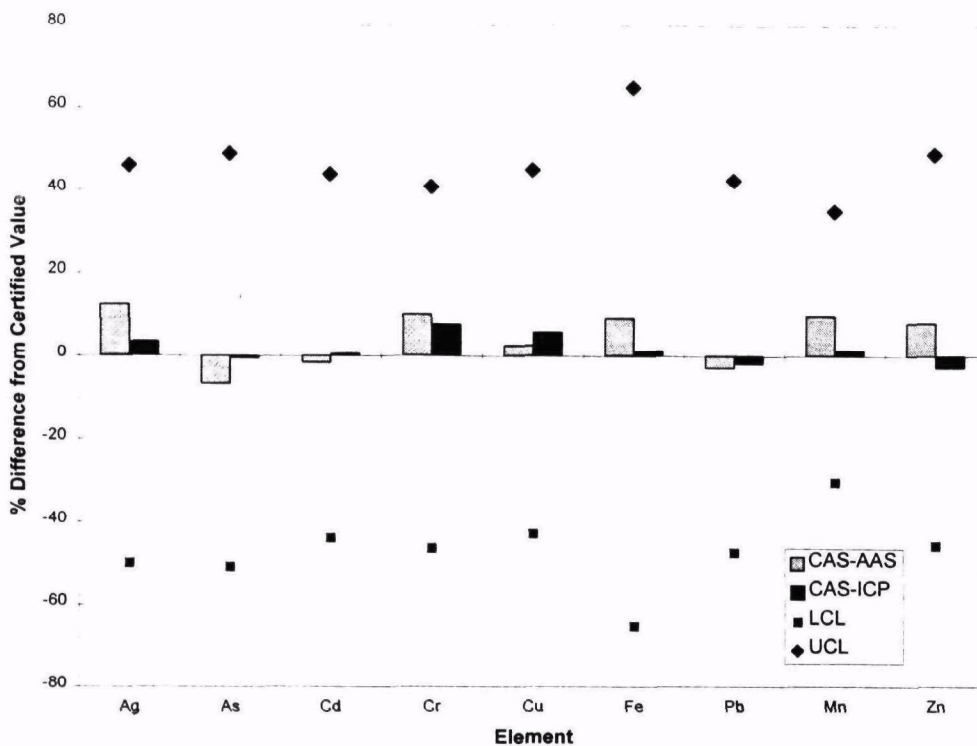


Figure 4-1. Control soil sample analysis results from CAS. The upper and lower 95 percent confidence limits with respect to the certified values are also shown.

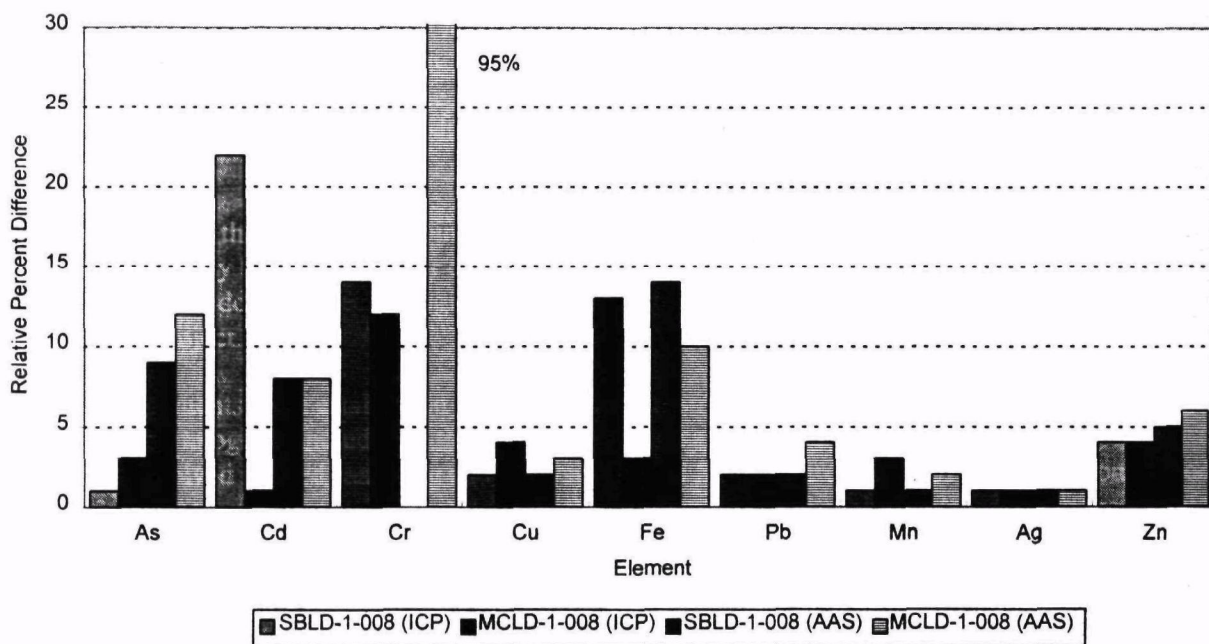


Figure 4-2. Duplicate soil sample analysis results from CAS.

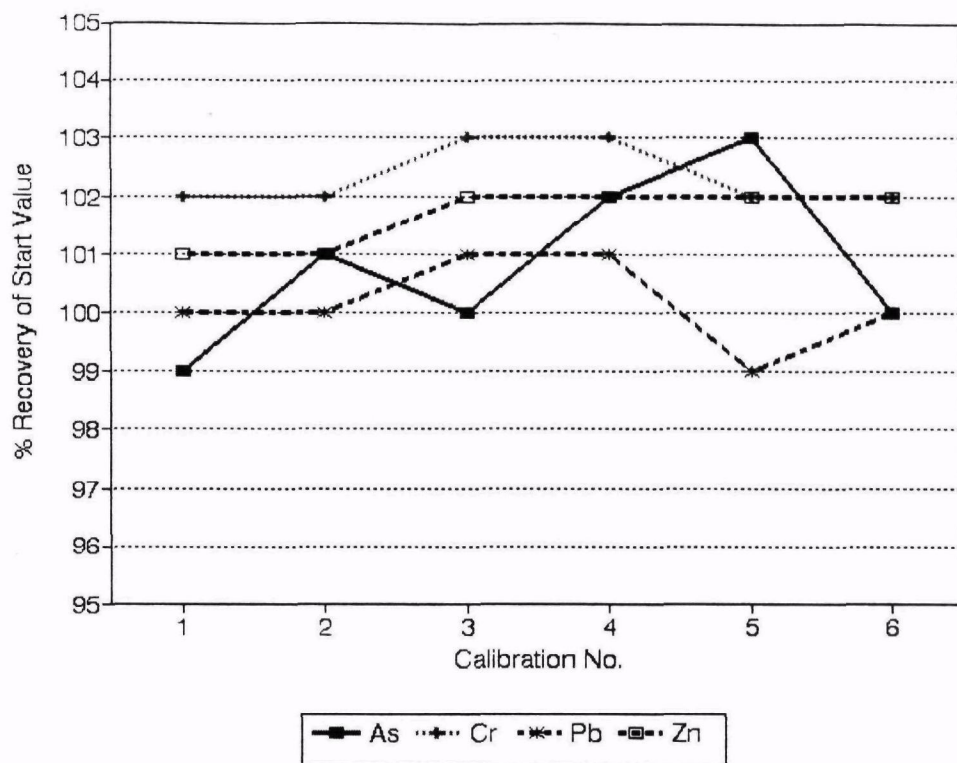


Figure 4-3. Continuing calibration verification results from CAS.

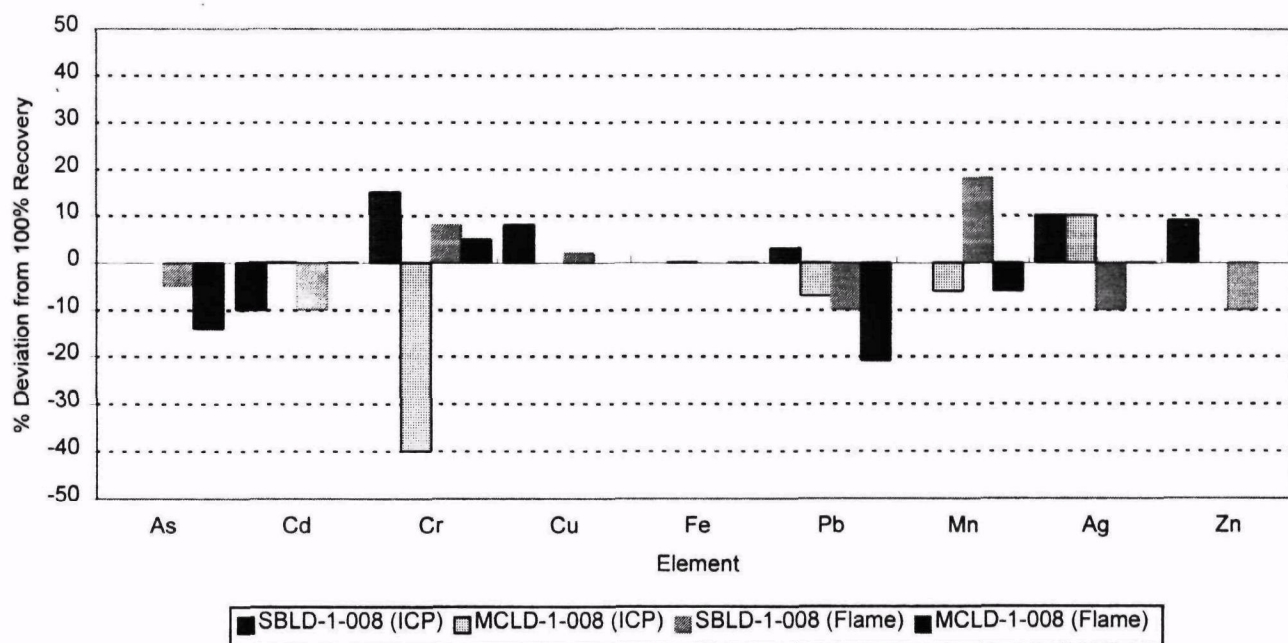


Figure 4-4. Spiked soil sample recovery results from CAS. See text for explanation of missing data.

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 ± 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 ± 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 (± 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 ± 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 ± 10 percent limit of these

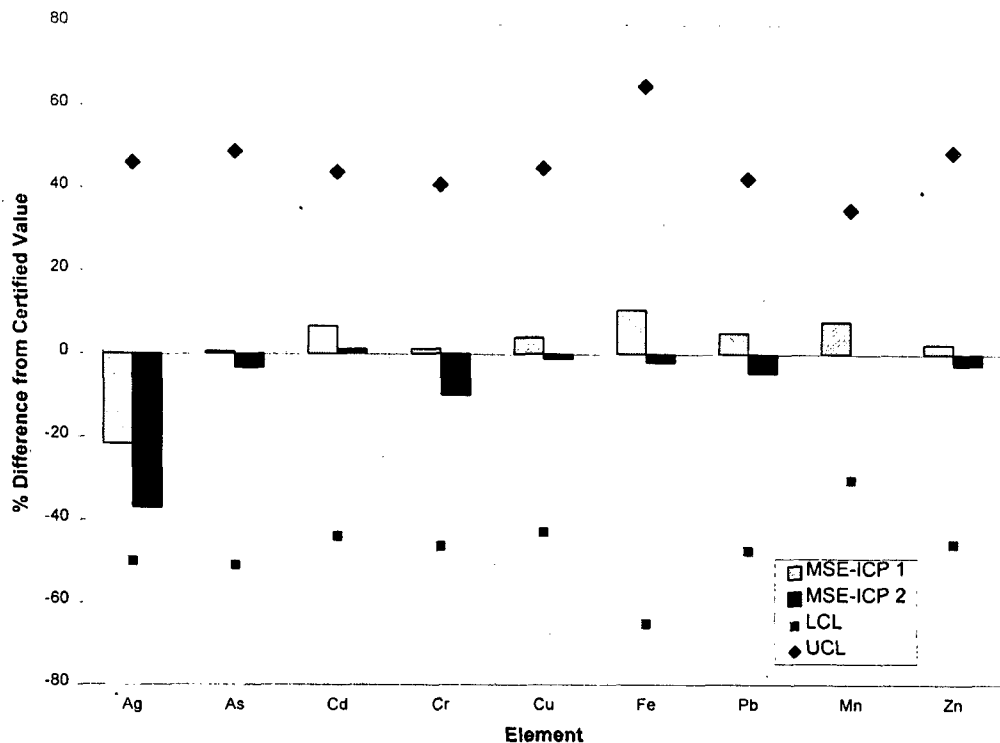


Figure 4-5. Control soil sample results from MSE. The upper and lower 95 percent confidence limits with respect to the certified values are also shown in the graph.

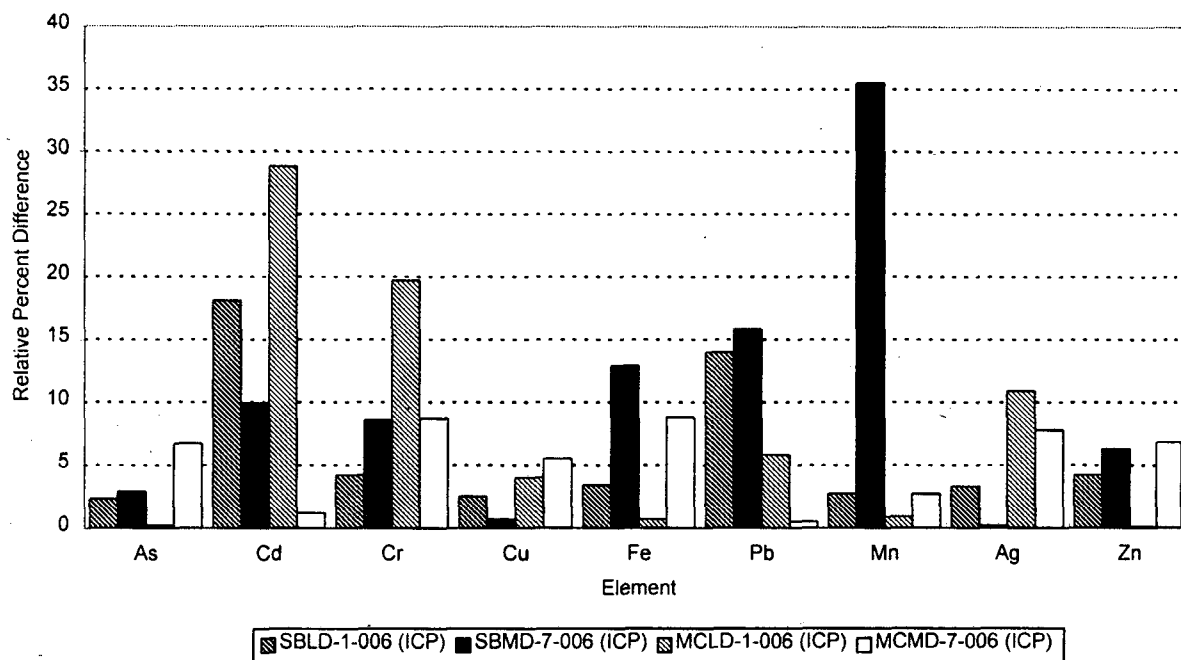


Figure 4-6. Duplicate soil sample results from MSE.

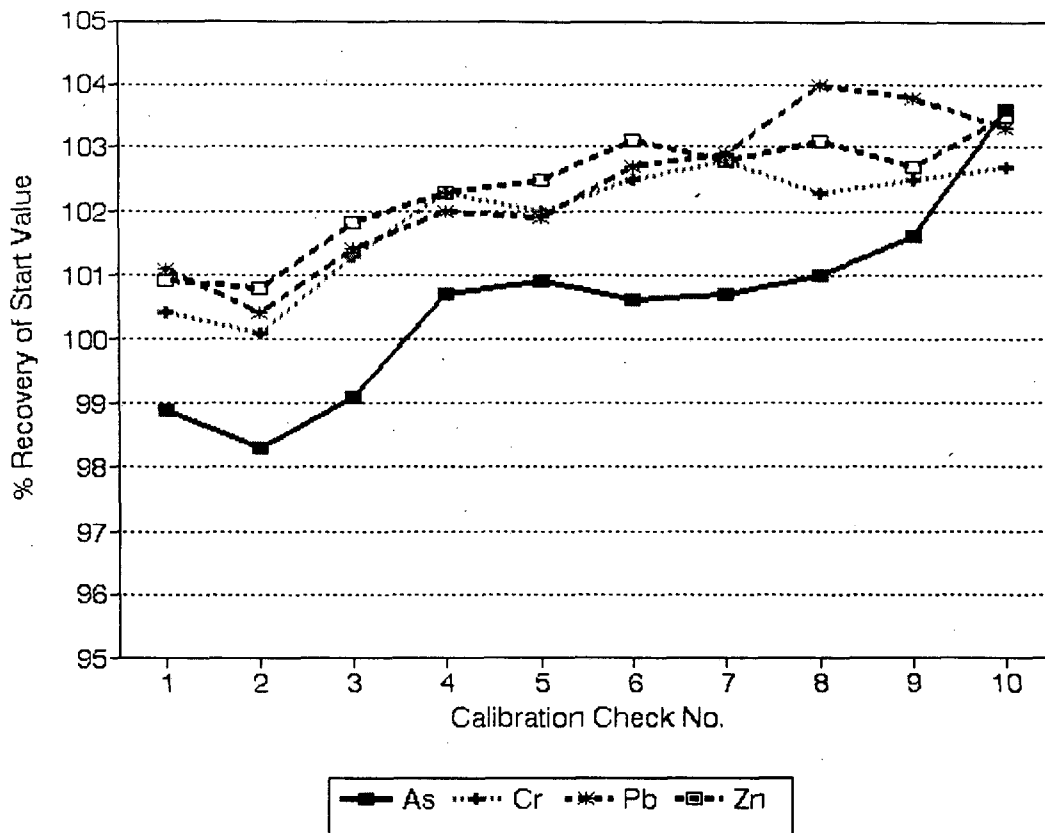


Figure 4-7. Continuing calibration verification results from MSE.

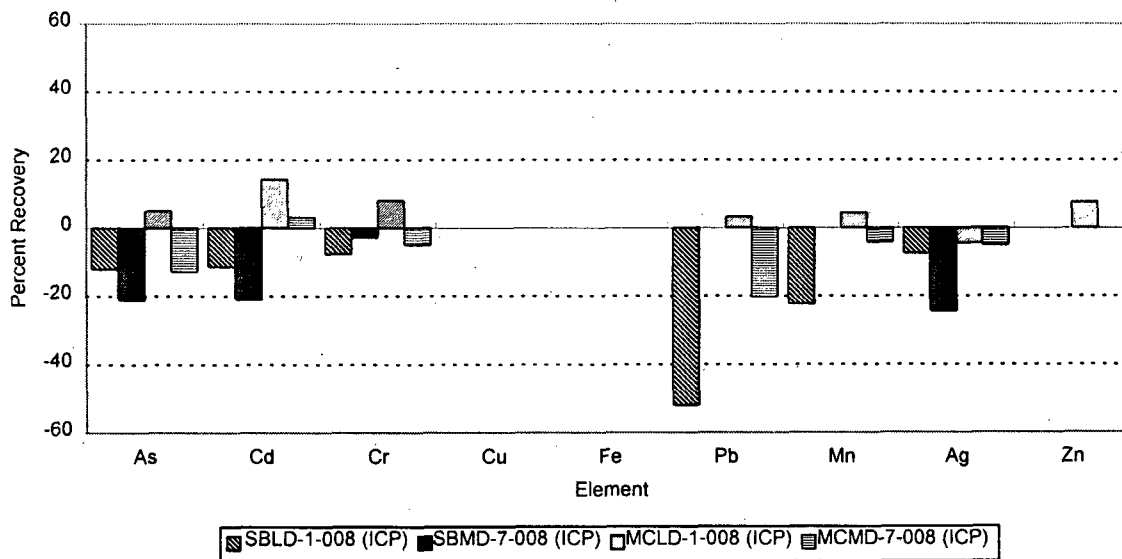


Figure 4-8. Spiked soil sample recovery results from MSE. See text for explanation of missing data.

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	62	2.7	4.2	100
As	24	0.9	4.1	6.8
Cd	48	8.3	64	39
Cr	17	71	7.0	11
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	13
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 ± 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 ± 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 ± 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 ± 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.

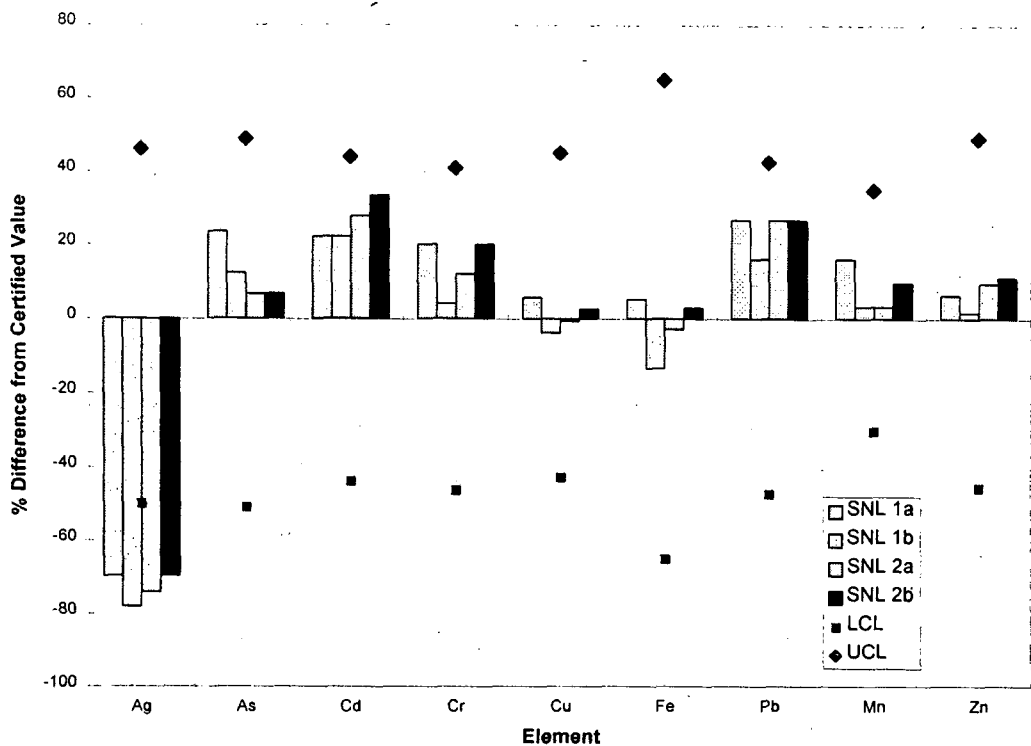


Figure 4-9. Control soil sample results from SNL. The upper and lower 95 percent confidence limits with respect to the certified values are also shown in the graph.

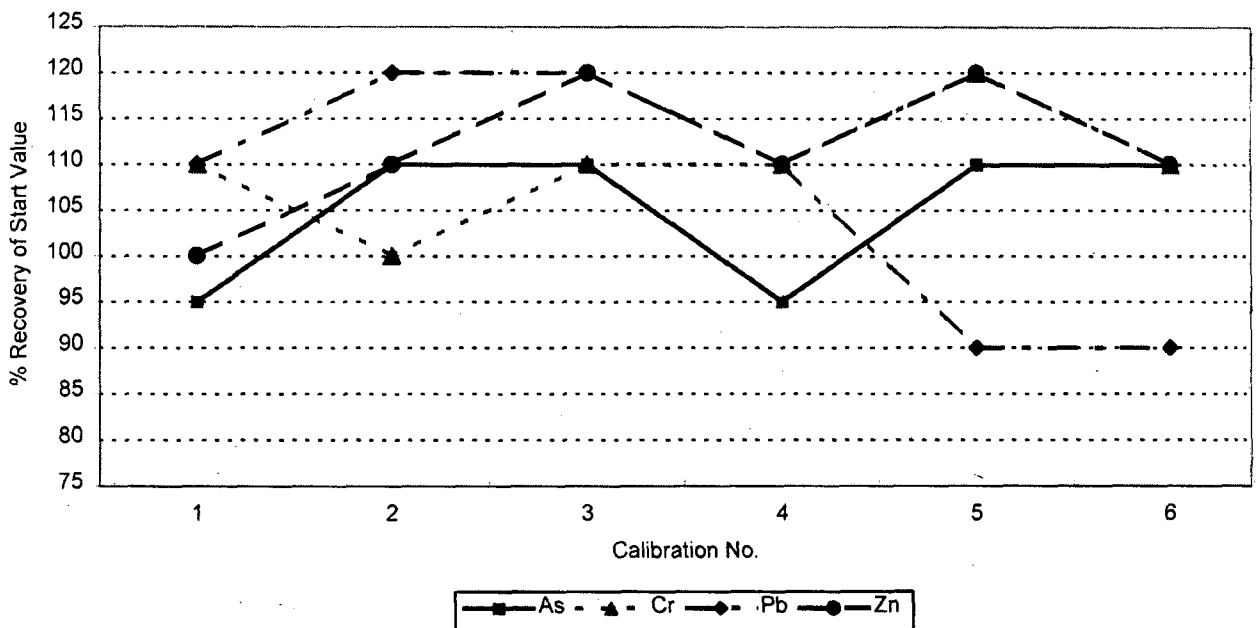


Figure 4-10. Continuing calibration verification results from SNL.

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 ± 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

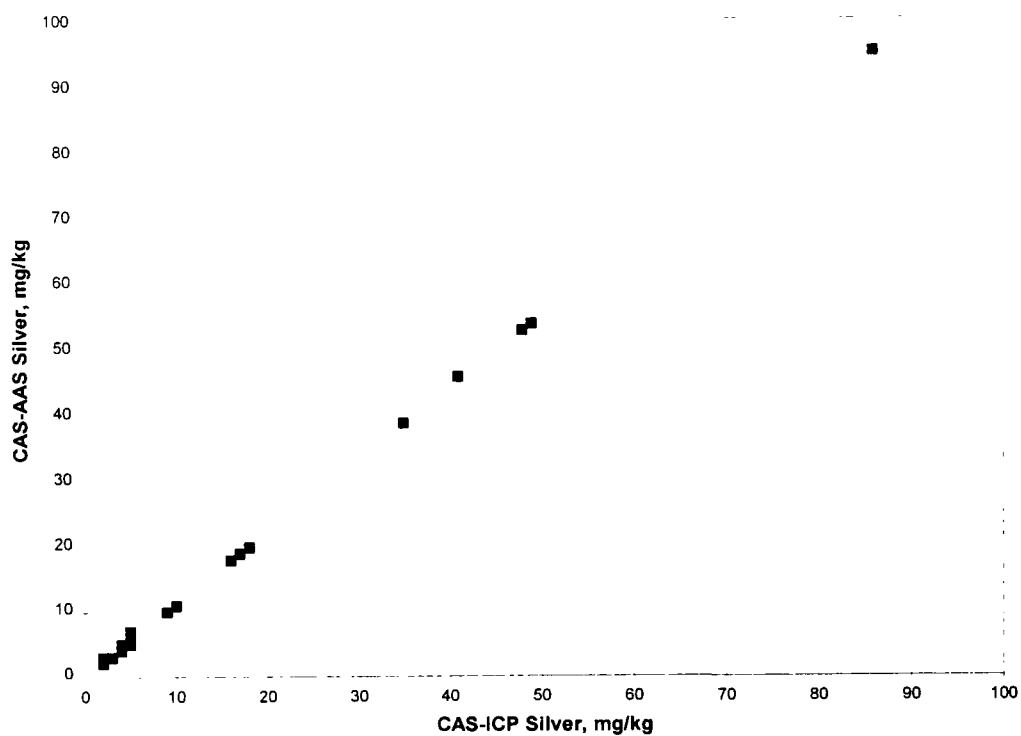


Figure 4-11. CAS AAS vs. CAS ICP silver measurements on field replicate soil samples.

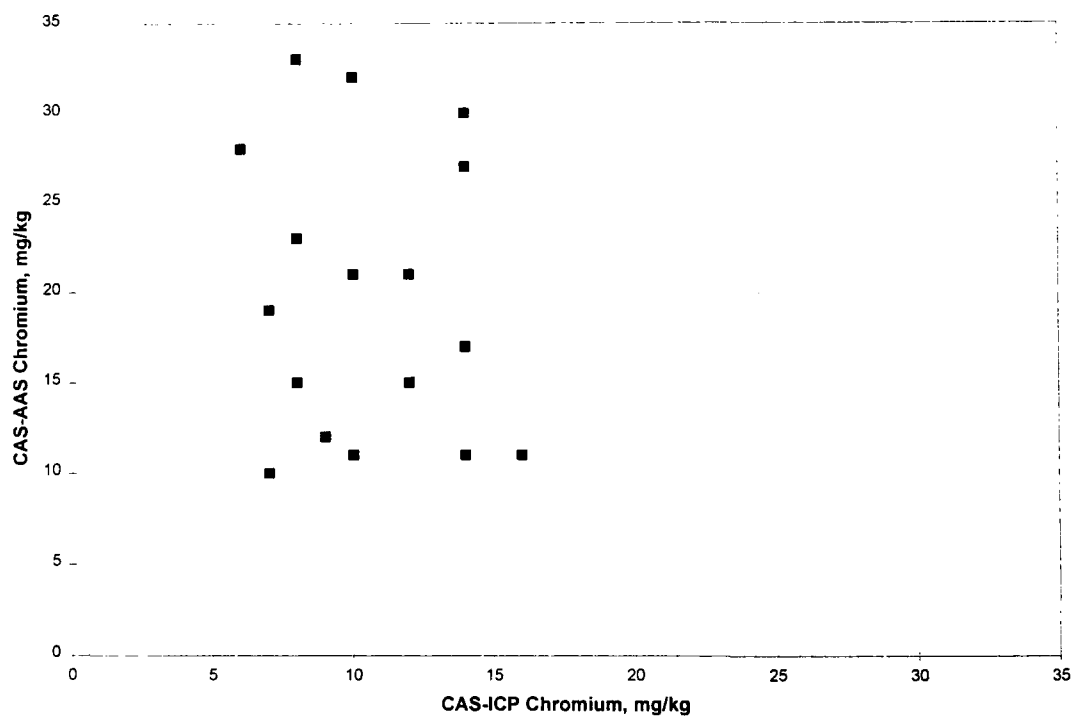


Figure 4-12. CAS AAS vs. CAS ICP chromium measurements on field replicate soil samples. Nondetectable results are not shown in the plot.

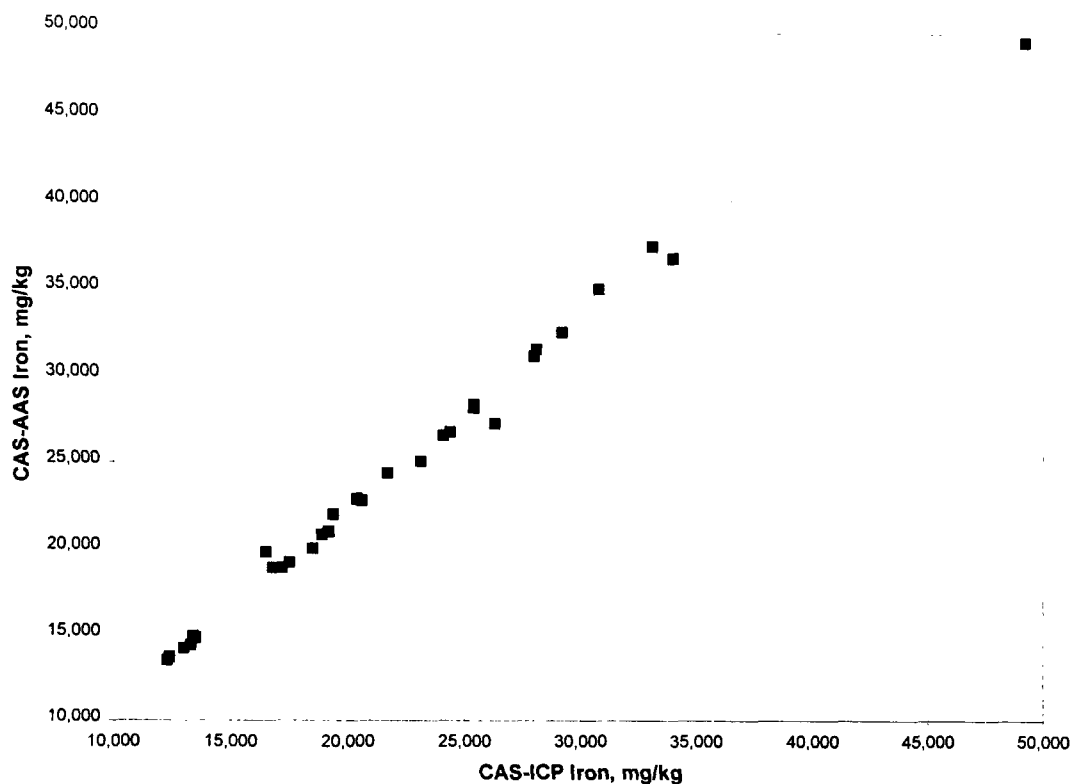


Figure 4-13. CAS AAS vs. CAS ICP iron measurements on field replicate soil samples.

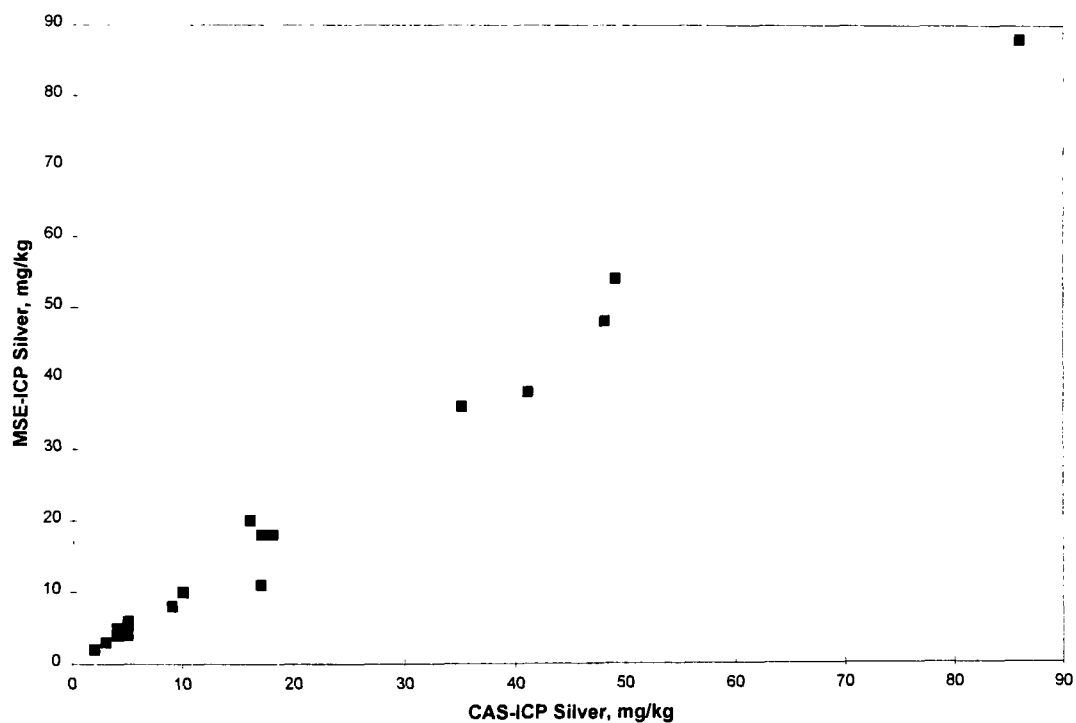


Figure 4-14. MSE ICP vs. CAS ICP silver measurements on field replicate soil samples.

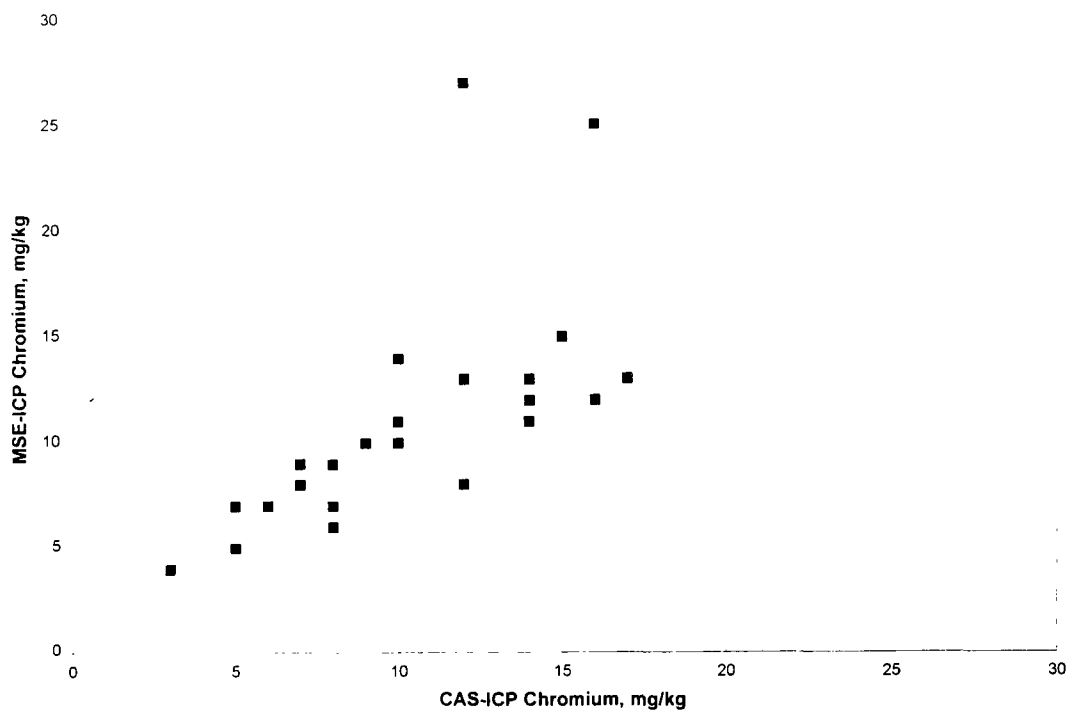


Figure 4-15. MSE ICP vs. CAS ICP chromium measurements on field replicate soil samples.

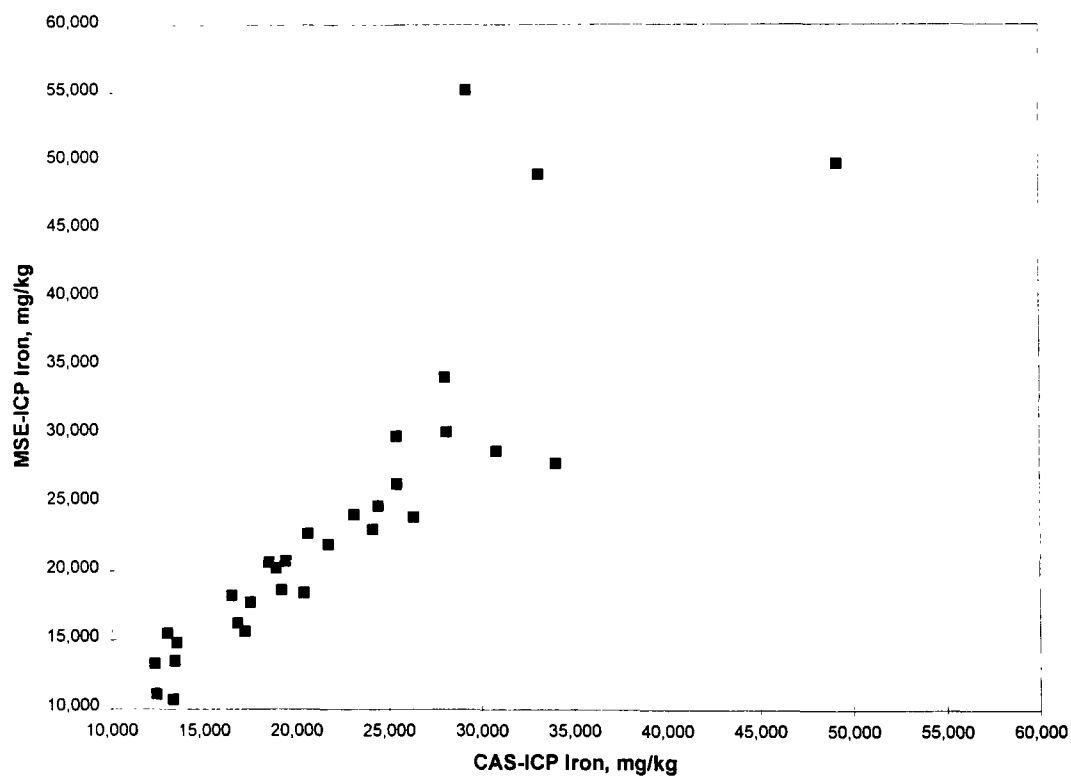


Figure 4-16. MSE ICP vs. CAS ICP iron measurements on field replicate soil samples.

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 ± 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 ± 10 percent is relatively small and acceptable in light of the ± 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-to-Laboratory Data Comparison Methods

The Pace AAS was designated a Level 2 technology. Consequently, a more rigorous evaluation was carried out than that done for a Level 1 technology. Performance indicators quantitatively evaluated in this process included instrument performance for each of the nine target elements relative to well-characterized control standards; instrument precision for the same target elements as determined from the analysis of replicate samples; and a comparison of Pace AAS data with the reference laboratory data set. The field soil sample analysis data are presented in Appendix A in tabular format with the results from each laboratory and the laboratory average shown alongside the Pace AAS results, sample-by-sample, for each target element. In this chapter the Pace AAS data are plotted against reference laboratory data. Linear regression analysis and nonparametric statistical analyses, virtually the same as those used for the reference laboratory data set intercomparison in Chapter 4, are also used to assess the overall comparability of the Pace AAS data relative to laboratory reference data.

Field Observations

Periodically during the demonstration, an observer checked in with the Pace AAS analysis team to monitor progress. With the exception of one hollow cathode lamp failure, for which a replacement was quickly obtained, no instrument malfunctions or breakdowns were encountered. The Pace team 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. Although the weather during the demonstration was occasionally rainy, windy, and cold, it did not appear to adversely affect the performance of the Pace-operated system.

General Description of Pace AAS Results

The Pace AAS analysis team produced a complete report in which an analysis result (either a detected amount or an indication of nondetectable) was obtained for all samples submitted for analysis. A total of 60 field soil samples plus 2 control soil samples and 2 blank soil samples were analyzed with the Pace AAS system for 9 target elements. Two of the field soil samples were also analyzed a second time in order to obtain an estimate of instrument analytical precision. The analysis team also prepared a number of internal quality control samples, such as method blanks and calibration standards, for additional evaluation of instrument performance.

Quality Control Sample Results

The results of the Pace AAS analyses of quality control samples are presented in the following sections. Where applicable, the results are presented in a format similar to that used in the evaluation of the reference laboratory data in Chapter 4.

Blank Soil Sample Analysis

A comparison of Pace AAS and certified levels for blank soil samples is given in Table 5-1. The MSE laboratory results are also shown in the table. The Pace AAS results compare reasonably well with certified and laboratory levels for all elements except As. The As detection limit was reported at a relatively high level of 15 mg/kg. The limit was high since analyses for all target elements, including As, were performed using direct sample aspiration into an air-acetylene flame. A comment is made in the Pace analysis report that As analysis should normally be done by either hydride flame AAS or by graphite furnace AAS. The system used had neither capability, so conventional air-acetylene flame aspiration was used, with a resulting loss in performance for As.

Table 5-1. Blank Soil Sample Results for Pace AAS

Element	Metal Concentration Level (mg/kg)		
	Pace AAS	MSE ICP	Certified Level
As	<15	2.1	<2
Cd	0.6	0.4	<1
Cr	6	6.7	7
Cu	6	5.6	<5
Fe	8,650	7,740	8,180
Pb	9	9.3	9
Mn	190	172	159
Ag	<2.5	0.4	<2
Zn	28	24.4	24

Notes: All Pace data shown are an average of two measurements. A "less than (<)" symbol indicates not detected. The number following the symbol is the reported detection limit for the instrument.

Control Soil Sample Analysis

Control soil samples, with well-defined concentration levels of target elements, were analyzed by all participants in the demonstration, including the Pace analytical team. Control sample results, expressed in terms of a percentage difference from a certified concentration level of each element in the control soil sample, are given for the Pace AAS system in Figure 5-1. The plotted data show Pace AAS analysis results within the 95 percent upper and lower confidence limits about the mean certified value for all elements except one As measurement. All other target element determinations fall within ± 25 percent of the certified soil control sample value. As noted earlier, this particular instrument configuration was not optimized for As analysis. Normally, As analysis is done with either a hydride flame or a graphite furnace accessory. In this case arsenic was analyzed by direct aspiration, with some resulting loss in sensitivity.

Duplicate Sample Analysis

Results from Pace AAS duplicate analyses of two specified soil samples are graphically shown in Figure 5-2. With a few exceptions, the reported relative percent difference of the target elements are 20 percent or less. A pair of Ag measurements resulted in a difference value of 47 percent, and a pair of Cr measurements had a value of 30 percent. The Cu analysis on sample MCMD-1-005 was reported at the same level for both analyses, resulting in a difference value of 0 percent, which is not indicated on the graph. The results of duplicate sample analysis indicate generally acceptable instrument performance with regard to analytical precision.

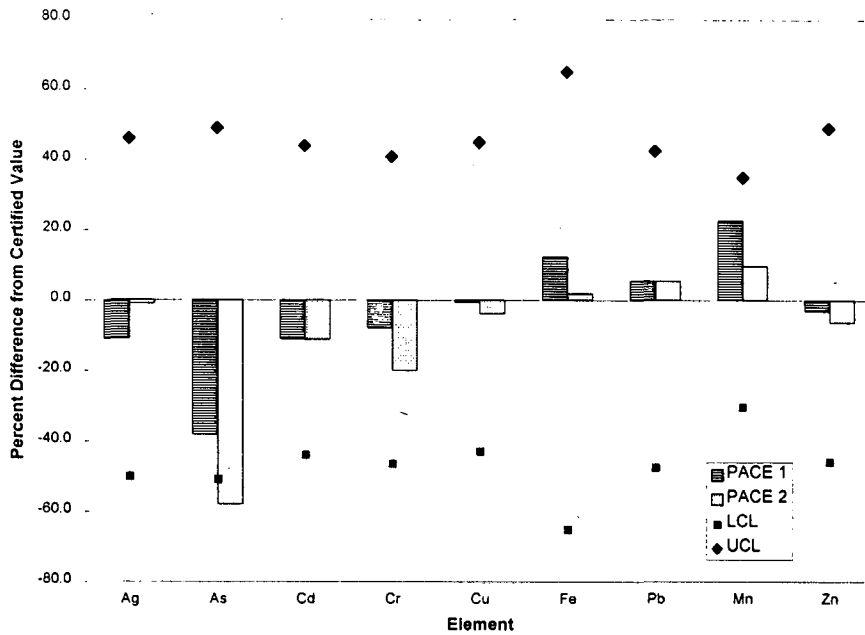


Figure 5-1. Control soil sample analysis results from the Pace AAS. The upper and lower confidence limits with respect to the certified levels are also shown on the graph.

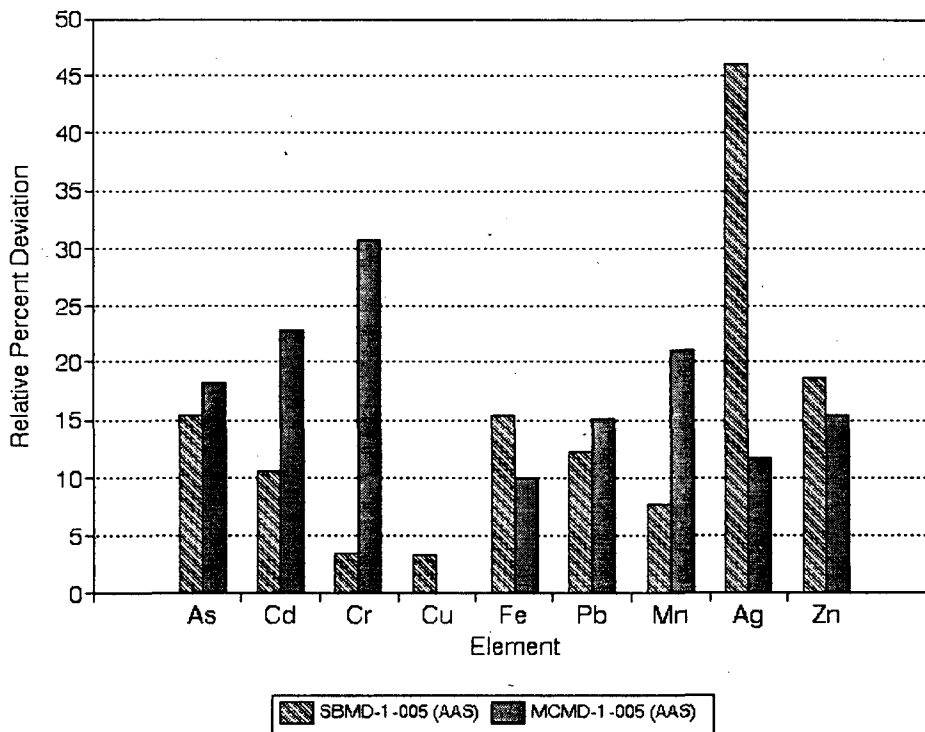


Figure 5-2. Duplicate sample analysis results from the Pace AAS.

Recovery Analysis

Spiked sample recovery analysis results are shown in Figure 5-3. Data are shown only for Ag, As, Cd, and Cr. The spike levels for the remaining target elements were less than 25 percent of the amount in the sample prior to the spike; consequently no recovery data are reported for these elements. Recovery data, where available, fall within the 75 to 125 percent (–25 to 25 percent deviation from 100 percent recovery) criteria specified in the EPA Method 7000A analysis protocol.

Field Soil Sample Analysis Results

Analysis results were reported for all 60 field soil samples submitted to the Pace AAS analysis team during the demonstration. The data are presented in two formats to assist in comparing the demonstration technology data against the data set produced from laboratory analysis of field replicates of soil samples. First, a series of eight plots (Figures 5-4 through 5-11) are given in which the Pace AAS field soil sample data for each target element are plotted against the reference laboratory data set. A scatter plot is not shown for Cr since the reference laboratory data were of unacceptable quality for particular elements. As a part of the laboratory data validation process, data from the CAS ICP, CAS AAS, and MSE ICP analyses were averaged together to yield a reference laboratory value. (See Chapter 4 for a discussion of the makeup of the reference laboratory data set.) Although all data are plotted, in many cases the dots on the scatter plots are overlaid and are thus indistinguishable from each other.

In general, the scatter plots reveal very good correlation between the Pace AAS and reference laboratory data sets. Although it is not shown, the worst comparison was for chromium. Chromium analysis results from all laboratories were highly variable and it appears that results from the mobile Pace AAS instrument are similarly uncertain. The Cr levels encountered in the field soil samples were in general very close to the detection limits of the various analytical methods used in these analyses. Consequently, the noise levels in the Cr determinations from all techniques are comparatively larger, contributing to greater uncertainty in the analysis results from the laboratory systems as well as the Pace mobile system.

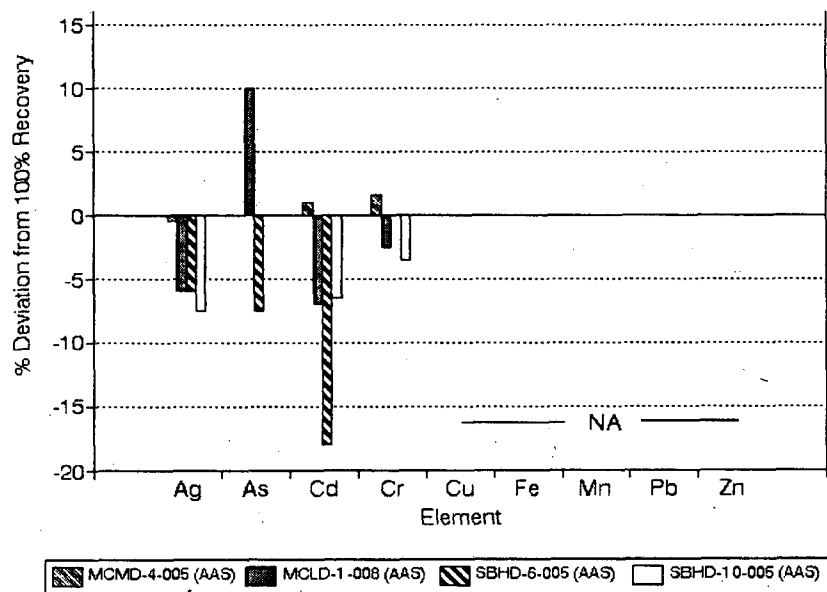


Figure 5-3. Spike recoveries for Pace AAS. The “NA” indicates that the spike level was too low for reliable quantification.

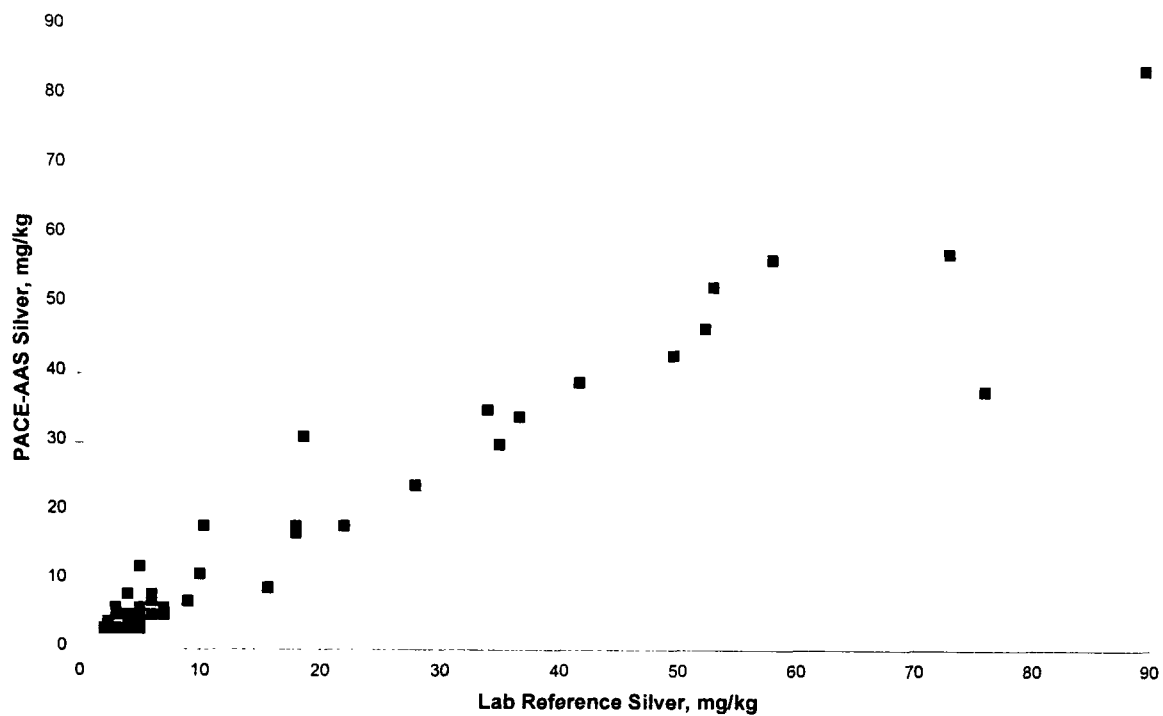


Figure 5-4. Pace AAS vs. reference laboratory silver.

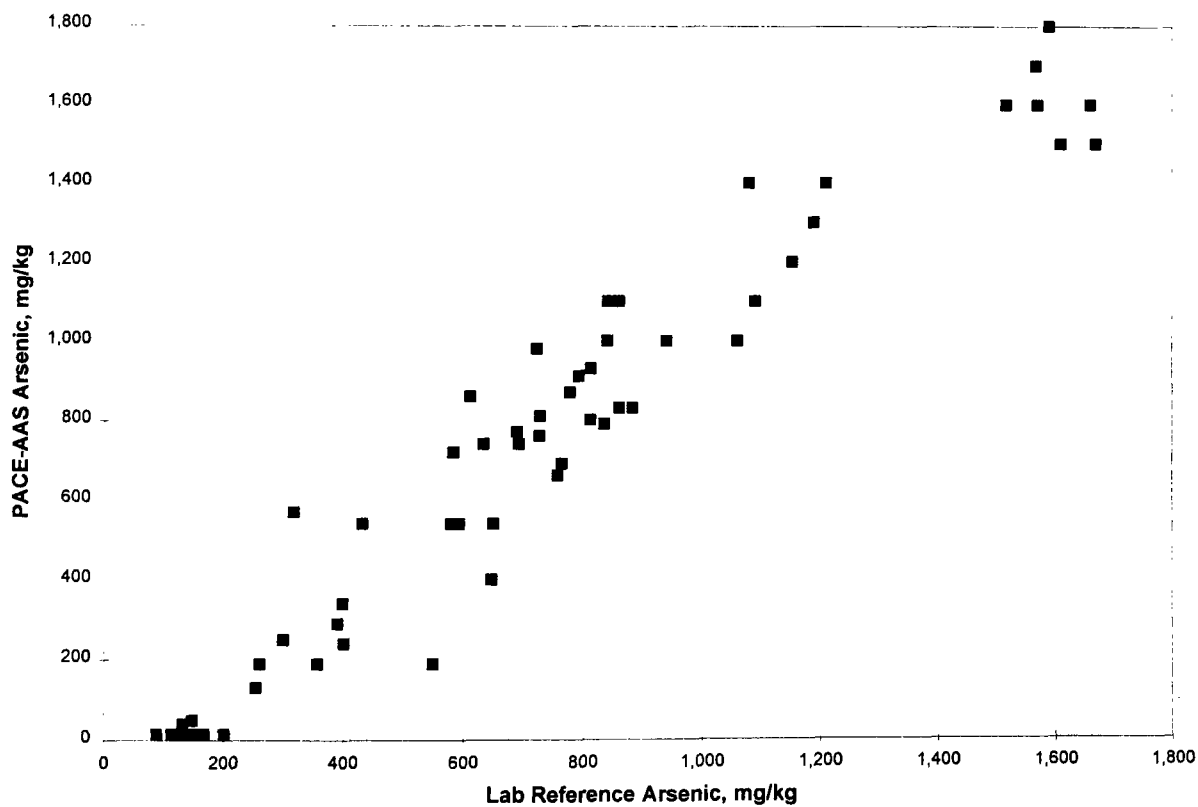


Figure 5-5. Pace AAS vs. reference laboratory arsenic.

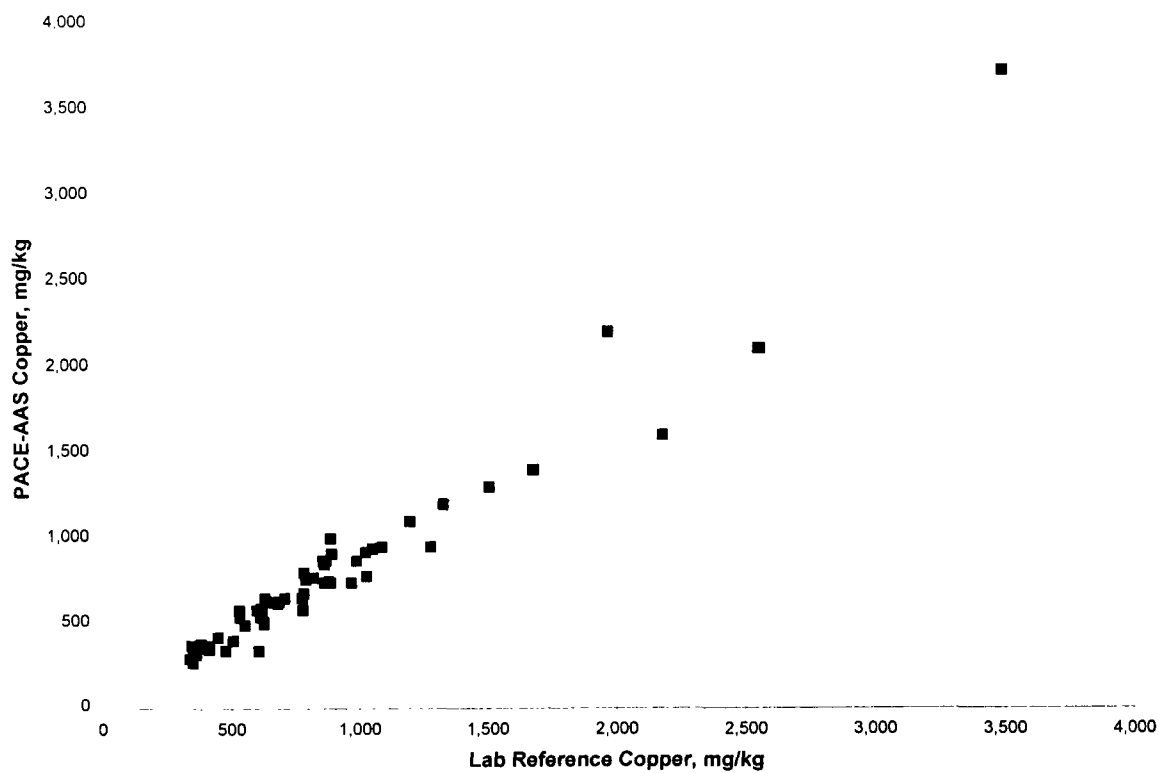


Figure 5-6. Pace AAS vs. reference laboratory copper.

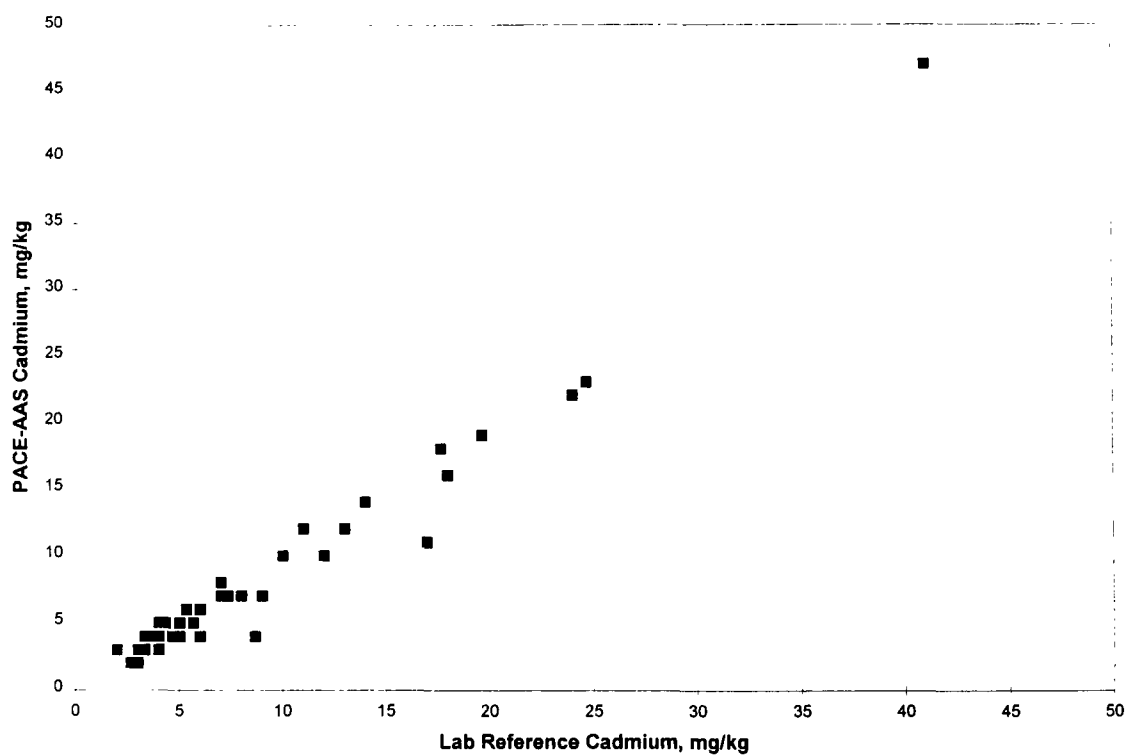


Figure 5-7. Pace AAS vs. reference laboratory cadmium.

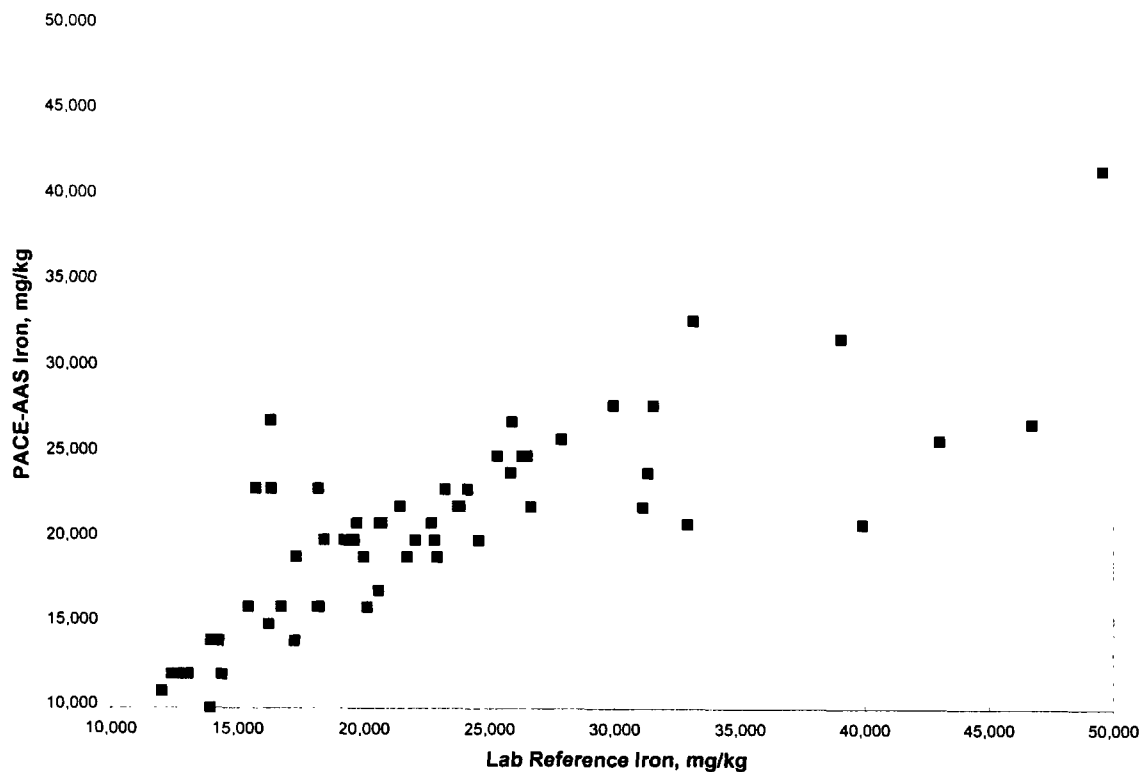


Figure 5-8. Pace AAS vs. reference laboratory iron.

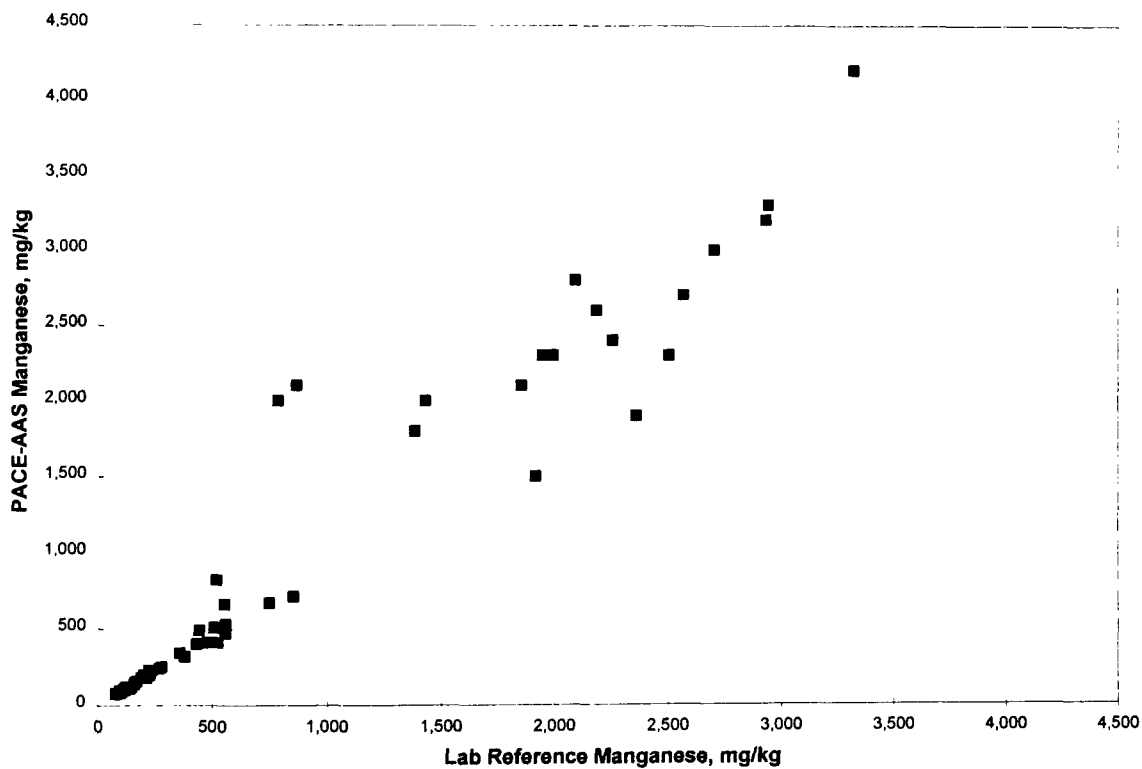


Figure 5-9. Pace AAS vs. reference laboratory manganese.

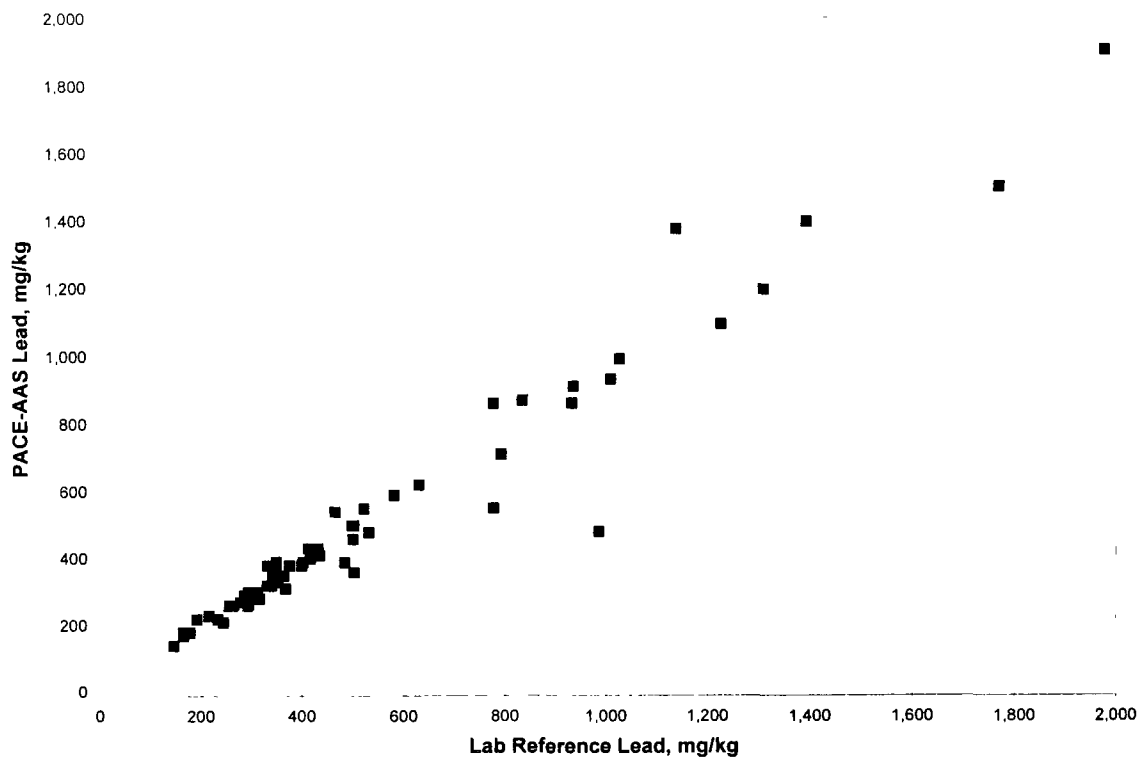


Figure 5-10. Pace AAS vs. reference laboratory lead.

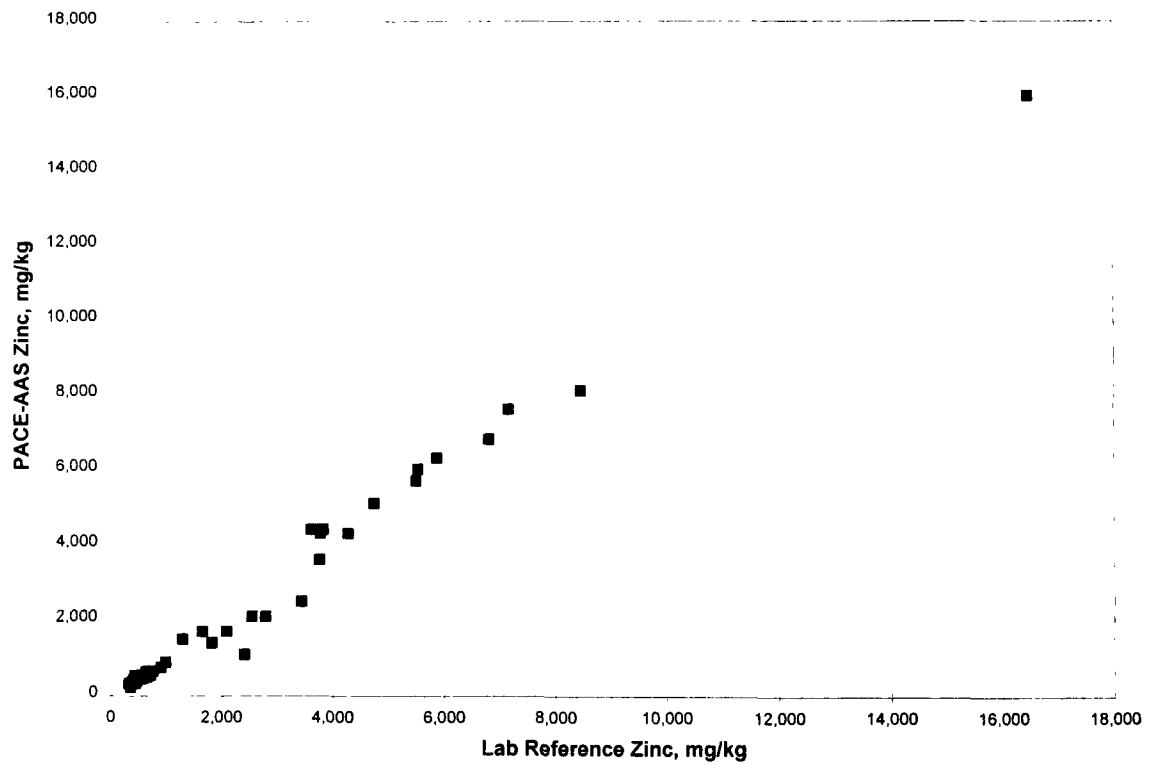


Figure 5-11. Pace AAS vs. reference laboratory zinc.

The Pace AAS data are also presented in tabular form in Appendix A to facilitate their comparison with individual reference laboratory results. A series of tables give the 60 sample analysis results for CAS ICP, CAS AAS, MSE ICP, reference laboratory, and Pace AAS analysis for each of the nine target elements.

Comparison of Pace AAS Results with Reference Laboratory Data

The following analytical approaches yield a quantitative measure of the agreement between the Pace AAS data and the laboratory reference data set.

Mean Percent Difference

The mean percent differences, as defined in Chapter 4, between Pace AAS and reference laboratory data sets are given in Table 5-2. A small value for the mean percent difference and an accompanying small low standard deviation is an indicator of good comparability between methods. In general, the results for the Pace AAS data are quite good. Mean percent difference levels are generally less than 10 percent, with accompanying small standard deviations. The poorest mean percent differences are encountered with Cr. Relatively low Cr levels were encountered in the soil samples, resulting in greater uncertainty in these measurements from both the Pace mobile system and reference laboratory systems used in this comparison.

Table 5-2. Mean Percent Difference for Pace AAS and Reference Laboratory Data

Element	Mean Percent Difference Laboratory Data
Ag	-6.5 ± 25.7
As	-16.2 ± 41.3
Cd	-6.0 ± 17.5
Cr	-24.7 ± 25.9
Cu	-10.2 ± 10.7
Fe	-7.2 ± 19.0
Mn	4.5 ± 31.6
Pb	-0.6 ± 11.8
Zn	-7.6 ± 14.2

Note: The mean value is followed by the standard deviation.

Correlation Coefficients

Linear regression results and correlation coefficients between the Pace AAS data set and the reference laboratory data set are given in Table 5-3. Correlation coefficients near unity reveal good linear correlation between the data sets. Values near zero reveal no data correlation. Correlation coefficients are greater than 0.9 for all elements except Cr and Fe. The slopes of the computed regression lines reveal additional information about the linear relationship between the two data sets. Slopes near unity indicate close comparability of the two methods. Nearly all elements have slopes in the range of 0.84 to 1.12. Two elements, Cr and Fe, have slopes significantly different from unity.

Table 5-3. Linear Regression Parameters for Pace AAS and Reference Laboratory Data

Element	Slope	Intercept (mg/kg)	Correlation Coefficient
Ag	0.84	1.0	0.96
As	1.12	-86	0.97
Cd	1.01	-0.5	0.98
Cr	0.28	4.9	0.43
Cu	0.92	-23	0.97
Fe	0.59	7000	0.80
Mn	1.12	0.6	0.97
Pb	0.91	33	0.97
Zn	1.00	-64	0.99

Statistical Bias Testing

The Wilcoxon matched pairs test was used to compare the Pace AAS and the reference laboratory data sets for statistically significant bias. The Wilcoxon test is a nonparametric test that assumes no underlying distribution in the data sets being compared and is well suited for paired data such as these. The test assesses the likelihood that observed differences between two methods are a result of random error.

The results of the Wilcoxon test for each of the nine target elements are summarized in Table 5-4. Varied results are noted. The Pace AAS and reference laboratory data are, statistically speaking, indistinguishable from each other for three of the nine target elements. The data sets for the other six elements are not statistically equivalent. These results must be understood in light of the correlation data shown in Table 5-3, however. The statistical test can detect a small bias in the two methods. For example, the slope of the comparison between Cd is reported as 1.01, with a correlation coefficient of 0.98, revealing very good agreement between the data sets. Nonetheless, the statistical test detects a consistent but small bias in the two data sets. The statistical test should be used in conjunction with a regression analysis or some other measure of overall differences between a reference and test method. The primary value of the statistical test is in the answer it yields for such elements as As, Mn, and Pb. The test indicates that no statistically significant bias exists between the two methods and that

Table 5-4. Results from the Wilcoxon Paired Sample Statistical Test

Element	Significant Bias? (p-value)
	Pace AAS vs. Laboratory Ref
Ag	Yes (<0.05)
As	No (0.72)
Cd	Yes (<0.05)
Cr	Yes (<0.05)
Cu	Yes (<0.05)
Fe	Yes (<0.05)
Mn	No (0.78)
Pb	No (0.50)
Zn	Yes (<0.05)

further bias comparisons are unwarranted for these particular elements. The observed differences between the two methods can be explained by random variability in the results. The p-value associated with the test is also given in the table. A p-value of 0.05 indicates that a 5 percent chance is associated with the assumption that the observed differences are caused by random variability alone. A p-value of 0.05 is normally used as the decision point for a statistically significant bias. Values less than 0.05 indicate bias and values greater than 0.05 reveal no bias.

The mean percent difference data in Table 5-2 give a measure of the method bias relative to the reference laboratory data. For seven of the nine target elements, the mean percent difference is ± 10 percent or less. Exceptions are encountered for As (-16 percent) and Cr (-25 percent).

Performance Evaluation Conclusions

Accuracy

The accuracy of the Pace AAS system was assessed by comparing Pace AAS results from control soil sample analyses with certified levels in the samples. In all determinations except one As measurement, the Pace AAS gave results consistent with known soil concentration levels for the nine target elements. A mean percent difference for each target element in the field soil samples was also computed using the reference laboratory data for comparison. In general, mean percent difference estimates by the Pace AAS method were within 10 percent of the reference laboratory data. Exceptions were noted for As and Cr. Poor results for As may be at least partially attributable to the fact that the analytical method used in the mobile laboratory was not optimized for As determinations. Poor results for Cr are at least partially attributable to the fact that Cr analysis results from the reference laboratories were highly variable as well, thus compromising the quality of reference laboratory data.

Precision

The precision of the Pace AAS, determined by duplicate analysis of soil sample splits, was 20 percent or less for most of the nine target elements. These results are consistent with the reported experiences of the Pace analysis team, as noted in Chapter 2.

General Observations

A comparison of the Pace AAS data with the reference laboratory data reveals good agreement between the two methodologies. This result is not surprising since the Pace AAS is essentially a laboratory instrument contained in a mobile platform. The performance of the system for As was somewhat compromised for low-level concentrations of As because the instrument configuration was not optimized for As analysis. Chromium analysis with the Pace AAS appears to be the most problematic of all the target elements selected for study in this demonstration. Chromium results were variable and did not compare well with the reference laboratory data. The laboratory reference data were also judged to be of marginal quality.

A detailed cost analysis was not carried out for this technology because it was designated Level 2. Overall cost comparisons between a conventional laboratory and this technology indicate generally equivalent costs since the instrumentation and required accessories for both analytical techniques are the same. The mobile system also requires the purchase of a mobile platform, however, which would result in higher on-site analytical costs. The on-site method does offer relatively quick turnaround of samples compared with off-site laboratory services.

Chapter 6

Developer's Comments

Sharyl Bergen from Pace Environmental Laboratories, Inc. of Minneapolis, Minnesota, reviewed this report in May 1996. Pace had no comments or suggested corrections following their review.

References

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Havlicek, L., and R. D. Crain, 1988. *Practical Statistics for the Physical Sciences*, American Chemical Society, Washington DC, pp. 84–93.

MSE, 1996. “Final Report for RCRA and Other Heavy Metals in Soils Demonstration,” MSE Technology Applications, Inc., Butte, Montana.

Appendix A

Tabular Data for Pace Flame AAS 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 1-3)
Column 6	Field Technology Results

Table A-1. Silver Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Ag (mg/kg)	C_IC_Ag (mg/kg)	C_AA_Ag (mg/kg)	Ref_Ag (mg/kg)	PACE_Ag (mg/kg)
SBHD1	38	41	46	42	39
SBHD2	53			53	53
SBHD3	36	35	39	37	34
SBHD4	34			34	35
SBHD5	88	86	95	90	85
SBHD6	58			58	57
SBHD7	48	48	53	50	43
SBHD8	73			73	58
SBHD9	54	49	54	52	47
SBHD10	35			35	30
SBMD1	10	10	11	10	18
SBMD2	22			22	18
SBMD3	11	17	19	16	9
SBMD4	76			76	38
SBMD5	18	18	20	19	31
SBMD6	28			28	24
SBMD7	18	17	19	18	18
SBMD8	18			18	18
SBMD9	20	16	18	18	17
SBMD10	10			10	11
SBLD1	2	2	2	2	3
SBLD2	2			2	3
SBLD3	2	2	3	2	3
SBLD4	3			3	3
SBLD5	2	2	3	3	4
SBLD6	3			3	5
SBLD7	4	5	6	5	6
SBLD8	3			3	5
SBLD9	4	5	6	5	6
SBLD10	5			5	6

Table A-2. Silver Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Ag (mg/kg)	C_IC_Ag (mg/kg)	C_AA_Ag (mg/kg)	Ref_Ag (mg/kg)	PACE_Ag (mg/kg)
MCHD1	3	3	3	3	6
MCHD2	5			5	12
MCHD3	4	4	4	4	8
MCHD4	4			4	4
MCHD5	6	5	7	6	8
MCHD6	6			6	8
MCHD7	5	4	5	5	5
MCHD8	5			5	6
MCHD9	8	9	10	9	7
MCHD10	5			5	6
MCMD1	4	4	5	4	3
MCMD2	4			4	4
MCMD3	4	4	4	4	3
MCMD4	4			4	3
MCMD5	4	4	4	4	5
MCMD6	5			5	5
MCMD7	5	5	5	5	3
MCMD8	5			5	4
MCMD9	6	5	7	6	7
MCMD10	7			7	5
MCLD1	4	4	5	4	3
MCLD2	4			4	3
MCLD3	4	4	4	4	3
MCLD4	4			4	3
MCLD5	4	4	4	4	3
MCLD6	5			5	3
MCLD7	5	5	5	5	4
MCLD8	5			5	4
MCLD9	6	5	7	6	5
MCLD10	7			7	6

Table A-3. Arsenic Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_As (mg/kg)	C_IC_As (mg/kg)	C_AA_As (mg/kg)	Ref_As (mg/kg)	PACE_As (mg/kg)
SBHD1	1,060	1,110	1,010	1,060	1,000
SBHD2	1,660			1,660	1,600
SBHD3	874	866	765	835	790
SBHD4	764			764	690
SBHD5	947	866	766	860	830
SBHD6	1,670			1,670	1,500
SBHD7	1,510	1,470	1,570	1,517	1,600
SBHD8	1,610			1,610	1,500
SBHD9	1,680	1,490	1,530	1,567	1,700
SBHD10	777			777	870
SBMD1	145	162	137	148	50
SBMD2	254			254	130
SBMD3	315	155	132	201	15
SBMD4	549			549	190
SBMD5	290	316	291	299	250
SBMD6	357			357	190
SBMD7	414	408	380	401	240
SBMD8	399			399	340
SBMD9	423	405	342	390	290
SBMD10	260			260	190
SBLD1	136	144	120	133	15
SBLD2	152			152	15
SBLD3	130	156	129	138	15
SBLD4	165			165	15
SBLD5	165	181	157	168	15
SBLD6	132			132	40
SBLD7	113	148	106	122	15
SBLD8	128			128	15
SBLD9	101	137	102	113	15
SBLD10	88			88	15

Table A-4. Arsenic Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_As (mg/kg)	C_IC_As (mg/kg)	C_AA_As (mg/kg)	Ref_As (mg/kg)	PACE_As (mg/kg)
MCHD1	637	629	565	610	860
MCHD2	1,570			1,570	1,600
MCHD3	326	347	275	316	570
MCHD4	583			583	720
MCHD5	1,260	1,240	1,130	1,210	1,400
MCHD6	813			813	930
MCHD7	466	461	366	431	540
MCHD8	812			812	800
MCHD9	697	716	663	692	740
MCHD10	882			882	830
MCMD1	586	604	587	592	540
MCMD2	860			860	1,100
MCMD3	717	757	708	727	810
MCMD4	689			689	770
MCMD5	1,240	1,190	1,030	1,153	1,200
MCMD6	940			940	1,000
MCMD7	907	828	789	841	1,100
MCMD8	1,090			1,090	1,100
MCMD9	1,650	1,680	1,440	1,590	1,800
MCMD10	1,080			1,080	1,400
MCLD1	640	704	604	649	540
MCLD2	647			647	400
MCLD3	576	580	581	579	540
MCLD4	757			757	660
MCLD5	619	668	612	633	740
MCLD6	726			726	760
MCLD7	814	811	753	793	910
MCLD8	722			722	980
MCLD9	877	837	808	841	1,000
MCLD10	1,190			1,190	1,300

Table A-5. Cadmium Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Cd (mg/kg)	C_IC_Cd (mg/kg)	C_AA_Cd (mg/kg)	Ref_Cd (mg/kg)	PACE_Cd (mg/kg)
SBHD1	23	27	24	24	23
SBHD2	13			13	12
SBHD3	22	22	15	20	19
SBHD4	10			10	10
SBHD5	49	54	20	41	47
SBHD6	18			18	16
SBHD7	19	18	16	18	18
SBHD8	18			18	16
SBHD9	16	14	12	14	14
SBHD10	24			24	22
SBMD1	6	6	3	5	5
SBMD2	12			12	10
SBMD3	8	15	3	9	4
SBMD4	17			17	11
SBMD5	15	11	7	11	12
SBMD6	8			8	7
SBMD7	10	7	10	9	7
SBMD8	5			5	4
SBMD9	7	6	5	6	6
SBMD10	6			6	6
SBLD1	5	5	4	5	4
SBLD2	4			4	3
SBLD3	4	3	3	3	3
SBLD4	3			3	2
SBLD5	3	3	3	3	2
SBLD6	5			5	4
SBLD7	7	8	7	7	7
SBLD8	3			3	3
SBLD9	2	4	3	3	3
SBLD10	4			4	4

Table A-6. Cadmium Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Cd (mg/kg)	C_IC_Cd (mg/kg)	C_AA_Cd (mg/kg)	Ref_Cd (mg/kg)	PACE_Cd (mg/kg)
MCHD1	4	3	3	3	3
MCHD2	4			4	3
MCHD3	3	3	2	3	2
MCHD4	4			4	3
MCHD5	5	4	3	4	3
MCHD6	3			3	2
MCHD7	4	3	2	3	2
MCHD8	6			6	4
MCHD9	27	25	22	25	23
MCHD10	4			4	4
MCMD1	3	4	3	4	4
MCMD2	4			4	3
MCMD3	4	3	3	3	3
MCMD4	4			4	3
MCMD5	6	5	5	5	6
MCMD6	5			5	5
MCMD7	7	5	5	5	5
MCMD8	7			7	7
MCMD9	8	7	6	7	8
MCMD10	6			6	6
MCLD1	2	2	2	2	3
MCLD2	4			4	3
MCLD3	4	3	3	3	4
MCLD4	4			4	4
MCLD5	4	4	3	4	4
MCLD6	4			4	5
MCLD7	5	4	4	4	5
MCLD8	4			4	5
MCLD9	5	3	3	4	4
MCLD10	7			7	8

Table A-7. Chromium Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Cr (mg/kg)	C_IC_Cr (mg/kg)	C_AA_Cr (mg/kg)	Ref_Cr (mg/kg)	PACE_Cr (mg/kg)
SBHD1	6	8		7	8
SBHD2	4			4	4
SBHD3	5	5		5	7
SBHD4	6			6	7
SBHD5	7	8	23	13	10
SBHD6	7			7	9
SBHD7	7	5		6	7
SBHD8	6			6	6
SBHD9	7	6		6.6	8
SBHD10	9			9	9
SBMD1	13	17		15	9
SBMD2	20			20	11
SBMD3	27	12	15	18	14
SBMD4	21			21	8
SBMD5	25	16	11	17	7
SBMD6	14			14	9
SBMD7	14	10		12	7
SBMD8	14			14	12
SBMD9	10	9		9	5
SBMD10	8			8	8
SBLD1	15	15		15	10
SBLD2	14			14	8
SBLD3	13	14	11	13	12
SBLD4	13			13	10
SBLD5	12	14		13	16
SBLD6	14			14	17
SBLD7	13	17		15	11
SBLD8	13			13	11
SBLD9	12	16		14	6
SBLD10	14			14	7

Table A-8. Chromium Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Cr (mg/kg)	C_IC_Cr (mg/kg)	C_AA_Cr (mg/kg)	Ref_Cr (mg/kg)	PACE_Cr (mg/kg)
MCHD1	8	7	10	8	6
MCHD2	10			10	8
MCHD3	4	3		4	3
MCHD4	6			6	7
MCHD5	11	10	11	11	6
MCHD6	10			10	6
MCHD7	7	6	28	14	4
MCHD8	10			10	6
MCHD9	10	9	12	10	6
MCHD10	13			13	10
MCMD1	11	10	21	14	9
MCMD2	10			10	8
MCMD3	11	14	30	18	8
MCMD4	13			13	8
MCMD5	13	14	17	15	6
MCMD6	10			10	8
MCMD7	13	12	21	15	9
MCMD8	12			12	11
MCMD9	12	14	27	18	7
MCMD10	13			13	8
MCLD1	7	8	33	16	8
MCLD2	8			8	4
MCLD3	9	7	19	12	7
MCLD4	12			12	9
MCLD5	8	12	21	14	7
MCLD6	11			11	8
MCLD7	10	10	32	17	9
MCLD8	7			7	7
MCLD9	9	8	15	11	8
MCLD10	11			11	8

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

Sample No.	MSE_Cu (mg/kg)	C_IC_Cu (mg/kg)	C_AA_Cu (mg/kg)	Ref_Cu (mg/kg)	PACE_Cu (mg/kg)
SBHD1	1,570	1,670	1,790	1,677	1,400
SBHD2	1,330			1,330	1,200
SBHD3	2,460	2,510	2,700	2,557	2,100
SBHD4	991			991	870
SBHD5	2,620	2,410	2,620	2,550	2,100
SBHD6	1,680			1,680	1,400
SBHD7	1,010	1,010	1,060	1,027	920
SBHD8	1,030			1,030	780
SBHD9	1,620	1,400	1,500	1,507	1,300
SBHD10	1,970			1,970	2,200
SBMD1	281	385	371	346	370
SBMD2	864			864	850
SBMD3	788	512	522	607	340
SBMD4	2,180			2,180	1,600
SBMD5	1,090	1,240	1,270	1,200	1,100
SBMD6	780			780	580
SBMD7	1,270	1,290	1,280	1,280	950
SBMD8	449			449	420
SBMD9	608	644	635	629	500
SBMD10	710			710	650
SBLD1	394	374	376	381	380
SBLD2	351			351	360
SBLD3	339	357	359	352	340
SBLD4	414			414	370
SBLD5	347	332	338	339	290
SBLD6	404			404	360
SBLD7	566	647	648	620	560
SBLD8	414			414	350
SBLD9	305	376	370	350	270
SBLD10	363			363	320

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

Sample No.	MSE_Cu (mg/kg)	C_IC_Cu (mg/kg)	C_AA_Cu (mg/kg)	Ref_Cu (mg/kg)	PACE_Cu (mg/kg)
MCHD1	682	663	701	682	620
MCHD2	792			792	760
MCHD3	419	400	420	413	360
MCHD4	687			687	630
MCHD5	956	828	880	888	740
MCHD6	533			533	540
MCHD7	589	626	668	628	510
MCHD8	859			859	870
MCHD9	3,340	3,490	3,640	3,490	3,700
MCHD10	889			889	1,000
MCMD1	631	631	657	640	630
MCMD2	532			532	580
MCMD3	585	621	651	619	590
MCMD4	632			632	650
MCMD5	825	795	845	822	770
MCMD6	893			893	910
MCMD7	890	821	885	865	740
MCMD8	871			871	870
MCMD9	1,020	1,010	1,130	1,053	940
MCMD10	784			784	800
MCLD1	476	513	535	508	400
MCLD2	477			477	340
MCLD3	595	598	610	601	580
MCLD4	554			554	490
MCLD5	721	775	837	778	650
MCLD6	971			971	740
MCLD7	853	878	916	882	750
MCLD8	784			784	680
MCLD9	624	598	622	615	540
MCLD10	1,090			1,090	950

Table A-11. Iron Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Fe (mg/kg)	C_IC_Fe (mg/kg)	C_AA_Fe (mg/kg)	Ref_Fe (mg/kg)	PACE_Fe (mg/kg)
SBHD1	28,700	30,800	35,100	31,533	28,000
SBHD2	19,200			19,200	20,000
SBHD3	21,900	21,700	24,400	22,667	21,000
SBHD4	26,300			26,300	25,000
SBHD5	30,100	28,100	31,600	29,933	28,000
SBHD6	26,500			26,500	25,000
SBHD7	20,700	19,400	22,000	20,700	21,000
SBHD8	22,900			22,900	19,000
SBHD9	29,800	25,400	28,400	27,867	26,000
SBHD10	23,700			23,700	22,000
SBMD1	27,800	34,000	36,900	32,900	21,000
SBMD2	43,000			43,000	26,000
SBMD3	55,200	29,200	32,600	39,000	32,000
SBMD4	46,700			46,700	27,000
SBMD5	49,000	33,100	37,600	39,900	21,000
SBMD6	31,300			31,300	24,000
SBMD7	34,100	28,000	31,200	31,100	22,000
SBMD8	33,100			33,100	33,000
SBMD9	26,300	25,400	28,200	26,633	22,000
SBMD10	23,200			23,200	23,000
SBLD1	15,500	13,000	14,200	14,233	14,000
SBLD2	13,900			13,900	10,000
SBLD3	13,300	12,300	13,500	13,033	12,000
SBLD4	13,900			13,900	9,200
SBLD5	13,500	13,400	14,900	13,933	14,000
SBLD6	12,700			12,700	12,000
SBLD7	11,100	12,400	13,700	12,400	12,000
SBLD8	12,000			12,000	11,000
SBLD9	10,700	13,300	14,400	12,800	9,400
SBLD10	11,400			11,400	9,100

Table A-12. Iron Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Fe (mg/kg)	C_IC_Fe (mg/kg)	C_AA_Fe (mg/kg)	Ref_Fe (mg/kg)	PACE_Fe (mg/kg)
MCHD1	24,100	23,100	25,100	24,100	23,000
MCHD2	21,400			21,400	22,000
MCHD3	23,900	26,300	27,300	25,833	24,000
MCHD4	25,900			25,900	27,000
MCHD5	24,700	24,400	26,800	25,300	25,000
MCHD6	23,800			23,800	22,000
MCHD7	23,000	24,100	26,600	24,567	20,000
MCHD8	22,800			22,800	20,000
MCHD9	49,800	49,200	49,500	49,500	42,000
MCHD10	15,400			15,400	16,000
MCMD1	14,800	13,500	14,800	14,367	12,000
MCMD2	16,700			16,700	16,000
MCMD3	15,600	17,200	18,900	17,233	14,000
MCMD4	16,200			16,200	15,000
MCMD5	17,700	17,500	19,200	18,133	16,000
MCMD6	15,700			15,700	23,000
MCMD7	18,200	16,500	19,800	18,167	23,000
MCMD8	16,300			16,300	27,000
MCMD9	16,200	16,800	18,900	17,300	19,000
MCMD10	16,300			16,300	23,000
MCLD1	18,600	19,200	21,000	19,600	20,000
MCLD2	20,100			20,100	16,000
MCLD3	20,600	18,500	20,000	19,700	21,000
MCLD4	21,700			21,700	19,000
MCLD5	18,400	20,400	22,900	20,567	17,000
MCLD6	20,600			20,600	21,000
MCLD7	20,200	18,900	20,800	19,967	19,000
MCLD8	18,400			18,400	20,000
MCLD9	22,700	20,600	22,800	22,033	20,000
MCLD10	18,200			18,200	16,000

Table A-13. Manganese Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Mn (mg/kg)	C_IC_Mn (mg/kg)	C_AA_Mn (mg/kg)	Ref_Mn (mg/kg)	PACE_Mn (mg/kg)
SBHD1	2,460	2,520	2,720	2,567	2,700
SBHD2	2,940			2,940	3,300
SBHD3	2,100	2,130	2,320	2183	2,600
SBHD4	1,380			1,380	1,800
SBHD5	2,000	1,900	2,070	1,990	2,300
SBHD6	2,700			2,700	3,000
SBHD7	1,920	1,870	2,040	1,943	2,300
SBHD8	2,930			2,930	3,200
SBHD9	1,800	1,780	1,970	1,850	2,100
SBHD10	1,960			1,960	2,300
SBMD1	935	794	847	859	2,100
SBMD2	2,500			2500	2,300
SBMD3	1,150	2,270	2,320	1,913	1,500
SBMD4	3,320			3,320	4,200
SBMD5	2,560	2,130	2,380	2,357	1,900
SBMD6	2,090			2,090	2,800
SBMD7	1,070	1,530	1,680	1,427	2,000
SBMD8	549			549	660
SBMD9	1,080	608	652	780	2,000
SBMD10	850			850	710
SBLD1	708	730	794	744	670
SBLD2	478			478	410
SBLD3	409	458	456	441	490
SBLD4	379			379	320
SBLD5	563	532	564	553	530
SBLD6	556			556	470
SBLD7	391	448	456	432	400
SBLD8	505			505	510
SBLD9	434	540	593	522	410
SBLD10	513			513	820

Table A-14. Manganese Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Mn (mg/kg)	C_IC_Mn (mg/kg)	C_AA_Mn (mg/kg)	Ref_Mn (mg/kg)	PACE_Mn (mg/kg)
MCHD1	113	115	115	114	110
MCHD2	122			122	120
MCHD3	71	78	82	77	74
MCHD4	94			94	97
MCHD5	121	124	105	117	100
MCHD6	75			75	78
MCHD7	88	96	98	94	81
MCHD8	161			161	150
MCHD9	2,180	2,230	2,350	2,253	2,400
MCHD10	222			222	230
MCMD1	284	267	280	277	250
MCMD2	202			202	200
MCMD3	263	266	271	267	240
MCMD4	210			210	200
MCMD5	222	206	210	213	180
MCMD6	170			170	160
MCMD7	288	270	277	278	250
MCMD8	235			235	230
MCMD9	219	225	236	227	200
MCMD10	188			188	180
MCLD1	119	124	125	123	110
MCLD2	102			102	86
MCLD3	120	113	113	115	110
MCLD4	139			139	120
MCLD5	132	138	143	138	110
MCLD6	146			146	120
MCLD7	163	155	158	159	140
MCLD8	139			139	120
MCLD9	115	108	108	110	100
MCLD10	357			357	340

Table A-15. Lead Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Pb (mg/kg)	C_IC_Pb (mg/kg)	C_AA_Pb (mg/kg)	Ref_Pb (mg/kg)	PACE_Pb (mg/kg)
SBHD1	1,170	1,220	1,290	1,227	1,100
SBHD2	1,010			1,010	940
SBHD3	946	902	955	934	870
SBHD4	936			936	920
SBHD5	2,080	1,850	2,000	1,977	1,900
SBHD6	1,310			1,310	1,200
SBHD7	1,030	992	1,060	1,027	1,000
SBHD8	1,770			1,770	1,500
SBHD9	1,500	1,310	1,370	1,393	1,400
SBHD10	1,140			1,140	1,380
SBMD1	410	1,260	1,290	987	490
SBMD2	631			631	630
SBMD3	456	513	539	503	370
SBMD4	779			779	870
SBMD5	677	823	883	794	720
SBMD6	836			836	880
SBMD7	696	798	840	778	560
SBMD8	466			466	550
SBMD9	537	471	494	501	470
SBMD10	342			342	390
SBLD1	200	166	171	179	190
SBLD2	166			166	190
SBLD3	139	147	154	147	150
SBLD4	245			245	220
SBLD5	173	161	165	166	180
SBLD6	217			217	240
SBLD7	324	374	393	364	360
SBLD8	193			193	230
SBLD9	264	302	315	294	270
SBLD10	294			294	310

Table A-16. Lead Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Pb (mg/kg)	C_IC_Pb (mg/kg)	C_AA_Pb (mg/kg)	Ref_Pb (mg/kg)	PACE_Pb (mg/kg)
MCHD1	391	391	417	400	390
MCHD2	582			582	600
MCHD3	384	415	452	417	410
MCHD4	312			312	310
MCHD5	520	521	556	532	490
MCHD6	484			484	400
MCHD7	355	361	388	368	320
MCHD8	376			376	390
MCHD9	388	396	423	402	400
MCHD10	332			332	390
MCMD1	229	235	240	235	230
MCMD2	350			350	400
MCMD3	267	283	294	281	280
MCMD4	256			256	270
MCMD5	442	424	441	436	420
MCMD6	265			265	270
MCMD7	362	336	362	353	340
MCMD8	349			349	390
MCMD9	484	495	529	503	510
MCMD10	413			413	440
MCLD1	298	306	319	308	300
MCLD2	316			316	290
MCLD3	291	279	288	286	300
MCLD4	331			331	330
MCLD5	264	275	297	279	280
MCLD6	342			342	360
MCLD7	350	330	340	340	330
MCLD8	432			432	440
MCLD9	540	497	530	522	560
MCLD10	499			499	510

Table A-17. Zinc Analysis Results for PACE-AAS and Reference Laboratories (Part 1, Silver Bow Site)

Sample No.	MSE_Zn (mg/kg)	C_IC_Zn (mg/kg)	C_AA_Zn (mg/kg)	Ref_Zn (mg/kg)	PACE_Zn (mg/kg)
SBHD1	7,410	8,590	9,340	8,447	8,100
SBHD2	3,830			3,830	4,400
SBHD3	6,750	6,540	7,130	6,807	6,800
SBHD4	3,620			3,620	4,400
SBHD5	14,800	16,600	18,000	16,467	16,000
SBHD6	5,530			5,530	6,000
SBHD7	5,440	5,240	5,810	5,497	5,700
SBHD8	5,870			5,870	6,300
SBHD9	4,710	4,510	5,000	4,740	5,100
SBHD10	7,160			7,160	7,600
SBMD1	1,270	2,040	2,190	1,833	1,400
SBMD2	3,440			3,440	2,500
SBMD3	1,410	2,810	3,040	2,420	1,100
SBMD4	3,760			3,760	3,600
SBMD5	4,080	3,390	3,860	3,777	4,300
SBMD6	2,550			2,550	2,100
SBMD7	2,810	2,640	2,950	2,800	2,100
SBMD8	1,300			1,300	1,500
SBMD9	2,020	2,040	2,230	2,097	1,700
SBMD10	1,660			1,660	1,700
SBLD1	426	396	442	421	390
SBLD2	327			327	330
SBLD3	310	343	381	345	310
SBLD4	404			404	380
SBLD5	343	341	375	353	310
SBLD6	413			413	410
SBLD7	543	700	773	672	550
SBLD8	363			363	230
SBLD9	325	429	473	409	330
SBLD10	420			420	420

Table A-18. Zinc Analysis Results for PACE-AAS and Reference Laboratories (Part 2, Mill Creek Site)

Sample No.	MSE_Zn (mg/kg)	C_IC_Zn (mg/kg)	C_AA_Zn (mg/kg)	Ref_Zn (mg/kg)	PACE_Zn (mg/kg)
MCHD1	609	640	141	463	549
MCHD2	525			525	490
MCHD3	577	623	137	446	540
MCHD4	662			662	590
MCHD5	640	611	673	641	500
MCHD6	474			474	420
MCHD7	538	588	657	594	470
MCHD8	669			669	590
MCHD9	4,080	4,130	4,600	4,270	4,300
MCHD10	430			430	490
MCMD1	388	417	462	422	340
MCMD2	447			447	440
MCMD3	406	441	483	443	350
MCMD4	387			387	360
MCMD5	722	686	739	716	590
MCMD6	596			596	540
MCMD7	746	671	741	719	550
MCMD8	657			657	610
MCMD9	858	887	1,000	915	760
MCMD10	698			698	660
MCLD1	437	468	517	474	400
MCLD2	543			543	450
MCLD3	587	541	586	571	550
MCLD4	529			529	480
MCLD5	591	651	727	656	500
MCLD6	687			687	650
MCLD7	755	751	805	770	660
MCLD8	642			642	640
MCLD9	654	610	668	644	570
MCLD10	994			994	890