

**COLORADO SMELTER SUPERFUND SITE  
PUEBLO, PUEBLO COUNTY, COLORADO**

**DEMONSTRATION OF METHODS APPLICABILITY AT  
COLORADO SMELTER  
DATA SUMMARY REPORT**

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**FINAL**

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## LIST OF ACRONYMS

AP	Apron
As	Arsenic
bgs	below ground surface
BY	Back Yard
CDPHE	Colorado Department of Public Health and Environment
CLP	Contract Laboratory Program
COPC	contaminant of potential concern
CPSA	Community Properties Study Area
CRQL	Contract Required Quantitation Limits
CSU	Colorado State University
DMA	demonstration of methods applicability
DMA QAPP PAL	Demonstration of Methods Applicability Project Action Level
DMA SL	Demonstration of Methods Applicability Screening Level
DQO	data quality objective
DSR	data summary report
DU	decision unit
DZ	Drip Zone
E2	E2 Consulting Engineers Inc.
ED	Earthen Drive
EPA	U.S. Environmental Protection Agency
EPA RSL	EPA Regional Screening Level
FY	Front Yard
GA	Garden
HHRA	human health risk assessment
HASP	Health and Safety Plan
ICP-MS	Inductively coupled plasma-mass spectrometry
ICS	incremental composite sampling
ICV	initial calibration verification
ID	identification number
IDW	Investigation-Derived Waste
IVBA	In-Vitro Bioaccessibility
JSAC	Japanese Society of Analytical Chemistry
LCS	laboratory control sample
LCL	lower confidence level
MDL	method detection limit
mg/kg	milligrams per kilogram
MS/MSD	matrix spike/matrix spike duplicate
NC	not calculated
NFG	National Functional Guidelines
NIST	National Institute of Standards and Technology
NS	not sampled
OU	operable unit
PA	Play Area
PARCCS	precision, accuracy, representativeness, comparability, completeness, and sensitivity
Pb	Lead
ppm	parts per million
PQL	practical quantitation limit

PWT	Pacific Western Technologies, Ltd.
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Project Plan
QC	quality control
R-sq	R-squared
RCRA	Resource Conservation and Recovery Act
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
RPD	relative percent difference
RSD	relative standard deviation
RSL	regional screening level
S3VE	Stage 3 criteria
S3VM	Stage 3 verification and validation
SCRIBE	USEPA's software tool used to assist in the process of managing environmental data
SDG	sample delivery group
SL	screening level
SOP	standard operating procedure
SRM	standard reference material
SY	Side Yard
SYE	Side Yard East
SYN	Side Yard North
SYS	Side Yard South
SYW	Side Yard West
TAL	Target Analyte List
TIIB	Technology Integration and Information Branch
TtEMI	Tetra Tech EM, Inc.
UCL	upper confidence limit
UFP QAPP	Uniform Federal Policy for Quality Assurance Project Plans
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	volatile organic compound
WP	Waste Piles
WSR	Wilcoxon Signed Rank
XRF	X-Ray Fluorescence Spectrophotometer



## **1.0 INTRODUCTION**

This Demonstration of Methods Applicability (DMA) Data Summary Report (DSR) was prepared by Pacific Western Technologies, Ltd. (PWT) and Tetra Tech EMI (TtEMI) under Remedial Action Contract (RAC2) Work Assignment No. 136-RICO-08UA, U.S. EPA Contract No. EP-W-06-006 to the United States Environmental Protection Agency (EPA) Region 8. This report documents the DMA, which assessed soils at 12 residential properties and 6 select locations of the former smelter/slag area. Sampling was conducted in accordance with the EPA-approved Uniform Federal Policy Quality Assurance Project Plan for Demonstration of Methods Applicability at Colorado Smelter, Revision 2 (QAPP), dated May 8, 2015.

Properties are located in the vicinity of the Colorado Smelter Superfund site (Site) located in Pueblo, Colorado. Figure 1-1 shows the location of the Site. Soils were assessed for the potential presence of arsenic, lead, and other heavy metals related to the historical Colorado Smelter. Data from the 12 properties and 6 smelter/slag areas evaluated during the DMA will be used to optimize sampling strategies, sample preparation, and analytical methods for the larger sampling effort planned for residential properties at the Site.

Data generated from the DMA will also support the long-term Remedial Investigation/Feasibility Study (RI/FS), help the EPA to determine the nature and extent of smelter related contamination at the Site, and support the EPA in conducting a human health risk assessment (HHRA). Data generated from the DMA will also support the determination of the contaminants of potential concern (COPCs) that will be established as part of the full RI/FS.

This document discusses the field sampling activities, analytical results, and data evaluations conducted for the DMA sampling event (i.e., May 2015 through June 2015). This document refers to the 2015 DMA sampling event as the DMA.

### **Site Description, History & Background**

The Colorado Smelter (also known as the Colorado Smelting Company and the Eiler's Smelter) was one of five smelters in Pueblo at the turn of the last century. This smelter processed silver-lead ore from the Monarch Pass area and operated from 1883 to 1908. There is a steel mill (Evraz/Rocky Mountain Steel/Colorado Fuel & Iron (CF&I)) located to the south of the Site that is still operating. The Colorado Department of Public Health and the Environment (CDPHE) Resource Conservation and Recovery Act (RCRA) program is the lead agency for that operating facility.

In 2006, a Colorado State University-Pueblo (CSU-Pueblo) professor and co-authors published a paper that described heavy metals in Pueblo surface soils. The authors found that in some areas, the topsoil in Pueblo has more arsenic, cadmium, mercury and lead than the average levels found nationally in soils. The areas identified in Pueblo were in low income and minority neighborhoods. The authors of the 2006 report recommended more soil sampling to identify hotspots within the city.

The CDPHE investigated the Blende Smelter, Fountain Foundry, and Colorado Smelter sites in Pueblo because they were in, or close to, residential neighborhoods, and previous soil sampling data indicated the need for more detailed sampling of these residential areas. The Blende Smelter was cleaned up using an EPA-lead Removal Action. One of the three remaining smelters, Pueblo Smelter/Rockwool facility, is bordered by commercial/industrial properties and

was addressed via a removal action in which source material was capped in place. The former New England/Massachusetts Smelter and the Philadelphia Smelters were located on the eastern edge of the steel mill facility. It is unknown if these smelters have impacted any nearby communities (CDPHE 2011).

Historical data that were collected by the CDPHE in 1994 and EPA contractors in 1995 indicated the presence of elevated levels of lead and arsenic; however, the studies were not systematic and lacked sufficient data density to clearly determine if metals posed a significant threat to residents living near the former smelter. In 2010, CDPHE collected 434 surface soil samples from 47 yards in the Eilers and Bessemer residential neighborhoods surrounding the Colorado Smelter, including the old slag pile area and two background locations. The former smelter site consists of an approximate 700,000 square foot slag pile that is 30 feet high in places. Lead levels in the slag pile ranged from 480 to 26,000 ppm; arsenic from 30 to 1,700 ppm. The lead levels measured using X-Ray Fluorescence spectrophotometry (XRF) on composite samples of residential soils collected from the area south and east of the former smelter ranged from 300 to 785 parts per million (ppm). The screening level benchmark that the EPA and CDPHE have typically used for lead is 400 ppm. Arsenic concentrations varied from 100 to 340 ppm range in an area immediately south of the former smelter site. The screening level benchmark that the EPA and CDPHE have typically used for arsenic have ranged from 40 to 70 ppm at similar sites in Region 8. In addition, these concentrations are well above preliminary background levels designated for that field effort (47 ppm for lead and 16 ppm for arsenic).

The 2010 Analytical Results Report (CDPHE 2011) provides the most recent historical data for the Site and helped determine the initial scope of the RI. This report will also be used to identify possible prioritization criteria for sampling, and possible early actions.

For additional information, refer to the DMA QAPP Worksheet #10 that addresses results of historical documentation and data review (PWT 2015b).

## **1.1 PROJECT SCOPE**

The DMA included sampling of residential properties and other select locations representative of properties and conditions that are likely to be encountered within the Colorado Smelter Community Properties Study Area (CPSA). For additional information on property selection, refer to the project-specific property selection SOP, PWT-COS-DMA-301 included in the DMA QAPP.

Sampling locations include:

1. Twelve residential properties ranging in size from approximately 0.07 to 0.47 acres,
2. Six select locations within the former smelter slag/contaminated soils area.

Contaminant types and assessment methods to be used in the selected areas include:

1. Lead and arsenic (target analytes), and antimony, cadmium, copper, and zinc (potential accessory analytes) in soil samples from select residential properties and former smelter area/contaminated soils area via field soils laboratory based XRF,
2. Target Analyte List (TAL) metals in soil samples from select residential properties and former smelter area/contaminated soils area using the EPA Contract Laboratory

- Program (CLP) inductively coupled plasma-mass spectrometry (ICP-MS) analysis using EPA method 6020B, under CLP contract ISM 01.3,
3. Bioaccessibility analysis for lead in site-specific matrices using US EPA's "*Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Lead in Soil*" (EPA 9200.2-86, April 2012), and
  4. Bioaccessibility analysis for arsenic in site-specific matrices using University of Colorado "*Standard Operating Procedure In Vitro Bioaccessibility (IVBA) Procedure for Arsenic*" (CU 2011),
  5. Geospeciation of lead and arsenic in select samples using special analytical services at the University of Colorado.

Results of bioaccessibility and geospeciation analysis are not addressed in this DMA DSR because decisions with respect to bioaccessibility will require a larger data set than was collected during the DMA. In addition, the evaluation of that data is not on the critical path to optimizing the RI sampling design and finalizing an RI QAPP for the Site. These results will be reported separately when sufficient data are available.

## **1.2 PROJECT OBJECTIVES**

The objective of the DMA is to evaluate the following questions to optimize data collection for the Colorado Smelter RI:

1. Can consistent comparability be established between XRF technology and fixed-laboratory methods (EPA Method 6020B for ICP-MS) to ensure adequate support for long-term decision-making at the site?
2. Is 30-point incremental sampling (30-point composite) necessary, or does 5-point composite sampling adequately address matrix heterogeneity and provide decision-quality data for the Site?
3. Are triplicate samples necessary for all decision units (DUs) and depths, or can triplicate samples be collected at a lower frequency?
4. Is sampling at all four of the depth ranges investigated during the DMA necessary?

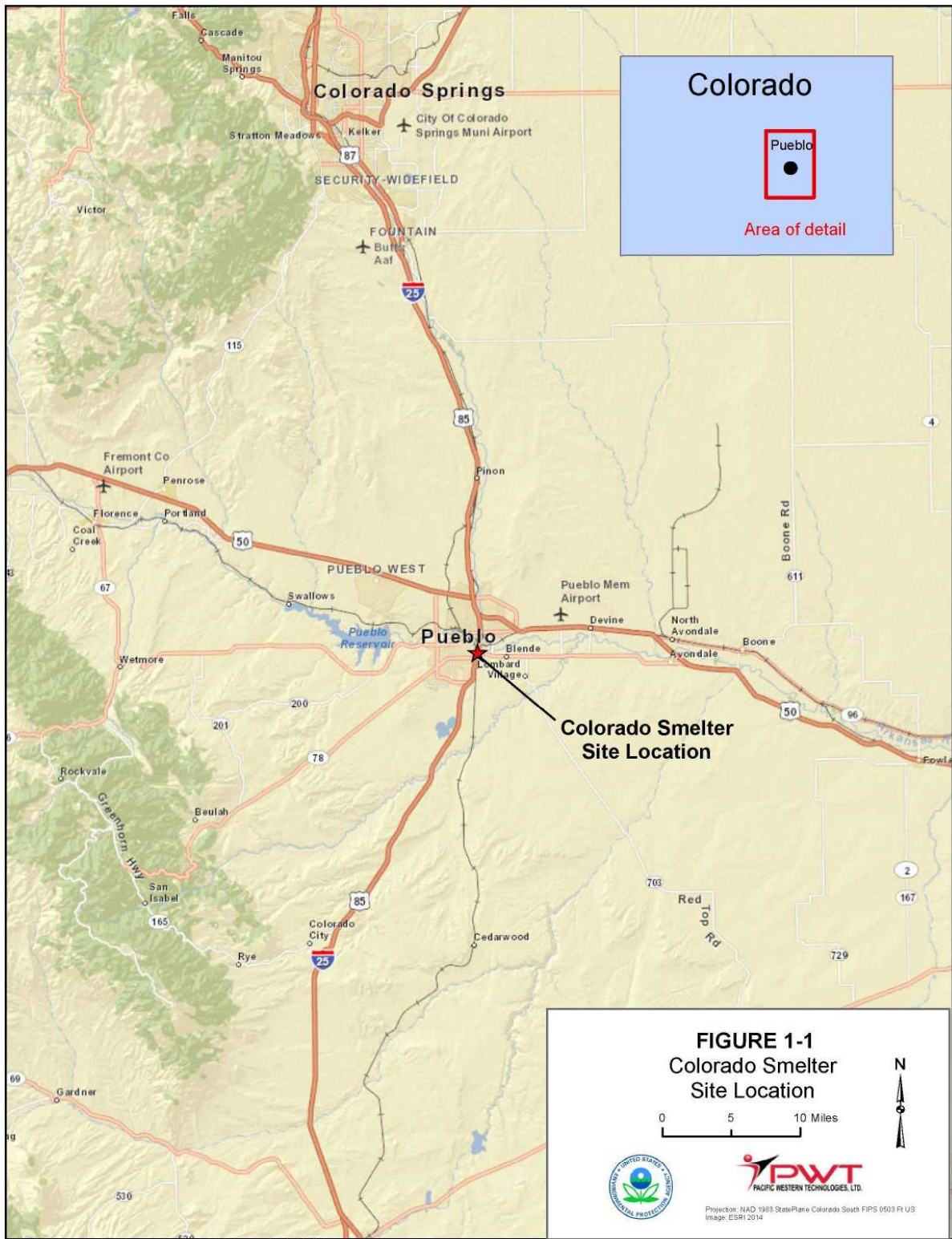
## **1.3 PROJECT DESCRIPTION**

The DMA QAPP identifies the following tasks:

1. Collect soil samples in accordance with the sample collection standard operating procedures (SOPs) and quality assurance/quality control (QA/QC) procedures specified in the DMA QAPP.
2. Prepare/process soil samples in accordance with the sample preparation SOPs and QA/QC procedures specified in the DMA QAPP.
3. Analyze soil samples in accordance with the sample analysis SOPs and QA/QC procedures specified in the DMA QAPP.

4. Collect subsamples from selected soil samples and analyze subsamples by XRF in accordance with the SOPs and QA/QC procedures specified in the DMA QAPP. Submit soil subsamples and appropriate QC samples (i.e., duplicate/replicate) for laboratory analysis through the EPA CLP.
5. Review and validate analytical data, prepare a database of the results, and assess paired data (XRF sample data and EPA CLP sample data) to evaluate overall comparability/reproducibility and possible bias.

For each property sampled, the lead and arsenic results are shown on a pair of figures included in Appendix A. This document discusses the field sampling activities, field laboratory sample preparation activities, analytical results, and data evaluations conducted for the DMA sampling effort. In addition, this document discusses any deviations from the DMA QAPP (PWT 2015b) that occurred during sample collection and handling, sample preparation, subsampling, and sample analysis and provides supporting field and field laboratory documentation.



## 2.0 SAMPLE COLLECTION

This section describes the field activities for the Colorado Smelter DMA, including: (1) sample collection objectives; (2) sample collection procedures, (3) sample designation, (4) field quality control, and (5) sample handling and custody requirements.

DMA soil sampling was completed in accordance with the approved DMA QAPP and sample collection SOPs. Between May 4, 2015 and May 31, 2015 a total of 51 decision units (DUs) in 12 residential yards were sampled at four depth intervals, with a combination of 5-point composite and 30-point incremental sampling approaches. Figure 2-1 shows the 12 yards selected for DMA sampling. A DU is defined as the smallest component of a residential yard for which a cleanup decision may be desired. The *Superfund Lead-Contaminated Residential Sites Handbook* was utilized to establish the yard components (i.e. DUs) to be sampled (USEPA 2003). In addition to the residential yard samples, six waste pile samples were also collected from the former smelter area. This generated 556 individual soil samples.

### 2.1 SAMPLE COLLECTION OBJECTIVES

The goal of residential yard soil sampling is to collect data which represents the true mean analyte concentration for a designated area (i.e., DU) and depth interval. One of the primary questions of the DMA was whether incremental sampling (30-point incremental) is necessary, or can 5-point composite sampling adequately address matrix heterogeneity and provide decision-quality data for the Site. As a result, DMA soil sample collection involved both 5-point composite and 30-point incremental approaches. A related secondary question that the DMA sampling was designed to answer requires an evaluation of variability within each DU, to determine whether triplicate sampling is required at every depth and DU, or whether triplicates can be collected on some less frequent basis.

In triplicate sampling, a primary 5-point composite along with a duplicate 5-point composite sample and triplicate 5-point composite sample, are collected at different locations within the DU, resulting in fifteen total soil sample locations. Triplicate 30-point incremental samples were also collected at some locations. Triplicate 30-point incremental samples were collected at 9 DUs and 20 DU/depth combinations, and triplicate 5-point composite samples were collected at 42 DUs and 154 DU/depth combinations.

Limited waste pile sampling was also conducted, in order to establish the efficacy of the sample preparation and analysis methods at higher concentrations, and to begin initial source characterization of the smelter material. Six samples were collected at different locations on the former smelter property for this purpose. Each waste pile sample was a five-point composite sample collected from the surface interval using a clean stainless steel scoop. Subsurface samples were not collected at the waste piles. Figure 2-2 shows the six waste pile sample locations.

### 2.2 SAMPLE COLLECTION PROCEDURES

Yards selected for DMA sampling were visited on March 31, 2015, and DUs were assigned at that time by the EPA RPM, a representative of EPA HQ and the EPA Risk Assessor. DU's were assigned based on the attributes of the property and apparent use as it relates to risk. A total of 51 DUs were identified for the 12 yards to be included in the DMA. When possible, each DU was further divided into four discrete depth intervals between the surface and a depth of 18

inches bgs. A total of 154 DUs/Depth intervals were sampled. In some DUs, particularly drip zones, the presence of underground utilities or other hazards prevented sampling at all four depth intervals. Figures A-1 through A-25 (included in Appendix A) show the DUs sampled for each property. Residential lots included in the DMA range in size from 0.07 acres to 0.47 acres. Half of the 12 lots were approximately 1/8 acre in size, three were smaller than 1/8 acre, and the remaining 3 were approximately 1/4 or 1/2 an acre. This distribution of lot sizes is generally representative of lot sizes throughout the Site. DUs varied in size from 25 square feet (sf) for the drip zone at PC-0269 up to a maximum of 12,626 sf for the eastern side yard at PC-0423. However, only one DU was larger than 2,000 sf. Excluding this outlier, the average DU sampled in the DMA was about 540 sf. Table 2-1 details information regarding the decision units sampled during the DMA, including size, sample depths, and sample collection methodology. For additional information regarding the property selection process, refer to the property selection SOP in the DMA QAPP (PWT2015b).

Subsequent to the March 31, 2015 site visit, and prior to soil sample collection, the following occurred at each yard:

1. Verification of appropriate signed access agreements,
2. Yard mapping was completed and a yard sketch identifying each DU was generated,
3. Utility locates were conducted,
4. Sample labels were generated in Scribe.

DMA sampling was conducted in accordance with the site-specific soil sample collection procedure described in PWT-COS-DMA-427 *Surface and Shallow Subsurface Sampling for Inorganics*, and the approved DMA QAPP (PWT 2015b). A soil sampling probe was utilized to collect either 5 or 30 increments of soil for the four depth intervals required. The ½ inch diameter soil cores for each depth interval was retrieved from the soil probe and placed in a sample container together with all other cores from that DU and depth interval. In cases where the 0-1 inch or 0-2 inch soil was loose, soil scoops were used. DMA sample collection began on May 4, 2015, in the eastern side yard at property PC-0423. This was the single largest DU sampled in the DMA, and it received the most extensive sampling effort, with both 5-point composite and 30-point incremental samples collected in triplicate from all four depths. For the remainder of the DMA, 30-point incremental sampling was limited to the upper 6 inches below ground surface (bgs).

Evaluations of the results obtained by analyzing these samples are presented in Section 6.

### **2.2.1 Field Documentation**

Information for each soil sample, such as the sample type (5-point composite or 30-point incremental and primary, duplicate or triplicate), sample location, DU sampled, depth interval sampled, sample date, sample time, and sample identification, was documented in a field sampling form, and recorded in the project Scribe database. The DMA field sampling records, including field sampling forms and completed chain-of-custody records are provided in Appendices B and D, respectively.

### **2.2.2 Health and Safety**

PWT developed a site specific Health and Safety Plan (HASP) for conducting the DMA. The HASP specifically addressed residential yard soil sampling activities (PWT 2015a). Sampling personnel conducted work in accordance with the HASP.

## 2.3 SAMPLE DESIGNATION

Soil samples were identified through the use of a coding system to identify sample locations and sample types. This coding system ensures that samples are uniquely identified by matrix, residential lot, decision unit, depth interval, and sample type.

Samples were numbered according to the following system:

Example Sample Number: S0136-FY-1218-03

Matrix: S – Soil

Location Code: 0136 – Property sampled corresponding to property identifier  
PC-0136, address and/or geocode specific

Decision Unit: AP – Soil collected from the Road Apron DU at a particular  
property

BY – Back Yard

DZ – Drip Zone

ED – Earthen Drive

FY – Front Yard

GA – Garden

PA – Play Area

SY – Side Yard

SYE – Side Yard East

SYW – Side Yard West

WP – Waste Pile, soil collected from one of the waste piles on the  
former smelter site.

Depth Intervals: 0002 – 0 to 2 inches bgs, Surface interval for a vegetated DU

0001 – 0 to 1 inch bgs, Surface interval for non-vegetated DU

0206 or 0106 – 2 to 6 inches bgs or 1 to 6 inches bgs

0612 – 6 to 12 inches bgs

1218 – 12 to 18 inches bgs

Sample Type: 01 – Primary 5-point composite sample

02 – Duplicate 5-point composite sample

03 – Triplicate 5-point composite sample

31 – Primary 30-point incremental sample

32 – Duplicate 30-point incremental sample

33 – Triplicate 30-point incremental sample



For example, the identification number S0136-FY-1218-03 indicates that the sample is from the residential property PC-0136. The sample is a 5-point composite, and was collected from the 12 to 18 inch bgs interval in the front yard. This sample was a triplicate, meaning that two other 5-point composite samples were collected from the same DU and depth (the primary and duplicate samples).

A field sampling record was completed for each soil sample. The field sampling record includes the soil sample designation. The DMA soil sampling records are provided in Appendix B. Review of these records indicates that appropriate sample designations were used in the DMA.

## **2.4 FIELD QUALITY CONTROL**

Quality control activities for the DMA were conducted in accordance with the DMA QAPP. Triplicate soil samples were collected to evaluate variability between field samples as one of the DMA objectives. Discussion of variability within and between triplicate sets is provided in Section 6.5 and Section 7.

Sample collection equipment decontamination was conducted in accordance with the equipment and personnel decontamination SOP included in the DMA QAPP (PWT 2015b). To verify the effectiveness of decontamination procedures, rinsate samples were collected at the end of each full day of sampling. These water samples were then shipped to an EPA CLP laboratory for total metals analysis by EPA Method 6020. No metals were detected in the rinsate samples above the CLP contract required quantitation limits (CRQLs). However, trace amounts of metals were detected in the samples, as expected, because distilled water, rather than deionized water, was used for the rinsate sampling. Equipment decontamination was judged to be effective. For the RI sampling effort, it may be acceptable to reduce the frequency of rinsate collection to once per week.

## **2.5 SAMPLE HANDLING AND CUSTODY**

Samples were labeled in the field and stored in coolers which were in custody of the field crew at all times. After completion of sampling activities at a given property, the field crew returned to the field office with the samples, which were then transferred into custody of the field laboratory personnel.

When the soil samples arrived at the field laboratory, the sample inventory on the field sampling form was compared to the labeled samples to ensure accuracy and completeness of sample identifications and other sample collection information. If errors or discrepancies were identified during sample check in, the field samplers were consulted, and the discrepancies resolved/corrected. The field sampling forms were then signed to serve as written acknowledgement that the samples had been transferred intact to the field laboratory. Sample collection information in Scribe was updated during or after sample check in, and sample preparation labels were generated in Scribe for each soil sample.

Based on the results of the DMA field discussion in this section, it can be concluded that the field equipment and sampling methodology identified in the DMA QAPP were adequate to conduct the DMA project and provide samples sufficient for analysis and characterization of soil conditions at the DMA properties.

**TABLE 2-1  
2015 DMA SOIL SAMPLES**

Property Code	Decision Unit	DU ft <sup>2</sup>	30 pt incremental	Sample Depth	Triplicate	5 pt composite	Sample Depths	Triplicate
PC0181	Front Yard	207				X	0-2, 2-6, 6-12, 12-18	X
	Side Yard	318				X	0-2, 2-6, 6-12, 12-18	X
	Back Yard	516				X	0-2, 2-6, 6-12, 12-18	X
	Garden	125				X	0-2, 2-6, 6-12, 12-18	
PC0269	Side Yard	1,025	X	0-2, 2-6	X	X	0-2, 2-6, 6-12, 12-18	X
	Back Yard	1,446				X	0-1, 1-6, 6-12, 12-18	X
	Apron	260				X	0-1, 1-6, 6-12, 12-18	X
	Drip Zone	25				X	0-1	X
PC0389	Front Yard	86				X	0-1, 1-6, 6-12, 12-18	X
	Side Yard	1526				X	0-1, 1-6, 6-12, 12-18	X
	Back Yard	1780	X	0-1, 1-6	X	X	0-1, 1-6, 6-12, 12-18	X
	Apron	300				X	0-1, 1-6, 6-12, 12-18	X
PC0423	Drip Zone	52				X	0-1	X
	Side Yard East	12,626	X	0-1, 1-6, 6-12, 12-18	X	X	0-1, 1-6, 6-12, 12-18	X
	Side Yard West	540				X	0-1, 1-6, 6-12, 12-18	X
	Back Yard	1623	X	0-2, 2-6	X	X	0-2, 2-6, 6-12, 12-18	X
	Drip Zone	129				X	0-1, 1-6	X
	Earthen Drive	1,234				X	0-1	X
PC1504	Garden					X	0-1, 1-6, 6-12, 12-18	
	Front/Side Yard	1738	X	0-2, 2-6	X	X	0-2, 2-6, 6-12, 12-18	X
	Back Yard	1896	X	0-1, 1-6	X	X	0-1, 1-6, 6-12, 12-18	X
	Drip Zone	158				X	0-2	X
PC1592	Front Yard	200				X	0-2, 2-6, 6-12, 12-18	X
	Back Yard	274				X	0-2, 2-6, 6-12, 12-18	X
	Garden	90				X	0-1, 1-6, 6-12, 12-18	
	Play Area	231				X	0-1, 1-6, 6-12, 12-18	X
PC1615	Play Area SAND	231	X	depth of sand	X			
	Front Yard	96				X	0-2, 2-6, 6-12, 12-18	X
	Side Yard	232				X	0-2	X
	Back Yard	990	X	0-2, 2-6	X	X	0-2, 2-6, 6-12, 12-18	X
	Apron	280				X	0-2, 2-6, 6-12, 12-18	X
	Earthen Drive (Car Port)	284				X	0-1, 1-6, 6-12, 12-18	
PC1654	Garden	90				X	0-1, 1-6, 6-12, 12-18	
	Front Yard	1,197	X	0-2, 2-6	X	X	0-2, 2-6, 6-12, 12-18	X
	Back Yard	968				X	0-2, 2-6, 6-12, 12-18	X
	Drip Zone	172				X	0-1	X
PC1835	Garden	144				X	0-1, 1-6, 6-12, 12-18	
	Front Yard	366				X	0-1, 1-6, 6-12, 12-18	X
	Back Yard	1,009				X	0-2, 2-6, 6-12, 12-18	X
	Drip Zone	74				X	0-2	X
PC0724	Apron	258				X	0-2, 2-6, 6-12, 12-18	X
	Front Yard	351				X	0-2, 2-6, 6-12, 12-18	X
	Side Yard West	306				X	0-2, 2-6, 6-12, 12-18	X
PC0496	Side Yard East	597				X	0-1, 1-6, 6-12, 12-18	X
	Front Yard	310				X	0-2, 2-6, 6-12, 12-18	X
	Side Yard	124				X	0-2, 2-6, 6-12, 12-18	X
PC1076	Back Yard	183				X	0-2, 2-6, 6-12, 12-18	X
	Front Yard	1,238				X	0-2, 2-6, 6-12, 12-18	X
	Back Yard	1,115	X	0-2, 2-6	X	X	0-2, 2-6, 6-12, 12-18	X
	Earthen Drive	1,000				X	0-1, 1-6, 6-12, 12-18	X
	Drip Zone	40				X	0-1	X
Waste Piles	Apron	343				X	0-2, 2-6, 6-12, 12-18	X
	WP1	NA				X	0-2	X
	WP2	NA				X	0-2	X
	WP3	NA				X	0-2	X
	WP4	NA				X	0-2	X
	WP5	NA				X	0-2	X
WP6	NA					X	0-2	X



Figure 2-1 Colorado Smelter Preliminary Study Area



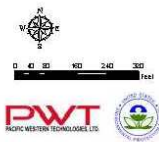
0 250 500 1,000 Feet

NAD 1983 StatePlane Colorado South FIPS 0503 Feet  
Imagery: Google Earth dated August 2013

**Legend**

- DMA Properties
- Preliminary Study Area
- Colorado Smelter Site Limit
- Site Parcels

Path: K:\GIS Library\Projects\Colorado Smelter\Maps\DMA\_20151014.mxd



**Colorado Smelter DMA Waste Pile Sample Location**

- CO\_Smelter\_Sample\_Points
- CO\_Smelter\_Site\_Limit

Figure 2-2

### **3.0 SAMPLE PREPARATION**

This section describes DMA soil sample preparation (drying, disaggregation, and sieving) and associated QA/QC activities.

#### **3.1 SAMPLE PREPARATION OBJECTIVES**

In order to evaluate the matrix heterogeneity within each DU, it was necessary to thoroughly homogenize each soil sample after sample collection and prior to sample analysis. This was accomplished through a standardized procedure of drying, disaggregation, and sieving, as described in PWT-COS\_DMA-302, which is included in the DMA QAPP (PWT 2015b). Disaggregation is the process of breaking clumps of soil into free flowing particles. It does not include fracturing, crushing, or pulverizing individual soil particles.

#### **3.2 SAMPLE PREPARATION PROCEDURE**

Soil samples were delivered to the field laboratory by the samplers, checked in from the field, then weighed. Initially, sample bags were left open overnight to promote air drying of soil. However, it was determined as the DMA progressed that leaving the sample bag open overnight did not significantly affect the sample moisture content, each sample still required further oven drying for a similar duration. Subsequent to this observation, sample bags were kept closed until soil was transferred to a drying oven. It is possible that this degree of sample drying may not be necessary during a period with less rainfall (the sampling occurred during an especially rainy period of time). Therefore no modification to the sample drying options in the standard procedure is recommended. A sample is dry enough to be sieved when soil particles move freely, and no color variation can be observed when the sample is stirred on the drying tray. A dry weight was recorded for each sample. The dried samples were disaggregated using a rolling pin, rubber mallets, and other methods as described in the sample preparation SOP.

Dried soil samples were transferred to a labeled stack of soil sieves which included a No. 10 sieve, a No. 60 sieve, and a solid bottomed catch pan. The purpose of the sieving process was to separate the samples by particle size. The weights of soil retained on the No. 10 screen, retained on the No. 60 screen, and passing the No. 60 screen were measured and recorded. The fractions of soil were stored separately in bags labeled with both the sample ID and the size fraction. The fine fraction of each soil sample, comprised of those particles smaller than 250 microns (passing the No. 60 sieve), was then analyzed by XRF as described in Section 4. The sample preparation log which details sample weights is included in Appendix C.

##### **3.2.1 Subsampling**

Field laboratory personnel also collected one or more 1-2 gram subsamples from 40 selected samples. In some cases, only one additional analysis was planned (usually ICP-MS), and so only one subsample was prepared. However, when multiple additional analyses were scheduled (i.e. ICP-MS, bioaccessibility, and geospeciation), more than one subsample bag was prepared. These subsamples were provided to the CLP laboratory for analysis by ICP-MS or to provide samples for bioaccessibility testing. The subsampling was conducted in accordance with the procedure described in Section 4.3 of the XRF sample analysis SOP (PWT-COS\_DMA-303) included in the DMA QAPP. Once a subsample was prepared, it was analyzed by XRF to determine whether it was sufficiently comparable to the source sample.

Samples which were determined not to be sufficiently comparable were mixed back into the source sample, and then a new subsample was prepared in accordance with the procedure. Subsample analysis and acceptance (or rejection) is discussed in Section 4.

### **3.2.2 Field Laboratory Documentation**

Sample preparation activities were documented using the sample preparation log format included in the sample preparation SOP. A scan of the handwritten Sample Preparation Log, as well as a table summarizing the sample preparation information, are included in Appendix C.

Calculations of percentage of dry mass lost were completed for each sample to help to identify cases of typographical or other human errors in the soil preparation process. Three samples with a calculated mass percent loss during sieving greater than 15 percent, and one sample with a calculated mass percent gain of greater than 7 percent, were identified as likely to have an error associated with sample preparation or sample preparation documentation.

Examination of these samples does not indicate a systematic error, and there is no reason to suspect that the error in sample preparation documentation would impact the quality or uncertainty of chemical analysis later performed on the samples.

An additional 18 samples did not have a calculated percent mass loss because one or more sample weights were not recorded during the sample preparation process. In four instances, one or more of the post-sieving masses were not recorded. For the other 14 of these 18 samples, the weight which was not recorded was the post drying/pre-sieving mass. These omissions appear to be random, and there is no reason to suspect that the error in sample preparation documentation would impact the quality or uncertainty of chemical analysis performed on the samples.

In order to improve preparation laboratory quality, and to reduce errors, the form used to document soil preparation activities will be adjusted prior to the RI sampling effort at the site. The primary adjustments will be to generate sample preparation forms including the sample identification in Scribe, rather than by hand, and to increase the height of each row on the sample preparation form. These adjustments will ensure the sample IDs are entered in a logical order and will be easier to locate, and will provide more room for personnel to record information or to make corrections when necessary. Other editorial changes to the sample preparation laboratory paperwork may also be implemented.

### **3.3 FIELD LABORATORY QUALITY CONTROL**

Field laboratory quality control included conducting routine calibration checks on the analytical balances used in the laboratory, routine decontamination of equipment which touched multiple samples, and collection of preparation equipment rinsate samples to verify that decontamination procedures were effective.

Daily calibration checks of analytical balances used for weighing soil samples and subsamples identified no issues with the balances. For the RI sampling effort, it may be acceptable to reduce the frequency of these quality checks from daily to weekly.

Routine decontamination was conducted for sieves and other sample preparation equipment which came in contact with multiple samples. Initially, decontamination consisted of brushing the sieves with appropriate gauge brushes after each sample, as recommended by the manufacturer and described in Section 4.7 of the XRF Sample Preparation SOP. However, it was observed that a fine coating of dust sometimes remained after this decontamination

process, which could not be removed by dry brushing alone. The decontamination process was adjusted to include the additional step of wiping with a damp paper towel between each sample.

To verify that decontamination procedures were effective, rinsate samples were collected. These samples consisted of distilled water which was allowed to contact sieves before collection in a sample bottle. The rinsate samples were sent to the CLP laboratory and analyzed for metals. Metals were not detected in any of the rinsate samples above CRQLs. However, trace amounts of metals were detected in the samples, as expected, because distilled water, rather than deionized water, was used for the rinsate sampling.

The decontamination procedure adopted during the DMA, utilizing a dry brush followed by a damp paper towel, was found to be effective, and is recommended for the larger sampling effort. However, the process of collecting rinsate samples through the soil sieves was observed to be damaging the sieves, causing rust to begin to form on the cut ends of the wires which made up the screens, where they were crimped into the crease on the side of the sieve. For this reason, the use of laboratory-grade silica to create rinsate samples through the sieves will be investigated for the larger sampling effort.

### **3.4 FIELD LABORATORY SAMPLE HANDLING AND CUSTODY REQUIREMENTS**

Samples were received in the field laboratory from the field sampling personnel. While sample preparation activities were conducted, samples were kept in or transferred between labeled bags or containers. Samples were handled by field samplers and field laboratory personnel, and were stored on a shelf in the sample preparation area (prior to sample processing), or on a storage shelf in a locked room across from the sample analysis area (after sample processing). No unauthorized personnel had access to the field laboratory during the DMA.

Based on the results of the DMA sample preparation discussion, it can be concluded that the lab preparation equipment and preparation methodologies identified in the DMA QAPP were adequate to conduct the DMA project and provide samples of sufficient quantity and quality for accurate XRF analysis.

## 4.0 SAMPLE ANALYSIS

This section describes soil sample analysis by XRF and associated QC activities for the DMA, including: 1) sample analysis objectives, 2) sample analysis procedures, 3) subsample analysis, 4) analytical documentation, and 5) analytical quality control. XRF sample analysis was conducted in accordance with the approved DMA QAPP and XRF Sample Analysis SOP (PWT-COS\_DMA-303).

The Thermo Scientific XL3t 955 GOLDD Ultra XRF Analyzer (XRF Instrument) was selected for use during the DMA. One XRF Instrument was provided by the EPA Technology Integration and Information Branch (TIIB), and a second XRF Instrument was rented for the DMA. Additional information regarding the XRF Instruments is provided in Appendix C.

This section also describes soil subsample analysis via ICP-MS, performed by the assigned offsite analytical CLP laboratory using EPA Method 6020B.

Measured concentrations of arsenic and lead for each DU and depth sampled are presented in Tables A-1 through A-13 in Appendix A. For sampling units where triplicate sample results are available, the mean of the three result concentrations is given.

### 4.1 SAMPLE ANALYSIS OBJECTIVES

The goal of XRF sample analysis was to determine the mean concentration of arsenic and lead in each sample and to provide quality control measurements and data to allow evaluation of the uncertainty associated with sample collection, sample preparation, and sample analysis. The goal of offsite laboratory ICP-MS analysis was to determine the concentration of TAL metals in each subsample analyzed. The primary intended purpose of the ICP-MS data is to evaluate whether and to what extent the concentrations of arsenic and lead measured by XRF in a processed soil sample are comparable to those measured by ICP-MS. The ICP-MS analyses also provide concentrations for additional TAL metals, as described in the approved DMA QAPP.

**Based on the results of the DMA sample XRF analysis discussion, it can be concluded that the XRF equipment and XRF analysis methodologies identified in the DMA QAPP (PWT 2015b) were adequate to support the DMA project and provide analytical results of sufficient quality for decision making on the forthcoming RI project.**

### 4.2 XRF SAMPLE ANALYSIS PROCEDURE

Samples were analyzed in a multi-step procedure. Each sample was initially inspected, and then analyzed. Initial quality control procedures were conducted at the start of the project, as well as when new lots of bags were used. Routine quality control procedures were conducted at the start of each day and periodically throughout the day. Corrective actions were performed as necessary, based on quality control results.

#### 4.2.1 Initial Inspection

Each sample was inspected before analysis. This inspection confirmed that the sample was in the correct type of plastic bag (polypropylene of 1.2 mil thickness). If crinkles or dimples were found in the bag which could interfere with the XRF measurement, the sample was transferred to a new bag. The sample was homogenized within the sample bag as described in the SOP. After homogenization, the sample material within the bag was visually inspected to verify that



the appearance of soil particles was the same on each side of the bag without any noticeable stratification of particles. If any differences were noted, additional homogenization within the sample bag was conducted as necessary until visual inspection showed no noticeable stratification.

#### **4.2.2 XRF Measurements for Full Samples and Subsamples**

For the Colorado Smelter DMA, the XRF instrument was secured in a test stand specifically designed for the purpose. All field laboratory XRF readings were taken using this test stand. The test stand protected the XRF instrument from damage during readings, provided a flat, level platform for consistent sample placement, and had a closable, lead lined lid which enhanced operator safety during readings. The XRF instrument was clicked into place in the stand and readings were taken through a small window designed for that purpose.

Analysis of investigative DMA samples was conducted only after routine XRF equipment startup and QC steps were completed and the sample had been inspected and homogenized.

The sample was placed flat over the window and two separate XRF readings were taken, and recorded on a spreadsheet. Then the bag was flipped over, and two additional readings were taken on the opposite side and recorded on the spreadsheet. The operator then checked if the statistical confidence goals for the sample had been met for arsenic and lead, as described in the XRF sample analysis SOP. If the goals had been met, analysis of the sample was complete. If the variability of the first four readings exceeded the limits defined in the SOP, then additional measurements were taken in pairs (one on each side of the bag) until both the mean and the lower 95% confidence limit (LCL) were above the decision limit, or both the mean and the upper 95% confidence limit (UCL) were below the decision limit.

For additional detail regarding the sample analytical procedure, management of variability, and determination of the number of measurements required, refer to the XRF sample analysis SOP in the approved DMA QAPP (PWT 2015b).

For subsamples, the XRF analysis procedure was similar. However, the subsampling bags were smaller, containing 1-2 grams of soil. The operator ensures that an adequate soil thickness (3 mm) was present when the subsample bag was placed over the window. Four readings were taken from the subsample bag, flipping the bag over after the first two readings. The subsample analysis procedure described in the approved SOP requires that the mean subsample concentration lie between the 95 percent LCL and the 95 percent UCL for the source soil sample. However, during subsample analysis, it was determined that this goal was not achievable, primarily due to the very low variability between the individual XRF measurements for each full sample.

Based on direction received from TIIB on May 28, 2015, the subsample acceptance criteria were modified to a tiered approach which allowed subsample analysis, and acceptance to proceed. The first tier was to compare the mean subsample concentration to the 95 percent LCL and the 95 percent UCL for the source soil sample, as described in the previous paragraph. If the mean subsample concentration was between the 95 percent LCL and UCL, the subsample was considered consistent with the source sample. If it was not, the second tier was to compare the mean subsample concentration to the mean of the source soil sample plus or minus 10 percent. If the mean subsample concentration fell within this range, the subsample was also considered consistent with the source sample. This was considered acceptable since the primary reason for assuring the subsample concentration was approximately equivalent to the source sample bag was to ensure a wide range of concentrations for comparison to the ICP-

MS method results. Subsample concentrations significantly different from the source sample could have resulted in insufficient coverage for comparability determinations. In summary, the 1-2 gram subsample was considered representative of the full sample if the mean concentration was +/- 10% and/or within the 95 percent LCL and 95% UCL on the mean concentration of the full sample XRF results.

#### **4.2.3 Field Laboratory Documentation**

Sample analysis activities were documented using a sample analysis log (Excel spreadsheet), control charts, and a daily logbook. Nonconformances, troubleshooting, and corrective actions were recorded in the daily logbook, and are summarized below. XRF data was initially recorded in the analytical spreadsheet, but was later replaced with a direct output from the XRF instrument to prevent transcription errors. This instrument output was imported into Scribe, the project analytical database, for ease of use as the project progresses.

Typical nonconformances, troubleshooting, and corrective actions included the following:

1. Nonconformances
  - a. No nonconformances were observed during the project
2. Troubleshooting
  - a. Sealing sample bag corners with adhesive tape when small leaks were observed
  - b. Cleaning the XRF instrument window when target analytes were detected in the blank, in accordance with the SOP
3. Corrective actions
  - a. Correction of sample ID entries in the logbook or instrument electronic logfile
  - b. Identification of sample scans not meeting SOP requirements (for example, aborted scans, sample not moved between scans, dimple in bag or gap in sample noted using instrument camera during analysis).
  - c. Reanalysis of blanks above criteria, in accordance with the SOP
  - d. Reanalysis of LCS outside criteria, in accordance with the SOP
  - e. Reanalysis of samples bracketed by LCS not meeting criteria, in accordance with the SOP

#### **4.2.4 Field Laboratory Quality Control**

Initial and routine quality control activities associated with XRF sample analysis included control charting of arsenic and lead, interference checks, blank analysis, LCS analysis, and instrument duplicate analysis, as described in the sample analysis SOP.

- Control charts were created at the start of the DMA to create control limits for assessing instrument performance. The control charts were created by analyzing SRM materials multiple times over a period of several days to capture instrument accuracy and instrument variability.
- Interference checks were conducted at the start of the DMA for each lot of bags to ensure the plastic bags used to analyze XRF samples did not significantly affect the results for the soil. The checks were performed by analyzing SRM materials several times with and without a layer of the bag material between the beam and the SRM cup. A Student's t-test was used to compare the results of the two sets of samples (with and without the plastic layer). Interference checks were not completed on a third lot of bags which was received during the DMA. This interference check will be completed before any of the newest lot of bags are used for RI sample analysis.

- Blank analysis was performed routinely during sample analysis. At the start and end of each sample batch, as well as periodically during the day, a blank sample was analyzed to confirm that the XRF membrane was clean.
- LCS analysis was performed routinely during sample analysis. At the start and end of each sample batch, as well as periodically during the day, LCS samples were analyzed and plotted on control charts to confirm that the instrument was in control.
- Instrument duplicates were analyzed semi-routinely during sample analysis. These duplicates were created by running an LCS twice consecutively without moving the sample. The data were used only for informational purposes in the event that an instrument was found to be out of control and could not be returned to an in control state. This did not occur during the DMA.

The results of these QC checks were evaluated as part of the data verification, and are discussed in Section 5.

### **4.3 ICP SAMPLE ANALYSIS PROCEDURE**

As described above, a subset of the DMA soil samples were selected for subsampling and subsample analysis by EPA Method 6020B. These subsamples were prepared as described in Section 3, analyzed by XRF as described above in Section 4.2, and then sent to an EPA specified commercial laboratory under the EPAs CLP. As a result, the laboratory analyses were conducted under the EPAs CLP protocols and QA/QC requirements, with slight modification to accommodate the requirements of the DMA. Chem Tech Consulting Group (Chem Tech) performed all of the analyses on the subsamples.

In accordance with the DMA QAPP, 1 to 2 gram subsamples of 40 individual soil samples were sent for laboratory analyses for total metals by Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS). The total metals analyte list (TAL) for ICP-MS, EPA Method 6020B, excludes aluminum, calcium, iron, magnesium, potassium, and sodium. Table 4-1 presents the TAL for EPA method 6020 and Table 4-2 provides the sample designation and type of analysis for each soil sample sent for offsite laboratory analysis. Appendix E contains copies of the laboratory case narratives and analytical results.

Based on the results of the DMA sample XRF analysis discussion, it can be concluded that the XRF equipment and XRF analysis methodologies identified in the DMA QAPP (PWT 2015b) were adequate to support the DMA project and provide analytical results of sufficient quality for decision making on the forthcoming RI project.

**Table 4-1**  
**CLP ANALYTICAL METHODS**

Analytical Method	Media	Analytes	MRL* (mg/Kg)	Instrumentation
<b>Inorganic Methods</b>				
ICP-MS 6020B	Soil	Antimony	1.0	Inductively Coupled Plasma / Mass Spectroscopy
		Arsenic	0.50	
		Barium	5.0	
		Beryllium	0.50	
		Cadmium	0.50	
		Chromium	1.0	
		Cobalt	0.50	
		Copper	1.0	
		Lead	0.50	
		Manganese	0.50	
		Nickel	0.50	
		Selenium	2.5	
		Silver	0.50	
		Thallium	0.50	
Vanadium	2.5			
Zinc	1.0			

\* MRL – Method reporting limit

**TABLE 4-2****DMA SAMPLE OFFSITE LABORATORY ANALYSIS**

<b>Sample Identification</b>	<b>Analyses</b>
S0000-WP3-0002-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0000-WP4-0002-01	Total Metals by ICP-MS (6020)
S0000-WP5-0002-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0000-WP6-0002-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0181-BY-1218-01	Total Metals by ICP-MS (6020)
S0181-FY-0612-01	Total Metals by ICP-MS (6020)
S0181-GA-0002-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0181-SY-0206-01	Total Metals by ICP-MS (6020)
S0181-SY-0612-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0181-SY-0612-03	Total Metals by ICP-MS (6020)
S0269-SY-0002-31	Total Metals by ICP-MS (6020)
S0389-AP-0001-01	Total Metals by ICP-MS (6020)
S0389-DZ-0001-01	Total Metals by ICP-MS (6020)
S0389-FY-0001-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0423-BY-0002-02	Total Metals by ICP-MS (6020)
S0423-SYE-0001-02	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0423-SYE-0001-31	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0423-SYE-0001-32	Total Metals by ICP-MS (6020)
S0423-SYE-0106-02	Total Metals by ICP-MS (6020)
S0423-SYE-0106-03	Total Metals by ICP-MS (6020)
S0423-SYE-0106-33	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S0423-SYE-0612-33	Total Metals by ICP-MS (6020)
S0496-SY-0002-01	Total Metals by ICP-MS (6020)
S0724-SYE-0001-01	Total Metals by ICP-MS (6020)
S1076-ED-0001-01	Total Metals by ICP-MS (6020)

\*Geospeciation and Bioaccessibility Analysis performed by University of Colorado in accordance with SOPs in the approved DMA QAPP.

**TABLE 4-2****DMA SAMPLE OFFSITE ANALYSIS**

<b>Sample Identification</b>	<b>Analyses</b>
S1504-BY-0612-02	Total Metals by ICP-MS (6020)
S1504-BY-1218-01	Total Metals by ICP-MS (6020)
S1504-FY-0206-02	Total Metals by ICP-MS (6020)
S1504-FY-0206-31	Total Metals by ICP-MS (6020)
S1592-FY-0206-01	Total Metals by ICP-MS (6020)
S1592-PA-0106-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S1592-PA-0106-03	Total Metals by ICP-MS (6020)
S1615-BY-0002-32	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S1615-BY-0206-31	Total Metals by ICP-MS (6020)
S1615-FY-0206-03	Total Metals by ICP-MS (6020)
S1615-SY-0002-03	Total Metals by ICP-MS (6020)
S1654-BY-0002-01	Total Metals by ICP-MS (6020)
S1654-DZ-0001-01	Total Metals by ICP-MS (6020)
S1654-FY-0002-01	Total Metals by ICP-MS (6020), Geospeciation & Bioaccessibility*
S1835-BY-0002-02	Total Metals by ICP-MS (6020)

\*Geospeciation and Bioaccessibility Analysis performed by University of Colorado in accordance with SOPs in the approved DMA QAPP.

## 5.0 DATA QUALITY EVALUATION

Before environmental data is used for project decision making, the data must be verified and validated, and the quality of the data should be quantitatively evaluated. The quality of the DMA data was evaluated for precision, accuracy, representativeness, comparability, and completeness (PARCC) against the data quality requirements for these parameters as described in the approved DMA QAPP, to determine if it met the data quality requirements for the DMA.

PWT submitted soil samples to Chem Tech for laboratory analyses through the EPA CLP. The quality of this data was also evaluated to determine whether it met project requirements. Selected soil samples were sent for bioaccessibility and geospeciation analysis at the University of Colorado laboratory, the results of those analyses will be reported separately.

### 5.1 PARCCS PARAMETERS

DMA data was evaluated against PARCC parameters to determine whether project goals defined in the approved DMA QAPP had been met. A discussion of this evaluation is provided below.

#### 5.1.1 Precision

Precision is the reproducibility of measurements under a given set of conditions. For most environmental projects, duplicate or replicate measurements are taken, and precision is often expressed as the relative percent difference (RPD) of a data pair. In general, analytical laboratory precision is assessed using the calculated RPD between the following data:

- Field replicate or duplicate sample pairs
- Matrix spike/matrix spike duplicate sample pairs (MS/MSD)

The RPD is calculated using the following formula:

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2)/2} \times 100$$

Where:

$C_1$  = reported concentration for "original" sample  
 $C_2$  = reported concentration for duplicate sample

Although the RPD is used for some of the Colorado Smelter DMA measures of precision, triplicate measurements were taken to evaluate field precision instead of duplicates. When triplicate data are collected, a relative standard deviation (RSD) is calculated instead of an RPD.

First, the standard deviation of the data is calculated using the following formula:

$$SD = \sqrt{\frac{\sum(C_i - \bar{C})^2}{N - 1}}$$

Where:

SD = the standard deviation

$C_i$  = the reported concentrations for  $i = 1$  to 3

$\bar{C}$  = the mean concentration

N = the number of samples

The RSD is then calculated by dividing the standard deviation by the mean concentration. The RSD is a fractional value that can be converted to the more convenient %RSD by multiplying by 100, as shown below:

$$\%RSD = \frac{SD}{\bar{C}} \times 100$$

An upper confidence limit (UCL) was also calculated for each DU and depth using the field triplicate sample results. The UCL for triplicate samples is calculated using the equation:

$$95\% t - UCL = \bar{C} + \frac{2.92 \times SD}{\sqrt{3}}$$

Where:

SD = the standard deviation

$\bar{C}$  = the mean concentration

2.92 is the value of the one-tailed Student's t-distribution at 95% confidence level and two degrees of freedom

RPD and %RSD values cannot be directly compared because a given RPD value does not represent the same amount of imprecision as the same value for %RSD. The values of RPD and %RSD are related by the square root of 2, such that  $\%RSD \times \text{sqrt}(2) = \text{RPD}$ . For example, the amount of imprecision given by an RPD of 35% is given by 25% RSD.

Inter-conversion between RPD and %RSD is useful when it is desirable to directly compare or combine RPD and %RSD values. The procedure would be to convert the RPD values into %RSD values (using the above equation) for direct comparison.

Care must also be employed when combining %RSD values to get an overall average %RSD for a group of replicates. The %RSD values must first be converted to relative variance by squaring all of the %RSD values. The average of the relative variances is determined the usual way, then the square root of the average relative variance is calculated to provide the average %RSD.

XRF laboratory precision was evaluated using several samples which were analyzed twice. This process of completing a full duplicate analysis on a sample should not be confused with the standard XRF analytical procedure mentioned in Section 4.2.2 and detailed in the XRF Analysis SOP, which involves taking replicate XRF measurements on a sample in pairs until statistical confidence goals are met. Table 5-2 summarizes the analytical results, mean, and RPD for each XRF laboratory duplicate pair. All RPDs were below 31%, with only two laboratory



duplicates that exceeded 25% RPD. These two duplicates were low concentration samples, one each for arsenic and lead.

In addition to laboratory duplicates, XRF laboratory precision was controlled using control charts for laboratory control sample (LCS) results. LCSs were standard reference materials (SRM) with certified concentrations in pre-assembled XRF cups. As noted in the DMA QAPP, whenever an LCS result fell outside control limits of 2 standard deviations from the mean, corrective actions were taken to ensure the instrument was in control. Instrument-specific control charts were developed before analysis of field samples began, and the control limits were re-evaluated on June 1, 2015 with the inclusion of additional data from the beginning of the DMA study. Several conclusions regarding XRF laboratory precision can be made based on the LCS data:

- With only two minor exceptions, all bracketing LCS results were within two standard deviations of the mean, indicating the instrument was in control. The two exceptions are described below:
  - One lead LCS result was within 1% of the lower limit and 5% of the mean reading for this SRM. This failure is not expected to significantly affect the accuracy of the readings affected by this LCS result.
  - One LCS result was for a low concentration SRM for lead (17.3 mg/kg) that is not near the range of decision-making on the project. This result also would have fallen within the re-evaluated control limits, and is not expected to significantly affect the accuracy of the bracketed readings, all of which were between 180 and 240 mg/kg).
- The RSDs for all passing LCS standards ranged from 1% to 27%, depending on the SRM material, analyte, and instrument. All were below 13% with the exception of a low-concentration lead SRM (17.3 mg/kg) for which the RSD was 27%. This indicates good instrumental precision for the XRF.
- Over the course of the project, approximately 6.4% of the LCS standards fell outside the  $\pm 2$  standard deviation range, which is slightly higher than the expected rate of 4.6% for a normal distribution. This slightly higher measured rate implies that the control charts did not capture the full variability of the LCS SRMs, but the difference is not so large as to be a concern.

Evaluation of ICP-MS laboratory precision was not possible based on the sample preparation procedures outlined in the DMA QAPP (PWT2015b). To prevent subsampling error at the analytical laboratory, all samples were provided to the CLP laboratory as a 2-gram aliquot in a plastic bag, and the laboratory was instructed to digest the entire sample. Laboratory duplicate sample analysis, as well as MS/MSD analysis was not possible because of these procedures. The laboratory precision for ICP-MS is expected to be within the observed field precision.

### 5.1.2 Accuracy

Accuracy is the degree of agreement between a measurement, or an average of measurements, and an accepted reference or “true” value, and is a measure of bias in the system. That is, the concentration determined by analysis (“measured”) is compared to the

actual known standard (“spiked”). Accuracy for most quality control samples is evaluated using percent recovery as calculated below:

$$\text{Percent Recovery} = \frac{C_{\text{measured}}}{C_{\text{spiked}}} \times 100$$

Where:

$C_{\text{measured}}$  = target analyte concentration determined analytically from the spiked sample

$C_{\text{spiked}}$  = known concentration of analyte in the spiked sample

For matrix spikes and matrix spike duplicates, accuracy is evaluated using a modified equation that accounts for the amount of analyte detected in the unspiked sample, as shown below:

$$\text{Percent Recovery} = \frac{|C_{\text{measured,spiked sample}} - C_{\text{measured,unspiked sample}}|}{C_{\text{spiked}}} \times 100$$

Where:

$C_{\text{measured, spiked sample}}$  = target analyte concentration determined analytically from the spiked sample

$C_{\text{measured, unspiked sample}}$  = target analyte concentrations determined analytically from separate analysis of the unspiked sample

$C_{\text{spiked}}$  = known concentration of spiked analyte added

Analytical laboratory accuracy for the XRF method was assessed using LCS results for three of the five different SRMs used during the DMA. The other two SRMs were not used consistently and therefore were not included in the accuracy evaluation. As noted in the DMA QAPP and in Section 5.1.1 above, whenever an LCS result fell outside control limits of 2 standard deviations from the mean corrective actions were taken to ensure the instrument was in control. Figure 5-1 summarizes the LCS results for arsenic, while Figure 5-2 summarizes the LCS results for lead. The average accuracy for the LCS results for the five SRMs assessed ranged from 63.6% to 104.8%, with an average of 91.9%. The figures show that the range of LCS results is wider at lower concentrations for both arsenic and lead, which is expected as the SRM concentration is closer to the XRF instrument detection limit. The accuracy at concentrations near the DMA SLs is excellent for both arsenic and lead. (Figure 5-1 USGS LCS for Arsenic, Figure 5-2 RCRA LCS for Lead)

- For arsenic, the SRMs with concentrations of 10.5 and 78 mg/kg bracket the DMA SL of 30 mg/kg for arsenic; the average LCS recoveries were between 76% and 129% for these SRMs.
- For lead, the SRMs with concentrations of 17.3 and 500 mg/kg bracket the DMA SL of 400 mg/kg for lead; the average LCS recoveries were between 63% and 95% for these SRMs. The 500 mg/kg SRM, with average LCS recovery of 95%, is expected to be more indicative of accuracy at concentrations near 400 mg/kg.

Analytical laboratory accuracy for the ICP-MS method was assessed quantitatively through the analysis of surrogate spikes, laboratory control samples (LCSs), and response factors for calibration standards and internal standard recoveries. Specific accuracy criteria, such as acceptable percent recovery values, are presented in the DMA QAPP. Accuracy for the ICP-MS method from surrogates and LCSs was evaluated as part of the data verification process

described in Section 5.3. In general, although deviations and exceptions occurred, the data are considered to be accurate as a whole.

Laboratory data were also evaluated for accuracy by assessing whether the holding time criteria were met. All holding times were met.

Evaluation of method blanks, trip blanks, equipment blanks, and interference checks were also used to assess accuracy.

- No method blank results were above the PQL.
- Trip blanks are only analyzed for VOCs and are submitted only when VOCs are to be analyzed in the sample. Therefore no trip blanks were submitted for analysis with the samples.
- Equipment blanks were analyzed on a regular basis. Arsenic and lead were not detected above the contract-required quantitation limit (CRQL) for water samples in any of the 14 equipment blanks submitted for ICP-MS analysis, indicating that cross-contamination from sampling equipment did not occur.

Interference checks were conducted for two of the three types of plastic bags used for XRF analysis. The third type was not tested, but will be tested during the RI. Interference for the plastic bags was found to be minimal and within DMA QAPP requirements.

### **5.1.3 Representativeness**

Representativeness is a qualitative expression of the degree to which sample data accurately and precisely represent a characteristic of a population, a sampling point, or an environmental condition. Representativeness criteria for specific parameters are presented in the DMA QAPP (PWT 2015b).

The goal for this project is for each composite and incremental sample to represent the true mean concentration of that DU and depth. Representativeness of the field data was achieved by following the DMA QAPP and SOPs during sample collection, processing, and analysis. Sample representativeness is measured by assessing the precision of the field replicates using the %RSD. The precision of field sampling procedures was evaluated with field triplicate samples for the XRF, and field duplicate samples for ICP-MS.

Most soil samples were collected in triplicate, with all three triplicates analyzed by XRF. RSD values were calculated for the triplicates. The DMA QAPP does not include a quantitative goal for RSDs, but the project performance criterion is that the standard deviation should be low enough for statistical decision-making to be made at the desired level of confidence. It is possible to set numerical criteria if the concentration range over which the criterion applies is specified. If setting a representativeness criterion is desired, it is best to use a criterion that is related to the ability to make confident decisions. For example, if 400 ppm Pb and 30 ppm As are used as benchmarks, tighter criteria are needed when the results are closer to the benchmarks.

Tables 5-3 and 5-4 summarize the analytical results, RSDs, and UCLs for field triplicates collected using the 5-point composite and 30-point incremental sampling approaches. The tables also include a column that shows whether the mean and UCL provide a clear decision –

that is, they are either both above or both below the DMA screening level (SL). Summary results are as follows:

- Arsenic RSDs for the 5-point composite sampling approach ranged from 0.8% to 49%, with a mean RSD of 13.7%. Of the 154 triplicates, 144 provided clear decisions, and 10 provided unclear decisions (this is 93.5% clear decisions).
- Lead RSDs for the 5-point composite sampling approach ranged from 0.8% to 117.3%, with a mean RSD of 18.7%. Of the 154 triplicates, 139 provided clear decisions, and 15 provided unclear decisions (this is 90.3% clear decisions).
- Arsenic RSDs for the 30-point incremental sampling approach ranged from 1.9% to 24.3%, with a mean RSD of 11.4%. Of the 20 triplicates, 18 provided clear decisions, and 2 provided unclear decisions (this is 90% clear decisions).
- Lead RSDs for the 30-point incremental sampling approach ranged from 1.4% to 69.7%, with a mean RSD of 11.8%. Of the 20 triplicates, 20 provided clear decisions, and none provided unclear decisions (this is 100% clear decisions).

In addition to the assessment of field precision by XRF described above, two of the triplicate samples at four DU/depth combinations were also analyzed by ICP-MS. The ICP-MS results for these pairs can be treated as field duplicates for an additional assessment of field precision. The DMA QAPP does not include a quantitative goal for RPDs, but the project performance criterion is that the standard deviation to be low enough for statistical decision-making to be made at the desired level of confidence. The RPD data are presented to show the precision for analytes in addition to arsenic and lead. The RPD was calculated only when both results were greater than the MRL (PWT 2015b).

Table 5-5 summarizes the analytical results and calculated RPDs for field duplicates analyzed by ICP-MS. The RPDs for all analytes ranged from 0% to 98.9%, with a mean RPD of 16.7%.

The results indicate that the data are representative of site conditions.

#### **5.1.4 Comparability**

Comparability is a qualitative parameter that expresses the confidence with which one data set may be compared to another. Comparability is dependent on similar QA objectives and is achieved using (1) standardized methods for sample collection and analysis, (2) standardized units of measure, (3) normalization of results to standard conditions, and (4) standard and comprehensive reporting forms as specified by the DMA QAPP.

For this DMA DSR, laboratory data were evaluated for comparability by assessing whether the laboratory followed the required analytical methods and provided the appropriate units of measure. The assessment showed that the comparability of the data to other methods was acceptable. A different comparability assessment involving statistical comparison of XRF results to ICP-MS results is discussed in Section 6.0.

#### **5.1.5 Completeness**

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount expected under correct, normal conditions. Laboratory data

completeness is a quantitative measure of valid data as a percentage of all analytical data as determined by the precision, accuracy, and holding time criteria evaluation. All of the analytical results for residential yard soil samples by XRF and ICP-MS analysis were considered valid. Completeness was at 100 percent, and therefore the completeness goal of 100 percent was met.

### **5.1.6 Sensitivity**

Sensitivity is an index of the ability of any analytical method or other detection procedure to make quantitative determinations at a range of levels. Sensitivity is typically discussed as it applies to very low levels; laboratory data sensitivity and method sensitivity (detection limit). The sensitivity assessment determined that both of the analytical methods used in the DMA (XRF and ICP-MS) were able to detect lead and arsenic below the DMA SLs.

## **5.2 DATA VERIFICATION AND VALIDATION SUMMARY**

The DMA QAPP indicates that data verification should be completed on 90 percent of the analytical records and data validation conducted on 10 percent of the results. Because data verification on a set of records should occur prior to data validation, 100 percent of the results are subject to verification. However, given the importance of the DMA data for decision making on the RI, the data were validated at 100 percent. Guidance documents utilized for the data validation and verification include:

- *DMA QAPP (PWT 2015b)*
- *USEPA Contract Laboratories Program National Functional Guidelines for Inorganic Data Review (USEPA 2014).*

Data validation and verification techniques include accepting, rejecting or qualifying the analytical data based on data quality acceptance criteria and requirements specified by the method, the laboratory, the DMA QAPP and the EPA *National Functional Guidelines (NFG)*. The PARCC parameters are also used to evaluate the quality of analytical data and determine whether the data quality objectives (DQOs) of the project were met. PARCC parameters are discussed above. The data verification/validation evaluation is discussed below.

Verification and/or validation of the analytical ICP-MS and XRF data generated from the DMA sampling event was reviewed to verify that the data meet the acceptance criteria of the DMA QAPP and the EPA guidance. Data verification and validation reports for ICP-MS and XRF are provided in Appendix E and summarized below.

### **5.2.1 ICP-MS Analytical Data Verification and Validation**

The DMA QAPP indicates that the following elements will be reviewed for compliance as part of data verification:

- Temperature
- Methodology
- Holding Times
- Calibration
- Blanks

- Laboratory Control Samples

Analysis of laboratory duplicate samples is typically a CLP laboratory requirement, however, the DMA QAPP specified that it was not required in this case because the laboratory was not scheduled to complete any subsampling. For the DMA, subsampling was completed at the Pueblo field laboratory and the 1-2 gram subsamples were digested completely during analysis at the CLP laboratory.

The function of matrix spikes (checking for aberrant matrix behavior) may be inferred based on the XRF-ICP comparability analysis. Any XRF-ICP pair that significantly deviates from the general relationship observed between XRF and ICP pairs may be an indication of potential matrix interference. If evaluation for matrix interference does not find evidence of it, other causal evidence for the aberrant pair will be sought. If an error can be identified, the data pair will be removed from comparability analysis. Potential matrix interference will be evaluated by:

- Looking in the field notebook to determine the type of matrix, and comparing the suspicious pair to other paired sample analyses from matrices that might be similar;
- Comparing the XRF spectrum for that sample to spectra from samples from a similar matrix; and
- Obtaining and investigating the ICP spectrum for unusual behavior.

One purpose of the data validation process is to evaluate the causes of nonconformance and to assess the impact on data quality. The data validation process is intended to check the quality of the data at a more detailed level than the data verification process, although the data verification results are an input to the data validation process. The DMA QAPP indicates that in addition to those elements reviewed for the data verification process, the following data elements will be evaluated as part of the full data validation:

- Practical quantitation limits
- Analyte identification
- Analyte quantification.

All soil and water QC samples were analyzed by ICP-MS for total metals by the assigned EPA CLP Laboratory. All data generated for the soil and water (rinsate) samples were labeled as electronically verified via Stage 3 criteria (S3VE) by the laboratory, as defined in *USEPA Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use (USEPA 2009)*. E2 Consulting Engineers, Inc. verified the S3VE flags electronically using NFG guidelines, and discrepancies are discussed in Appendix E. Manual Stage 3 verification and validation (S3VM) was performed on data submitted in each of six sample delivery groups (SDGs) containing soil samples. Calibration standards and batch QC samples were processed correctly by the laboratory, and the example calculations for sample result, initial calibration verification (ICV) recovery, interference check sample (ICS) recoveries, and laboratory control sample (LCS) recoveries were confirmed.

E2's electronic verification confirmed that the S3VE-flagged data were accurate compared to NFG rules, with the exception of the application of U/UJ flags in cases where professional judgment is directed. Additionally, the CLP laboratory reported data using laboratory-established

RLs instead of the (higher) CRQLs. There were no other discrepancies discovered during the manual Stage 3 review (S3VM). Since all data were electronically and manually verified and validated, all data for this monitoring event are considered verified and validated and are acceptable for the purposes of the DMA project.

### 5.2.2 XRF Data Verification

This review and verification addresses the procedures set forth in the XRF sample analysis SOP during the 2015 DMA soil sampling project completed at the Site.

The XRF sample analysis SOP was used to analyze all soil samples collected during the 2015 DMA. The QC procedures for XRF soil analysis were reviewed for completeness and general quality and quantification for the final data set. The quality control guidelines followed the project sample analysis SOP, and the EPA XRF method 6200 - *Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment* (USEPA 2007).

The procedures that are addressed are as follows:

- Initial Control Charting

- Interference Checks

- Blank Analysis

- LCS Analysis

- Instrument Duplicates

- Calibration of XRF

- XRF Sample Precision Measurements

The review and verification utilized, whenever possible, the raw data output files from the XRF instrument to recreate and recalculate control charts, calibrations, and %RSD's. The original raw data files were also used to verify the daily quality controls and frequencies of the standards and blanks. It is also noted that only data pertaining to arsenic and lead were reviewed and utilized for any verification and recalculations.

The review and verification of the XRF analyses for the DMA project are complete and follow the guidelines set forth in the SOP and EPA Method 6200. Initial control charts, performance evaluations, and interference checks were completed and indicated that the instruments were in control for the duration of the project. Frequency of blanks and other SRM standards were documented and complete. Statistical goals for individual sample sets were met and the data are acceptable for the purposes of the DMA project.

TABLE 5-1

CHEMICAL DATA QUALITY CONTROL EVALUATION IN TERMS OF PARCC PARAMETERS

PARCC*	Quality Control Program	Evaluation Criteria
Precision	Field Duplicate/Replicate Sample Pairs Matrix Spike/Matrix Spike Duplicate Sample Pairs Investigative/Matrix Duplicate Sample Pairs Laboratory Control Sample/Laboratory Control Sample Duplicate Pairs	Relative Percent Difference <sup>(a)</sup> Relative Percent Difference Relative Percent Difference Relative Percent Difference
Accuracy	Surrogate Spikes Matrix Spikes Matrix Spike Duplicates Laboratory Control Sample Laboratory Control Sample Duplicate Standard Reference Materials	Percent Recovery <sup>(b)</sup> Percent Recovery Percent Recovery Percent Recovery Percent Recovery Percent Recovery
Representativeness	Holding Times Method Blanks Trip Blanks Equipment Blanks Temperature Blanks Field Duplicates	Qualitative, Degree of Confidence Qualitative, Degree of Confidence Qualitative, Degree of Confidence Qualitative, Degree of Confidence Qualitative, Degree of Confidence Qualitative, Degree of Confidence
Comparability	Standard Field Procedures Standard Analytical Procedures Standard Units of Measure	Qualitative, Degree of Confidence Qualitative, Degree of Confidence Qualitative, Degree of Confidence
Completeness	Valid Data	Relative Valid Data <sup>(c)</sup>

Notes: \* PARCC – Precision, Accuracy, Representativeness, Completeness, and Comparability

Where “C” equals concentration and “n” = number:

$$(a) \quad \text{Relative Percent Difference} = \frac{|C_{\text{sample}} - C_{\text{duplicate}}|}{\left(\frac{C_{\text{sample}} + C_{\text{duplicate}}}{2}\right)} \times 100$$

$$(b) \quad \text{Relative Standard Deviation} = \frac{SD}{C_{\text{mean}}} \times 100, \text{ where } SD = \sqrt{\frac{\sum(C_i - \bar{C})^2}{N-1}}$$

$$(c) \quad \text{Percent Recovery} = \frac{C_{\text{measured, spiked sample}}}{C_{\text{spiked}}} \times 100$$

$$(d) \quad \text{Percent Recovery} = \frac{|C_{\text{measured, spiked sample}} - C_{\text{measured unspiked sample}}|}{C_{\text{spiked}}} \times 100$$

$$(e) \quad \text{Relative Valid Data} = \frac{n_{\text{acceptable data points}}}{n_{\text{total measurements}}} \times 100$$



**TABLE 5-2**

**XRF LABORATORY DUPLICATE RESULTS**

Property Code	DU	Depth (inches bgs)	Analyte	Original Result	Duplicate Result	RPD (%)
0181	BY	12-18	Arsenic	30.2	28.3	6.5
0181	BY	12-18	Lead	825	846	2.5
0181	FY	6-12	Arsenic	11.3	12.4	9.3
0181	FY	6-12	Lead	236	235	0.4
0181	SY	2-6	Arsenic	29.5	24	20.6
0181	SY	2-6	Lead	722	720	0.3
0269	SY	2-6	Arsenic	10.3	10.8	4.7
0269	SY	2-6	Lead	263	263	0.0
0423	SYE	0-1	Arsenic	6.84	6.32	7.9
0423	SYE	0-1	Lead	103	89.4	14.1
0423	SYE	12-18	Arsenic	4.84	4.78	1.2
0423	SYE	12-18	Lead	34.3	32.8	4.5
0423	SYE	12-18	Arsenic	3.74	3.57	4.7
0423	SYE	12-18	Lead	5.46	7.09	26.0
1504	FY	2-6	Arsenic	11	10.6	3.7
1504	FY	2-6	Lead	376	373	0.8
1504	FY	6-12	Arsenic	8.69	11.8	30.4
1504	FY	6-12	Lead	318	308	3.2
1835	BY	0-2	Arsenic	12.4	13.7	10.0
1835	BY	0-2	Lead	398	406	2.0

**Notes:**

All results reported in mg/kg.

- bgs Below ground surface
- BY Back yard
- DU Decision unit
- FY Front yard
- RPD Relative percent difference
- SY Side yard
- SYE Side yard east
- XRF X-ray fluorescence

**TABLE 5-3**

**XRF FIELD TRIPLICATE RESULTS, 5-POINT COMPOSITE SAMPLING APPROACH**

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
0181	BY	0-2	As	14.4	13.2	15.5	14.4	8.0	16.3	Yes
0181	BY	2-6	As	15.1	15.4	14.7	15.1	2.3	15.7	Yes
0181	BY	6-12	As	16.7	14.6	14.9	15.4	7.4	17.3	Yes
0181	BY	12-18	As	30.2	28	23.7	27.3	12.1	32.9	No
0181	FY	0-2	As	10.8	9.02	7.76	9.19	16.6	11.8	Yes
0181	FY	2-6	As	14.4	15	11.8	13.7	12.4	16.6	Yes
0181	FY	6-12	As	11.3	12.3	13.2	12.3	7.7	13.9	Yes
0181	FY	12-18	As	6.86	7.48	9.63	7.99	18.2	10.4	Yes
0181	SY	0-2	As	15.7	14.1	16.6	15.5	8.2	17.6	Yes
0181	SY	2-6	As	29.5	18.5	20.3	22.8	25.9	32.7	No
0181	SY	6-12	As	36.4	26.4	23.5	28.8	23.5	40.2	No
0181	SY	12-18	As	11.6	16.1	10.2	12.6	24.5	17.8	Yes
0269	AP	0-1	As	8.87	8.76	7.83	8.49	6.7	9.5	Yes
0269	AP	1-6	As	6.31	8.16	6.7	7.06	13.8	8.7	Yes
0269	AP	6-12	As	5.18	3.65	3.86	4.23	19.6	5.6	Yes
0269	AP	12-18	As	3.23	3.6	3.09	3.31	8.0	3.8	Yes
0269	BY	0-1	As	10.8	11.9	11.6	11.4	5.0	12.4	Yes
0269	BY	1-6	As	13.4	11.2	12.9	12.5	9.2	14.4	Yes
0269	BY	6-12	As	10.7	9.84	13.4	11.3	16.4	14.4	Yes
0269	BY	12-18	As	7.82	7.16	9.48	8.15	14.7	10.2	Yes
0269	DZ	0-1	As	9.33	11.2	15.6	12	26.8	17.4	Yes
0269	SY	0-2	As	8.46	11.5	11.7	10.6	17.1	13.7	Yes
0269	SY	2-6	As	9.7	9.1	10.9	9.9	9.3	11.4	Yes
0269	SY	6-12	As	11.1	10.8	8.5	10.1	14.1	12.5	Yes
0269	SY	12-18	As	7.97	7.91	8.8	8.23	6.0	9.1	Yes
0389	AP	0-1	As	92.6	119	128	113	16.3	144.0	Yes
0389	AP	1-6	As	49.4	57.1	61.1	55.9	10.6	65.9	Yes
0389	AP	6-12	As	22.8	23.1	24.3	23.4	3.4	24.7	Yes
0389	AP	12-18	As	7.03	5.66	5.3	6	15.2	7.5	Yes
0389	BY	0-1	As	13.9	12.7	9.4	12	19.4	15.9	Yes
0389	BY	1-6	As	26	25.3	31.4	27.6	12.1	33.2	No
0389	BY	6-12	As	15.3	15.8	18.7	16.6	11.1	19.7	Yes
0389	BY	12-18	As	10.1	16.6	6.02	10.9	49.0	19.9	Yes
0389	DZ	0-1	As	70.5	49.5	52.3	57.4	19.9	76.6	Yes
0389	FY	0-1	As	25.6	26.6	36.1	29.4	19.7	39.2	No
0389	FY	1-6	As	14.6	15.1	17	15.6	8.1	17.7	Yes
0389	FY	6-12	As	6.9	9.58	8.17	8.22	16.3	10.5	Yes
0389	FY	12-18	As	3.65	6.4	3.58	4.54	35.4	7.3	Yes
0389	SY	0-1	As	38.3	43.9	42	41.4	6.9	46.2	Yes
0389	SY	1-6	As	48.1	60.2	70.2	59.5	18.6	78.2	Yes
0389	SY	6-12	As	58.6	55.2	52.8	55.5	5.3	60.4	Yes
0389	SY	12-18	As	33.3	18.2	23.2	24.9	30.9	37.9	No
0423	BY	0-2	As	7.59	6.46	7.69	7.25	9.4	8.4	Yes

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
0423	BY	2-6	As	8.63	8.06	8.44	8.38	3.5	8.9	Yes
0423	BY	6-12	As	8.13	7.66	6.56	7.45	10.8	8.8	Yes
0423	BY	12-18	As	8.93	8.43	5.72	7.69	22.5	10.6	Yes
0423	DZ	0-1	As	14.4	11.8	10.5	12.2	16.3	15.5	Yes
0423	DZ	1-6	As	14.8	11.6	13.9	13.4	12.3	16.2	Yes
0423	ED	0-1	As	7.66	6.35	7.17	7.06	9.4	8.2	Yes
0423	SYE	0-1	As	6.82	6.84	7.44	7.03	5.0	7.6	Yes
0423	SYE	1-6	As	4.98	8.94	6.84	6.92	28.6	10.3	Yes
0423	SYE	6-12	As	4.02	5	3.22	4.08	21.9	5.6	Yes
0423	SYE	12-18	As	3.06	4.84	3.99	3.96	22.5	5.5	Yes
0423	SYW	0-1	As	9.37	8.02	8.33	8.57	8.3	9.8	Yes
0423	SYW	1-6	As	11.4	9.84	8.78	10	13.2	12.2	Yes
0423	SYW	6-12	As	17.6	9.64	11	12.7	33.5	19.9	Yes
0423	SYW	12-18	As	13.1	14.4	16.8	14.8	12.7	18.0	Yes
0496	BY	0-2	As	6.99	7.79	8.92	7.9	12.3	9.5	Yes
0496	BY	2-6	As	6.66	6.71	9.27	7.55	19.8	10.1	Yes
0496	BY	6-12	As	8.41	7.37	9.33	8.37	11.7	10.0	Yes
0496	BY	12-18	As	5.59	7.08	6.54	6.4	11.8	7.7	Yes
0496	FY	0-2	As	4.41	2.7	3.87	3.66	23.9	5.1	Yes
0496	FY	2-6	As	4.04	4.36	4.3	4.23	4.0	4.5	Yes
0496	FY	6-12	As	6.57	7.34	7.21	7.04	5.9	7.7	Yes
0496	FY	12-18	As	4.79	3.65	4.41	4.28	13.6	5.3	Yes
0496	SY	0-2	As	13.1	10.5	8.1	10.6	23.6	14.8	Yes
0496	SY	2-6	As	9.49	13.7	10.6	11.3	19.3	15.0	Yes
0496	SY	6-12	As	8.56	6.04	8.42	7.67	18.5	10.1	Yes
0496	SY	12-18	As	5.16	5.42	6.08	5.55	8.5	6.3	Yes
0724	FY	0-2	As	10.8	13.8	11.7	12.1	12.7	14.7	Yes
0724	FY	2-6	As	15	16.1	14.5	15.2	5.4	16.6	Yes
0724	FY	6-12	As	14.3	15.4	14.7	14.8	3.8	15.7	Yes
0724	FY	12-18	As	11.9	15.5	10.1	12.5	22.0	17.1	Yes
0724	SYE	0-1	As	9.56	10.4	8.26	9.41	11.5	11.2	Yes
0724	SYE	1-6	As	9.9	9.76	11.4	10.4	8.7	11.9	Yes
0724	SYE	6-12	As	11	11	7.07	9.69	23.4	13.5	Yes
0724	SYE	12-18	As	10.1	11.3	6.78	9.39	24.9	13.3	Yes
0724	SYW	0-2	As	7.8	8.52	6.56	7.63	13.0	9.3	Yes
0724	SYW	2-6	As	8.98	10.9	8.77	9.55	12.3	11.5	Yes
0724	SYW	6-12	As	7.28	7.65	6.77	7.23	6.1	8.0	Yes
0724	SYW	12-18	As	8.04	8.4	7.33	7.92	6.9	8.8	Yes
1076	AP	0-2	As	10.4	9.27	9.42	9.7	6.3	10.7	Yes
1076	AP	2-6	As	8.21	8.49	6.57	7.76	13.4	9.5	Yes
1076	AP	6-12	As	7.58	5.17	6.37	6.37	18.9	8.4	Yes
1076	AP	12-18	As	5.34	3.89	5.43	4.89	17.7	6.3	Yes
1076	BY	0-2	As	12.3	14.4	17.3	14.7	17.1	18.9	Yes
1076	BY	2-6	As	14.9	15.9	15.7	15.5	3.4	16.4	Yes
1076	BY	6-12	As	10.7	9.13	11.9	10.6	13.1	12.9	Yes
1076	BY	12-18	As	4	4.32	3.91	4.08	5.3	4.4	Yes
1076	DZ	0-1	As	11.5	12	9.57	11	11.7	13.2	Yes
1076	ED	0-1	As	14.2	14.2	14.4	14.3	0.8	14.5	Yes

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
1076	ED	1-6	As	15.4	15.8	17.1	16.1	5.5	17.6	Yes
1076	ED	6-12	As	12.7	12.5	15.2	13.5	11.1	16.0	Yes
1076	ED	12-18	As	8.63	7.7	11.2	9.18	19.7	12.2	Yes
1076	FY	0-2	As	9.45	12	9.5	10.3	14.2	12.8	Yes
1076	FY	2-6	As	8.42	10.5	9.94	9.62	11.2	11.4	Yes
1076	FY	6-12	As	8.86	8.63	5.28	7.59	26.4	11.0	Yes
1076	FY	12-18	As	5.59	9.12	5.13	6.61	33.0	10.3	Yes
1504	BY	0-1	As	10.2	10.7	8.1	9.67	14.3	12.0	Yes
1504	BY	1-6	As	9.74	10.4	10.6	10.2	4.4	11.0	Yes
1504	BY	6-12	As	14.9	18.1	15.8	16.3	10.1	19.1	Yes
1504	BY	12-18	As	11.8	12.1	9.07	11	15.2	13.8	Yes
1504	DZ	0-2	As	13.2	14.5	13.5	13.7	5.0	14.8	Yes
1504	FY	0-2	As	14.1	11.2	12.5	12.6	11.5	15.0	Yes
1504	FY	2-6	As	11	9.69	13.5	11.4	17.0	14.7	Yes
1504	FY	6-12	As	8.69	9.24	8.61	8.85	3.9	9.4	Yes
1504	FY	12-18	As	6.72	7.61	8.91	7.75	14.2	9.6	Yes
1592	BY	0-2	As	60.7	51	47.6	53.1	12.8	64.6	Yes
1592	BY	2-6	As	68	58.3	71.1	65.8	10.1	77.1	Yes
1592	BY	6-12	As	152	84	103	113	31.0	172.1	Yes
1592	BY	12-18	As	119	160	150	143	14.9	179.0	Yes
1592	FY	0-2	As	42.8	44.6	42.9	43.4	2.3	45.1	Yes
1592	FY	2-6	As	60.8	63.4	64.8	63	3.2	66.4	Yes
1592	FY	6-12	As	95.1	87.4	92.3	91.6	4.3	98.2	Yes
1592	FY	12-18	As	65.4	62.2	56	61.2	7.8	69.3	Yes
1592	PA	0-1	As	85.8	78.2	77.1	80.4	5.9	88.4	Yes
1592	PA	1-6	As	161	144	144	150	6.5	166.5	Yes
1592	PA	6-12	As	118	130	145	131	10.3	153.8	Yes
1592	PA	12-18	As	115	97.4	126	113	12.8	137.3	Yes
1615	AP	0-2	As	18.4	22.4	18.6	19.8	11.4	23.6	Yes
1615	AP	2-6	As	24.7	26	29.9	26.9	10.1	31.5	No
1615	AP	6-12	As	31.1	32.7	29.4	31.1	5.3	33.9	Yes
1615	AP	12-18	As	21.1	27.6	26.4	25	13.8	30.8	No
1615	BY	0-2	As	26.9	26.4	30.5	27.9	8.0	31.7	No
1615	BY	2-6	As	30.8	26	35.7	30.8	15.7	39.0	Yes
1615	BY	6-12	As	15.5	17.1	22	18.2	18.6	23.9	Yes
1615	BY	12-18	As	17.4	14.1	15.5	15.7	10.5	18.5	Yes
1615	FY	0-2	As	25.8	22.4	22.8	23.7	7.8	26.8	Yes
1615	FY	2-6	As	29	28.1	27.5	28.2	2.7	29.5	Yes
1615	FY	6-12	As	21.5	20.5	20.4	20.8	2.9	21.8	Yes
1615	FY	12-18	As	9.01	9.38	8.33	8.91	6.0	9.8	Yes
1615	SY	0-2	As	16.4	11.9	17.1	15.1	18.7	19.9	Yes
1654	BY	0-2	As	47.4	94.2	86.9	76.2	33.0	118.6	Yes
1654	BY	2-6	As	135	252	222	203	29.9	305.4	Yes
1654	BY	6-12	As	150	134	63.2	116	39.8	193.9	Yes
1654	BY	12-18	As	38.4	32.3	26	32.2	19.3	42.7	Yes
1654	DZ	0-1	As	21.2	18.7	26.4	22.1	17.8	28.7	Yes
1654	FY	0-2	As	80.7	51.2	72.3	68.1	22.3	93.7	Yes
1654	FY	2-6	As	66.3	80	53.2	66.5	20.2	89.1	Yes

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
1654	FY	6-12	As	22.5	26.8	36.4	28.6	24.9	40.6	No
1654	FY	12-18	As	18	19.6	19	18.9	4.3	20.3	Yes
1835	AP	0-2	As	14.1	11.9	10.4	12.1	15.4	15.2	Yes
1835	AP	2-6	As	12.1	12.8	15.7	13.5	14.1	16.7	Yes
1835	AP	6-12	As	7.85	9.22	9.75	8.94	11.0	10.6	Yes
1835	AP	12-18	As	4.79	5.09	4.9	4.93	3.1	5.2	Yes
1835	BY	0-2	As	12.4	15	15.4	14.3	11.4	17.0	Yes
1835	BY	2-6	As	12.7	17.5	13.2	14.5	18.2	18.9	Yes
1835	BY	6-12	As	13.1	13.2	15.7	14	10.5	16.5	Yes
1835	BY	12-18	As	8.4	10.5	7.99	8.96	15.0	11.2	Yes
1835	DZ	0-2	As	20.5	20.7	19.8	20.3	2.3	21.1	Yes
1835	FY	0-2	As	12.2	10.2	10.6	11	9.6	12.8	Yes
1835	FY	2-6	As	10.6	11.2	12.6	11.5	8.9	13.2	Yes
1835	FY	6-12	As	6.59	7.39	6.38	6.79	7.8	7.7	Yes
1835	FY	12-18	As	4.94	4.49	4.05	4.49	9.9	5.2	Yes
<b>Arsenic summary results</b>							<b>Average</b>	13.7	<b>Clear</b>	144
							<b>Minimum</b>	0.8	<b>Unclear</b>	10
							<b>Maximum</b>	49.0	<b>Total</b>	154
0181	BY	0-2	Pb	445	451	400	432	6.5	479.0	Yes
0181	BY	2-6	Pb	437	460	474	457	4.1	488.5	Yes
0181	BY	6-12	Pb	445	467	444	452	2.9	473.9	Yes
0181	BY	12-18	Pb	825	771	763	786	4.3	842.9	Yes
0181	FY	0-2	Pb	239	270	226	245	9.2	283.1	Yes
0181	FY	2-6	Pb	337	372	323	344	7.3	386.5	Yes
0181	FY	6-12	Pb	236	213	253	234	8.6	267.8	Yes
0181	FY	12-18	Pb	31.8	41.5	133	68.8	81.2	162.9	Yes
0181	SY	0-2	Pb	416	399	415	410	2.3	426.1	Yes
0181	SY	2-6	Pb	722	566	569	619	14.4	769.4	Yes
0181	SY	6-12	Pb	915	666	523	701	28.3	1035.4	Yes
0181	SY	12-18	Pb	186	317	148	217	40.9	366.5	Yes
0269	AP	0-1	Pb	192	173	169	178	6.9	198.7	Yes
0269	AP	1-6	Pb	84	66.3	83.4	77.9	12.9	94.8	Yes
0269	AP	6-12	Pb	34.6	19.8	19.9	24.8	34.3	39.2	Yes
0269	AP	12-18	Pb	20.4	9.12	19.7	16.4	38.5	27.1	Yes
0269	BY	0-1	Pb	321	335	352	336	4.6	362.2	Yes
0269	BY	1-6	Pb	344	327	364	345	5.4	376.2	Yes
0269	BY	6-12	Pb	224	219	255	233	8.4	265.9	Yes
0269	BY	12-18	Pb	83.7	99.8	133	106	23.7	148.4	Yes
0269	DZ	0-1	Pb	441	408	529	459	13.6	564.4	Yes
0269	SY	0-2	Pb	285	280	287	284	1.3	290.1	Yes
0269	SY	2-6	Pb	239	224	271	245	9.8	285.5	Yes
0269	SY	6-12	Pb	170	163	150	161	6.3	178.1	Yes
0269	SY	12-18	Pb	88.4	73.2	102	87.9	16.4	112.2	Yes
0389	AP	0-1	Pb	319	483	497	433	22.9	599.9	Yes
0389	AP	1-6	Pb	107	148	169	141	22.4	194.2	Yes
0389	AP	6-12	Pb	24.7	35.5	18.5	26.2	32.8	40.7	Yes
0389	AP	12-18	Pb	13.4	12.8	9.4	11.9	18.1	15.5	Yes
0389	BY	0-1	Pb	271	289	260	273	5.4	297.7	Yes

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
0389	BY	1-6	Pb	336	343	390	356	8.2	405.5	No
0389	BY	6-12	Pb	246	216	233	232	6.5	257.4	Yes
0389	BY	12-18	Pb	114	140	48.8	101	46.5	180.2	Yes
0389	DZ	0-1	Pb	569	482	490	514	9.4	595.1	Yes
0389	FY	0-1	Pb	371	342	488	400	19.3	530.3	No
0389	FY	1-6	Pb	276	223	297	265	14.4	329.3	Yes
0389	FY	6-12	Pb	49.9	97.8	72.5	73.4	32.6	113.8	Yes
0389	FY	12-18	Pb	25.2	57.3	18.3	33.6	61.9	68.7	Yes
0389	SY	0-1	Pb	521	535	519	525	1.7	539.7	Yes
0389	SY	1-6	Pb	555	660	684	633	10.8	748.7	Yes
0389	SY	6-12	Pb	668	647	659	658	1.6	675.8	Yes
0389	SY	12-18	Pb	486	259	403	383	30.0	576.6	No
0423	BY	0-2	Pb	182	186	173	180	3.7	191.2	Yes
0423	BY	2-6	Pb	202	226	218	215	5.7	235.6	Yes
0423	BY	6-12	Pb	117	76.8	111	102	21.3	138.6	Yes
0423	BY	12-18	Pb	118	144	92.7	118	21.7	161.2	Yes
0423	DZ	0-1	Pb	346	358	349	351	1.8	361.5	Yes
0423	DZ	1-6	Pb	517	629	466	537	15.5	677.6	Yes
0423	ED	0-1	Pb	170	203	193	189	9.0	217.5	Yes
0423	SYE	0-1	Pb	102	103	126	110	12.3	132.9	Yes
0423	SYE	1-6	Pb	31.7	152	54.7	79.5	80.3	187.2	Yes
0423	SYE	6-12	Pb	10.9	68.3	14.6	31.3	102.6	85.5	Yes
0423	SYE	12-18	Pb	6.16	34.3	12.4	17.6	84.0	42.5	Yes
0423	SYW	0-1	Pb	198	230	193	207	9.7	240.8	Yes
0423	SYW	1-6	Pb	213	218	207	213	2.6	222.3	Yes
0423	SYW	6-12	Pb	641	325	279	415	47.5	747.2	Yes
0423	SYW	12-18	Pb	576	434	451	487	15.9	617.7	Yes
0496	BY	0-2	Pb	251	271	250	257	4.6	277.0	Yes
0496	BY	2-6	Pb	286	261	314	287	9.2	331.7	Yes
0496	BY	6-12	Pb	346	278	287	304	12.2	366.3	Yes
0496	BY	12-18	Pb	135	261	109	168	48.4	305.1	Yes
0496	FY	0-2	Pb	85.2	85.5	90.9	87.2	3.7	92.6	Yes
0496	FY	2-6	Pb	130	116	125	124	5.7	136.0	Yes
0496	FY	6-12	Pb	209	195	201	202	3.5	213.8	Yes
0496	FY	12-18	Pb	83.3	108	81.5	90.9	16.3	115.9	Yes
0496	SY	0-2	Pb	461	513	517	497	6.3	549.7	Yes
0496	SY	2-6	Pb	511	555	544	537	4.3	575.6	Yes
0496	SY	6-12	Pb	220	216	347	261	28.5	386.6	Yes
0496	SY	12-18	Pb	65.9	73.2	97.5	78.9	21.0	106.8	Yes
0724	FY	0-2	Pb	179	173	171	174	2.4	181.0	Yes
0724	FY	2-6	Pb	174	188	181	181	3.9	192.8	Yes
0724	FY	6-12	Pb	115	137	112	121	11.3	144.0	Yes
0724	FY	12-18	Pb	52.7	49.2	54.1	52	4.9	56.3	Yes
0724	SYE	0-1	Pb	169	182	173	175	3.8	186.2	Yes
0724	SYE	1-6	Pb	183	215	247	215	14.9	268.9	Yes
0724	SYE	6-12	Pb	146	163	367	225	54.7	432.3	No
0724	SYE	12-18	Pb	103	138	876	372	117.3	1107.9	No
0724	SYW	0-2	Pb	149	124	165	146	14.2	180.8	Yes

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
0724	SYW	2-6	Pb	184	185	182	184	0.8	186.6	Yes
0724	SYW	6-12	Pb	138	141	133	137	2.9	143.8	Yes
0724	SYW	12-18	Pb	126	176	126	143	20.2	191.7	Yes
1076	AP	0-2	Pb	255	231	264	250	6.8	278.8	Yes
1076	AP	2-6	Pb	193	186	238	206	13.7	253.6	Yes
1076	AP	6-12	Pb	112	69.7	127	103	28.8	153.1	Yes
1076	AP	12-18	Pb	109	56	70.3	78.4	35.0	124.6	Yes
1076	BY	0-2	Pb	477	508	557	514	7.8	582.0	Yes
1076	BY	2-6	Pb	494	560	517	524	6.4	580.5	Yes
1076	BY	6-12	Pb	256	251	354	287	20.2	384.9	Yes
1076	BY	12-18	Pb	22.6	32.4	52.2	35.7	42.2	61.1	Yes
1076	DZ	0-1	Pb	400	443	387	410	7.1	459.4	Yes
1076	ED	0-1	Pb	676	511	476	554	19.3	734.1	Yes
1076	ED	1-6	Pb	577	473	587	546	11.6	652.4	Yes
1076	ED	6-12	Pb	354	304	431	363	17.6	470.9	No
1076	ED	12-18	Pb	284	231	182	232	22.0	318.0	Yes
1076	FY	0-2	Pb	275	282	274	277	1.6	284.3	Yes
1076	FY	2-6	Pb	236	248	234	239	3.2	251.8	Yes
1076	FY	6-12	Pb	218	269	142	210	30.4	317.7	Yes
1076	FY	12-18	Pb	310	396	135	280	47.5	504.2	No
1504	BY	0-1	Pb	356	394	367	372	5.3	405.0	No
1504	BY	1-6	Pb	288	410	431	376	20.5	506.2	No
1504	BY	6-12	Pb	402	705	446	518	31.6	794.0	Yes
1504	BY	12-18	Pb	217	265	158	213	25.2	303.4	Yes
1504	DZ	0-2	Pb	420	484	429	444	7.8	502.4	Yes
1504	FY	0-2	Pb	330	323	349	334	4.0	356.7	Yes
1504	FY	2-6	Pb	376	325	343	348	7.4	391.6	Yes
1504	FY	6-12	Pb	318	243	133	231	40.3	387.9	Yes
1504	FY	12-18	Pb	40	262	195	166	68.6	358.0	Yes
1592	BY	0-2	Pb	386	366	359	370	3.8	393.6	Yes
1592	BY	2-6	Pb	409	413	453	425	5.7	466.0	Yes
1592	BY	6-12	Pb	546	400	484	477	15.4	600.5	Yes
1592	BY	12-18	Pb	400	557	780	579	33.0	900.9	Yes
1592	FY	0-2	Pb	346	282	323	317	10.2	371.7	Yes
1592	FY	2-6	Pb	432	432	440	435	1.1	442.8	Yes
1592	FY	6-12	Pb	661	615	606	627	4.7	676.7	Yes
1592	FY	12-18	Pb	409	396	317	374	13.3	457.9	No
1592	PA	0-1	Pb	473	489	466	476	2.5	495.9	Yes
1592	PA	1-6	Pb	649	650	612	637	3.4	673.5	Yes
1592	PA	6-12	Pb	384	428	444	419	7.4	471.4	Yes
1592	PA	12-18	Pb	378	323	397	366	10.5	430.8	No
1615	AP	0-2	Pb	448	429	405	427	5.0	463.3	Yes
1615	AP	2-6	Pb	546	573	535	551	3.5	584.0	Yes
1615	AP	6-12	Pb	574	574	557	568	1.7	584.5	Yes
1615	AP	12-18	Pb	413	489	480	461	9.0	531.0	Yes
1615	BY	0-2	Pb	445	479	453	459	3.9	489.0	Yes
1615	BY	2-6	Pb	492	448	485	475	5.0	514.9	Yes
1615	BY	6-12	Pb	290	296	373	320	14.5	398.0	Yes

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
1615	BY	12-18	Pb	400	195	254	283	37.3	460.9	No
1615	FY	0-2	Pb	598	633	545	592	7.5	666.7	Yes
1615	FY	2-6	Pb	806	846	729	794	7.5	894.3	Yes
1615	FY	6-12	Pb	459	772	508	580	29.0	863.8	Yes
1615	FY	12-18	Pb	76.3	101	72.4	83.2	18.6	109.3	Yes
1615	SY	0-2	Pb	411	441	487	446	8.6	510.5	Yes
1654	BY	0-2	Pb	858	1250	986	1030	19.4	1367.0	Yes
1654	BY	2-6	Pb	1790	3280	2880	2650	29.1	3950.1	Yes
1654	BY	6-12	Pb	2030	1960	952	1650	36.6	2666.9	Yes
1654	BY	12-18	Pb	458	140	78.2	225	90.6	568.6	No
1654	DZ	0-1	Pb	533	503	555	530	4.9	574.0	Yes
1654	FY	0-2	Pb	831	503	536	623	29.0	927.5	Yes
1654	FY	2-6	Pb	971	1190	834	998	18.0	1300.7	Yes
1654	FY	6-12	Pb	31.5	134	359	175	95.7	457.4	No
1654	FY	12-18	Pb	20.4	48.4	62.1	43.6	48.7	79.4	Yes
1835	AP	0-2	Pb	350	365	351	355	2.4	369.1	Yes
1835	AP	2-6	Pb	343	368	374	362	4.5	389.7	Yes
1835	AP	6-12	Pb	182	208	195	195	6.7	216.9	Yes
1835	AP	12-18	Pb	29.4	41.3	25.4	32	25.8	45.9	Yes
1835	BY	0-2	Pb	398	404	429	410	4.0	437.7	Yes
1835	BY	2-6	Pb	439	485	440	455	5.8	499.3	Yes
1835	BY	6-12	Pb	417	420	476	438	7.6	494.0	Yes
1835	BY	12-18	Pb	190	271	142	201	32.4	310.9	Yes
1835	DZ	0-2	Pb	675	741	734	717	5.1	778.1	Yes
1835	FY	0-2	Pb	370	307	378	352	11.0	417.6	No
1835	FY	2-6	Pb	348	314	350	337	6.0	371.1	Yes
1835	FY	6-12	Pb	117	145	110	124	14.9	155.2	Yes
1835	FY	12-18	Pb	22.7	26.3	27.5	25.5	9.8	29.7	Yes
<b>Lead summary results</b>							<b>Average</b>	18.7	<b>Clear</b>	139
							<b>Minimum</b>	0.8	<b>Unclear</b>	15
							<b>Maximum</b>	117.3	<b>Total</b>	154

**Notes:**

All results reported in mg/kg.

As Arsenic

bgs Below ground surface

BY Back yard

DU Decision unit

Pb Lead

RSD Relative standard deviation

SY Side yard

SYE Side yard east

U Not detected

UCL Upper confidence limit

UJ Not detected - detection limit is estimated

XRF X-ray fluorescence



TABLE 5-4

XRF FIELD TRIPLICATE RESULTS, 30-POINT INCREMENTAL SAMPLING APPROACH

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
0269	SY	0-2	As	13.1	13	13.9	13.3	3.7	14.1	Yes
0269	SY	2-6	As	10.3	10.6	10.8	10.6	2.4	11.0	Yes
0389	BY	0-1	As	19.8	18.4	23	20.4	11.6	24.4	Yes
0389	BY	1-6	As	23.1	22.8	29.1	25	14.2	31.0	No
0423	BY	0-2	As	7.87	7.32	8.35	7.85	6.6	8.7	Yes
0423	BY	2-6	As	9.85	8.94	9.58	9.46	4.9	10.2	Yes
0423	SYE	0-1	As	4.76	5.55	5.6	5.3	8.9	6.1	Yes
0423	SYE	1-6	As	5.62	5.51	4.09	5.07	16.8	6.5	Yes
0423	SYE	6-12	As	4.11	3.44	4.21	3.92	10.7	4.6	Yes
0423	SYE	12-18	As	3.74	3.21	3.29	3.41	8.4	3.9	Yes
1076	BY	0-2	As	11.1	13.8	15.2	13.4	15.6	16.9	Yes
1076	BY	2-6	As	15.3	13.1	13.6	14	8.2	15.9	Yes
1504	BY	2-6	As	9.72	9.5	9.36	9.53	1.9	9.8	Yes
1504	BY	1-6	As	11.1	10.2	9.62	10.3	7.2	11.6	Yes
1504	FY	0-2	As	11.8	13.8	8.37	11.3	24.3	15.9	Yes
1504	FY	2-6	As	7.04	9.7	11.3	9.35	23.0	13.0	Yes
1615	BY	0-2	As	27.1	22.7	25.6	25.1	8.9	28.9	Yes
1615	BY	2-6	As	27.9	21.6	31.8	27.1	19.0	35.8	No
1654	FY	0-2	As	62.3	84.2	73.8	73.4	14.9	91.9	Yes
1654	FY	2-6	As	64.2	51.5	47.7	54.5	15.9	69.1	Yes
<b>Arsenic summary results</b>							<b>Average</b>	11.4	<b>Clear</b>	18
							<b>Minimum</b>	1.9	<b>Unclear</b>	2
							<b>Maximum</b>	24.3	<b>Total</b>	20
Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
0269	SY	0-2	Pb	332	320	309	320	3.6	339.4	Yes
0269	SY	2-6	Pb	263	249	267	260	3.6	275.9	Yes
0389	BY	0-1	Pb	260	268	274	267	2.6	278.8	Yes
0389	BY	1-6	Pb	307	283	333	308	8.1	350.2	Yes
0423	BY	0-2	Pb	189	197	200	195	2.9	204.6	Yes
0423	BY	2-6	Pb	253	205	233	230	10.5	270.6	Yes
0423	SYE	0-1	Pb	79.3	85.6	79.3	81.4	4.5	87.5	Yes
0423	SYE	1-6	Pb	28	34	37.3	33.1	14.2	41.0	Yes
0423	SYE	6-12	Pb	10.8	19.4	36.9	22.4	59.4	44.8	Yes
0423	SYE	12-18	Pb	5.46	12.1	24.8	14.1	69.7	30.7	Yes
1076	BY	0-2	Pb	437	469	461	456	3.7	484.1	Yes
1076	BY	2-6	Pb	469	475	462	469	1.4	480.0	Yes
1504	BY	2-6	Pb	349	337	342	343	1.8	353.2	Yes
1504	BY	1-6	Pb	376	346	341	354	5.3	385.9	Yes
1504	FY	0-2	Pb	315	327	323	322	1.9	332.3	Yes
1504	FY	2-6	Pb	282	327	280	296	9.0	340.8	Yes
1615	BY	0-2	Pb	468	451	473	464	2.5	483.4	Yes
1615	BY	2-6	Pb	512	466	515	498	5.5	544.3	Yes
1654	FY	0-2	Pb	527	632	578	579	9.1	667.5	Yes

Property Code	DU	Depth (inches bgs)	Analyte	Triplicate Sampling Results			Mean	RSD (%)	UCL	Clear Decision?
1654	FY	2-6	Pb	699	620	495	605	17.0	778.4	Yes
<b>Lead summary results</b>							<b>Average</b>	11.8	<b>Clear</b>	20
							<b>Minimum</b>	1.4	<b>Unclear</b>	0
							<b>Maximum</b>	69.7	<b>Total</b>	20

**Notes:**

All results reported in mg/kg.

- As        Arsenic
- bgs      Below ground surface
- BY       Back yard
- DU       Decision unit
- Pb        Lead
- RSD      Relative standard deviation
- SY        Side yard
- SYE      Side yard east
- U         Not detected
- UCL      Upper confidence limit
- UJ        Not detected - detection limit is estimated
- XRF      X-ray fluorescence

TABLE 5-5

## ICP-MS FIELD DUPLICATE RESULTS

Property Code	DU	Depth (inches bgs)	Analyte	Original Result	Duplicate Result	RPD (%)
0181	SY	6-12	Antimony	2.4	1.8	28.6
0181	SY	6-12	Arsenic	41.3	23.6	54.5
0181	SY	6-12	Barium	204	222	8.5
0181	SY	6-12	Beryllium	0.49	0.6	20.2
0181	SY	6-12	Cadmium	10.4	6.8	41.9
0181	SY	6-12	Chromium	9.2	10.4	12.2
0181	SY	6-12	Cobalt	5.6	6	6.9
0181	SY	6-12	Copper	99	85.4	14.8
0181	SY	6-12	Lead	918	514	56.4
0181	SY	6-12	Manganese	462	488	5.5
0181	SY	6-12	Nickel	31.5	30.5	3.2
0181	SY	6-12	Selenium	1.2 UJ	1.3 UJ	NC
0181	SY	6-12	Silver	3.8	2.3	49.2
0181	SY	6-12	Thallium	0.31 U	0.32 U	NC
0181	SY	6-12	Vanadium	32.3	32.4	0.3
0181	SY	6-12	Zinc	575	573	0.3
0423	SYE	0-1	Antimony	0.82	0.97	16.8
0423	SYE	0-1	Arsenic	6.6	6.3	4.7
0423	SYE	0-1	Barium	162	147	9.7
0423	SYE	0-1	Beryllium	0.49	0.42	15.4
0423	SYE	0-1	Cadmium	1.4	1.4	0.0
0423	SYE	0-1	Chromium	21.1	19.2	9.4
0423	SYE	0-1	Cobalt	5.4	5.4	0.0
0423	SYE	0-1	Copper	27.5	26.5	3.7
0423	SYE	0-1	Lead	74.5	75.5	1.3
0423	SYE	0-1	Manganese	383	370	3.5
0423	SYE	0-1	Nickel	18.7	18.4	1.6
0423	SYE	0-1	Selenium	0.58 UJ	0.48 UJ	NC
0423	SYE	0-1	Silver	0.23 U	0.21 U	NC
0423	SYE	0-1	Thallium	0.19 U	0.19 U	NC
0423	SYE	0-1	Vanadium	30.5	32.4	6.0
0423	SYE	0-1	Zinc	230	233	1.3
0423	SYE	1-6	Antimony	0.73	0.78	6.6
0423	SYE	1-6	Arsenic	7.3	8.9	19.8
0423	SYE	1-6	Barium	207	198	4.4
0423	SYE	1-6	Beryllium	0.61	0.52	15.9
0423	SYE	1-6	Cadmium	2.3	1.1	70.6
0423	SYE	1-6	Chromium	14.3	11.8	19.2
0423	SYE	1-6	Cobalt	5.5	5.4	1.8
0423	SYE	1-6	Copper	36	20.7	54.0
0423	SYE	1-6	Lead	147	49.7	98.9
0423	SYE	1-6	Manganese	319	272	15.9
0423	SYE	1-6	Nickel	20.9	33.1	45.2
0423	SYE	1-6	Selenium	0.48 UJ	0.5 UJ	NC
0423	SYE	1-6	Silver	0.39	0.18 U	NC
0423	SYE	1-6	Thallium	0.2 U	0.21 U	NC

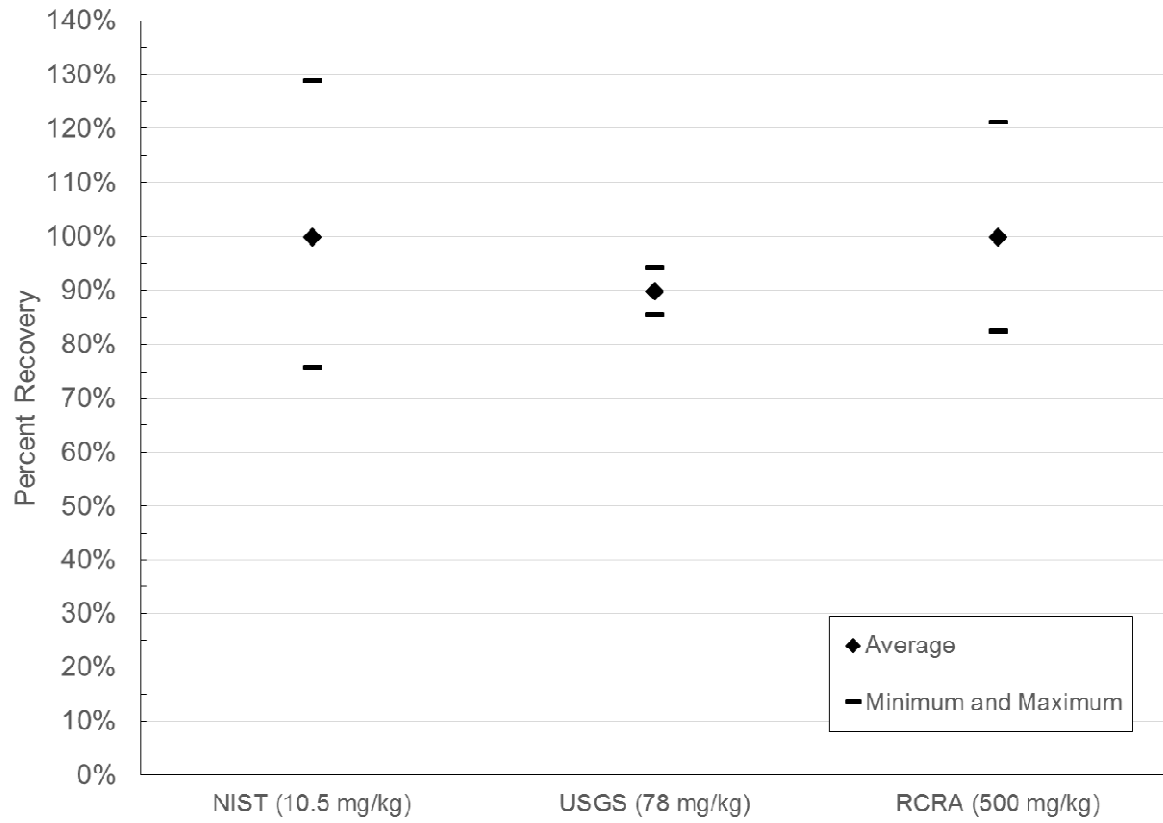
Property Code	DU	Depth (inches bgs)	Analyte	Original Result	Duplicate Result	RPD (%)
0423	SYE	1-6	Vanadium	28.2	33	15.7
0423	SYE	1-6	Zinc	229	125	58.8
1592	PA	1-6	Antimony	4.5	3.6	22.2
1592	PA	1-6	Arsenic	282	249	12.4
1592	PA	1-6	Barium	229	231	0.9
1592	PA	1-6	Beryllium	0.71	0.7	1.4
1592	PA	1-6	Cadmium	6.4	6.7	4.6
1592	PA	1-6	Chromium	14.6	14.2	2.8
1592	PA	1-6	Cobalt	6.8	6.9	1.5
1592	PA	1-6	Copper	102	99.9	2.1
1592	PA	1-6	Lead	647	646	0.2
1592	PA	1-6	Manganese	997	869	13.7
1592	PA	1-6	Nickel	28.8	26.2	9.5
1592	PA	1-6	Selenium	1.1 UJ	0.97 UJ	NC
1592	PA	1-6	Silver	1.7	1.6	6.1
1592	PA	1-6	Thallium	0.27 U	0.25 U	NC
1592	PA	1-6	Vanadium	28.8	25.7	11.4
1592	PA	1-6	Zinc	1000	915	8.9

**Notes:**

All results reported in mg/kg.

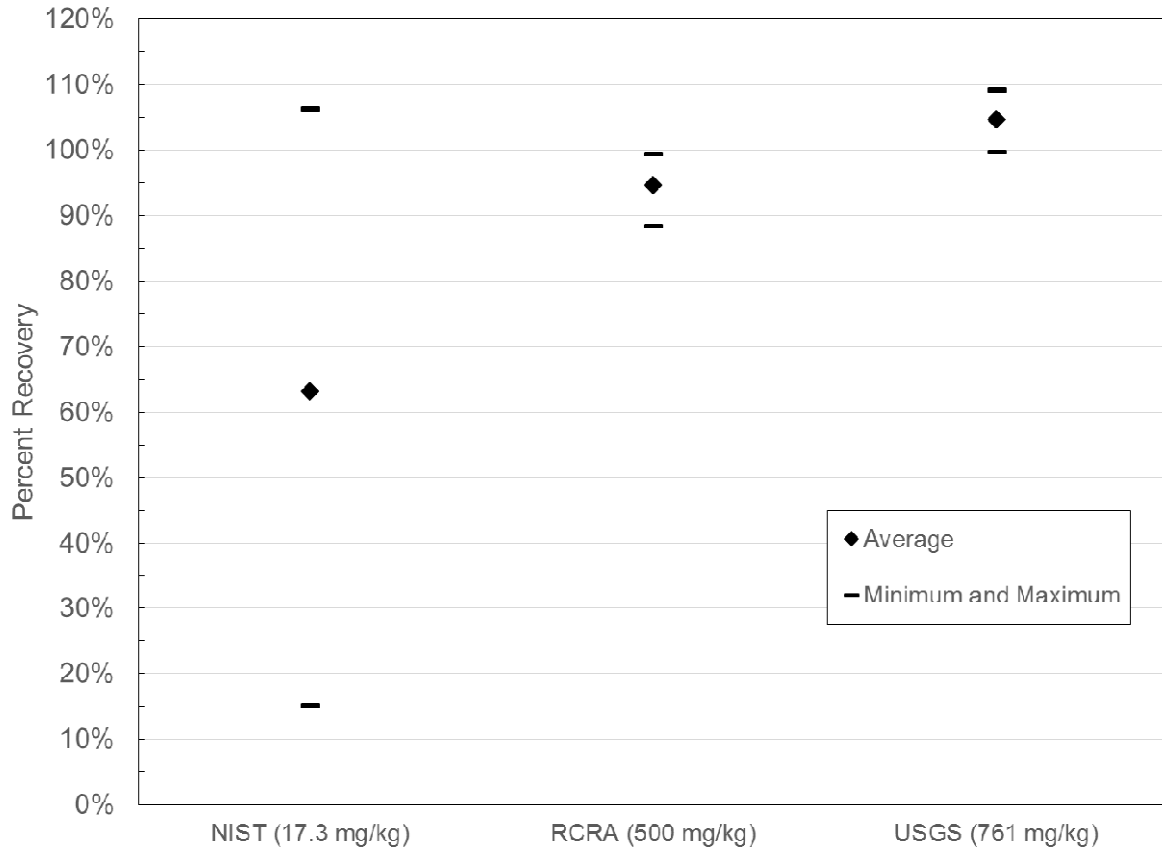
- bgs Below ground surface
- DU Decision unit
- ICP-MS Inductively-coupled plasma mass spectrometry
- PA Play area
- RPD Relative percent difference
- SY Side yard
- SYE Side yard east
- U Not detected
- UJ Not detected - detection limit is estimated

**FIGURE 5-1 LCS PERCENT RECOVERY RESULTS FOR ARSENIC**



Notes: LCS = Laboratory Control Sample  
NIST = National Institute of Standards and Technology  
USGS = U.S. Geological Survey  
RCRA = Resource Conservation and Recovery Act  
mg/kg = milligram/kilogram

**Figure 5-2 LCS PERCENT RECOVERY RESULTS FOR LEAD**



Notes: LCS = Laboratory Control Sample  
NIST = National Institute of Standards and Technology  
USGS = U.S. Geological Survey  
RCRA = Resource Conservation and Recovery Act  
mg/kg = milligram/kilogram

## 6.0 DATA ASSESSMENT

This section discusses data assessment procedures that were conducted to evaluate (1) the analytical results generated by the XRF equipment relative to ICP-MS results and (2) the sampling approaches used during the DMA. During the DMA, other data were collected for preliminary assessment of COPCs, bioaccessibility, and geospeciation; however, this DMA DSR does not assess these data, which will be assessed later in the project when a complete data set has been collected and evaluated.

### 6.1 DATA PROCESSING

The raw data from the XRF instruments were processed for analysis after evaluation against the instrument logbooks used to document data collection. Several steps were taken to generate a final analytical result for each sample:

- Data entries were corrected where necessary for errors noted in the instrument logbooks. This included removal of data from sample scans that were noted as unusable in the instrument logbooks.
- Sample means, standard deviations, RSDs, and UCLs were calculated.
- For samples with one or more sample scans that were non-detect by XRF for a specific metal, means and standard deviations were calculated using the Kaplan-Meier approach using EPA ProUCL software version 5.0 software (USEPA 2013). This affected arsenic results for 14 samples and no lead results. Lead was detected in all sample scans.
- After initial examination of XRF linearity (Section 6.3) and comparability of the XRF results to ICP-MS results (Section 6.4), adjusted XRF data were calculated for arsenic and lead. These adjusted data were used for all subsequent data assessment steps.

### 6.2 COMPARISON OF ICP RESULTS TO DMA SCREENING LEVELS

The ICP-MS results were compared to DMA screening levels (SLs) as an initial assessment of COPCs. Where no DMA SL was identified for a metal in the DMA QAPP, EPA Regional Screening Levels (RSLs) were used as the DMA SLs. Based on the small number of homes sampled for the DMA, the DMA approach and findings are not intended as a final decision about COPCs for the site. Table 6-1 shows the range of detected data for each metal analyzed by ICP-MS in comparison to the DMA SLs or RSLs.

In the DMA data set, three metals exceeded the DMA SL or RSL in at least one sample:

- Arsenic
- Lead
- Manganese

These three metals were evaluated for XRF linearity, as discussed in the next section.

### 6.3 EVALUATION OF XRF LINEARITY

Raw (unadjusted) XRF data were evaluated against the SRMs used for LCS analysis in the XRF method. These SRMs included (1) three which were used for control charting and (2) two

which were not used for control charting, but were evaluated during the latter part of the DMA for possible replacement of these SRMs in the overall RI effort:

- National Institute of Standards and Technology (NIST) SRM 2709a (charted)
- U.S. Geological Survey (USGS) SdAR-M2 (charted)
- Resource Conservation and Recovery Act (RCRA) (charted – this SRM is not certified but was mixed by weight instead)
- Japanese Society of Analytical Chemistry (JSAC) 0461 (not charted)
- JSAC 0466 (not charted)

Figures 6-1 and 6-2 show the average results for each SRM from each instrument used during the course of the DMA study; Figure 6-1 shows the results for arsenic and Figure 6-2 for lead. Table 6-2 shows a tabular comparison of results for both instruments. The results are summarized below:

- The linearity for arsenic was excellent for all 5 SRMs on both XRF instruments used during the DMA. The differences between the two instruments were slight and mostly appear to affect the highest concentration SRM, which is well above the DMA SL.
- The linearity for lead was very good for all 5 SRMs. The ratios of measured to certified concentration were below 60 percent for two SRMs when analyzed on one of the instruments (serial number 82347), but the concentrations of these SRMs are well below the DMA SL. The other three SRMs showed excellent linearity for both instruments. The differences between the two instruments were very minor and mostly appear to affect the highest concentration SRM, which is well above the DMA SL. For future RI work, it may be useful to obtain an SRM for lead with a certified concentration between 250 and 350 mg/kg. One possible candidate is JSAC 0464, with a lead concentration of 302.7 mg/kg and an arsenic concentration of 271.1 mg/kg.
- There were only two SRMs covering only a limited range of certified concentrations for manganese (529 to 1,000 mg/kg). Therefore, linearity for manganese could not be accurately assessed and manganese was not evaluated for XRF comparability to ICP-MS based on the DMA data set. Manganese may be evaluated for linearity and comparability to ICP-MS if data collected during the RI indicate that it is a COPC.

## 6.4 COMPARABILITY OF XRF TO ICP RESULTS

The DMA was designed to assess whether XRF could be used to accurately measure concentrations of COPCs at the Colorado Smelter site. Of the approximately 640 samples collected and analyzed by XRF, 40 were submitted to the EPA CLP for analysis by ICP-MS. These 40 samples were used to assess the XRF results. The samples were selected based on measured XRF concentration to provide a wide range for comparability analysis.

XRF results for metals with concentrations exceeding DMA SLs (see Section 6.2), and with adequate linearity and sufficient SRMs (see Section 6.3) were compared to the ICP results. This included only arsenic and lead, and only these metals are analyzed further in Sections 6.4.1 and 6.4.2 below.

Each analyte was compared using Q-Q plots, paired Wilcoxon Signed Rank (WSR) tests, and linear regression. All comparisons were made using EPA ProUCL software, version 5.0 (EPA 2013).



Q-Q plots were used to show the two distributions side-by-side for qualitative comparison. For the Q-Q plots shown in this section, the ICP-MS and XRF results are treated as two distributions and plotted separately.

Paired WSR tests were used to test for statistically significant bias between the methods. A two-sided test at a 95% confidence level was used for each test. The null hypothesis was that the difference between the paired XRF and ICP-MS results was statistically equivalent to zero. The alternative hypothesis was that the difference between the paired results was statistically different from zero.

Linear regressions were prepared to compare the results of the two methods quantitatively. 95% confidence limits and 95% prediction intervals are included on the linear regression plots.

If the Q-Q plots and paired WSR tests indicated differences between the two methods, the use of an adjustment equation based on the linear regression was investigated. Adjustment of the XRF data to values comparable to ICP-MS results is only appropriate when bias is indicated between the methods, and it can be documented that the adjustment does not increase variability of the data.

#### **6.4.1 Arsenic**

The Q-Q plot and WSR test results for arsenic are shown in Figure 6-3. The Q-Q plot shows a clear separation of the XRF and ICP-MS results, indicating a bias between the methods. It is possible that this bias is related to a real difference in methods, since the XRF method may effectively probe the inside of soil particles that are not digested by the sample preparation method used for the ICP-MS method (SW-846 Method 3050B). Based on a review of Figure 6-3, XRF results for As are consistently higher than ICP. This bias is not unexpected since the ICP method relies on a digestion while XRF represents a total metals analysis.

Figure 6-4 shows the linear regression of the ICP-MS results for arsenic against the XRF results. The ICP-MS results are plotted on the y-axis (i.e., as the dependent variable) so that the regression may be used to adjust the XRF results such that the XRF results can be used to predict the corresponding ICP-MS results. The correlation is excellent, with an R-squared (R-sq) value of 0.9868. The slope is less than 1, confirming that the XRF analysis is biased high compared to the Method 3050B digestion and ICP analysis. No obvious outliers are present. There are a few gaps at the higher end of the concentration range, which can cause the R-sq value to be biased high. There are signs of correlated residuals at lower concentrations, which may be caused by the nonlinearity at the high end of the range. The data have a somewhat curved appearance, with positive residuals dominating the low end of the range, and negative residuals dominating the middle of the range. There are no signs of heteroscedasticity (variability that varies over the concentration range).

The overall pattern of the residuals indicates non-linearity at higher concentrations, so a second linear regression was performed using only the results for which arsenic concentrations were below 90 mg/kg. This regression is shown on the bottom of Figure 6-4. The correlation is still very good, with an R-sq value of 0.8997. The slope is still less than 1, the intercept moves to zero nearly, the data balance is improved, and there are no signs of correlated residuals or heteroscedasticity. Since the regression data set is trimmed at 90 ppm, XRF results that are greater than 90 ppm and adjusted using this equations will have more uncertainty associated with them than those below 90 ppm. However, concentrations above 90 ppm are expected to

be above the screening level for decision-making on the project, so this increased uncertainty is not expected to affect decisions for the RI.

To assess whether the trimmed regression can be used as an adjustment equation, the adjusted data were calculated to assess whether the adjustment caused any unexpected results. A Q-Q plot of the adjusted data was created, and the WSR test was conducted. Figure 6-5 shows the Q-Q plot and the WSR test results for the adjusted data. The Q-Q plot shows excellent agreement for adjusted XRF data when the raw XRF concentrations are below 90 mg/kg. The WSR test shows a significant difference between the adjusted data and the ICP-MS data when all of the data are included; however, when only the data used to develop the adjustment equation are included, there is no significant difference.

As a further check on the performance of the adjustment equation, Figure 6-6 shows the linear regression for the ICP-MS results against the adjusted XRF results for arsenic. The correlation is still very good, with an R-sq value of 0.9000, and otherwise the correlation appears nearly identical to the correlation for ICP-MS concentration against unadjusted arsenic XRF concentrations below 90 mg/kg. No significant variability appears to be introduced by using the adjustment equation, so the adjusted XRF data will be used for arsenic in all further data evaluations. The adjustment equation for XRF may be updated based on additional data collected during the RI.

#### **6.4.2 Lead**

Figure 6-7 shows the Q-Q plot and WSR test results for lead. The Q-Q plot shows a slight separation of the XRF and ICP results, indicating a possible bias between the methods. It is possible that this bias is related to a real difference in methods, since the XRF method may effectively probe the inside of soil particles that are not digested by the sample preparation method used for the ICP-MS method. The WSR test indicates that there is a statistically significant bias at the 95% confidence level.

Figure 6-8 shows the linear regression of the ICP results for lead against the XRF results. The ICP-MS results are shown on the y-axis so that the regression may be used to adjust the XRF results as a means to predict corresponding ICP-MS results. The correlation is excellent, with an R-sq value of 0.9851. The slope is less than 1, confirming that the XRF analysis provides a high bias relative to the ICP method. No obvious outliers are present. The data are balanced, with no large gaps between the lower and higher concentration data points. The regression slope of 0.934 is near the ideal of 1, and the intercept of -2 is near the ideal of zero. There are no signs of heteroscedasticity (variability that varies over the concentration range).

To assess whether the regression can be used as an adjustment equation, the adjusted data were calculated to assess whether the adjustment caused any unexpected results. A Q-Q plot of the adjusted data was created, and the WSR test was conducted. Figure 6-9 shows the Q-Q plot and the WSR test results for the adjusted data. The Q-Q plot shows excellent agreement for adjusted XRF data. The WSR test shows no statistically significant difference at the 95% confidence level between the adjusted data and the ICP-MS when all the data are included.

Figure 6-10 shows the linear regression for the ICP-MS results against the adjusted XRF results for lead. The correlation remains excellent, with the R-sq at 0.9851. The correlation appears nearly identical to the correlation for ICP-MS concentration against unadjusted XRF lead concentration. No significant variability appears to be introduced by using the adjustment

equation, so the adjusted XRF data will be used for lead in all further data evaluations. The adjustment equation for XRF may be updated based on additional data collected during the RI.

### 6.4.3 Summary

The bullets below summarize the results of the comparability analysis for arsenic and lead:

- The raw XRF results for both metals appeared visually different from ICP-MS results on Q-Q plots, and were shown to be statistically different at the 95% confidence level.
- Linear regression of the raw XRF results against the ICP-MS results showed excellent correlation, and adjustment equations were developed for each metal.
- After the adjustment equations were used to calculate adjusted concentrations, the adjusted XRF results were examined in the same way as the raw results.
- The adjusted XRF results for both metals appeared visually similar to ICP-MS results on Q-Q plots, and were shown to be statistically identical at the 95% confidence level.
- Linear regression of the adjusted XRF results against the ICP-MS results showed excellent correlation, with no decrease in correlation relative to the raw XRF versus ICP-MS correlations.

In conclusion, the DMA data indicate that the XRF appears to provide defensible data for arsenic and lead for soil samples from the Colorado Smelter site.

## 6.5 COMPARABILITY OF SAMPLING APPROACHES

The DMA was designed to assess whether a 5-point composite sampling approach could be used to make accurate decisions at the Colorado Smelter site. Of the approximately 154 DU/depth combinations sampled using a triplicate 5-point composite sampling approach, 20 were sampled using both that approach and a 30-point incremental sampling approach. These 20 DU/depth combinations were used to compare the 5-point composite approach to the 30-point incremental approach.

The variability and decision error of the sampling approaches were compared. The variability of the 5-point composite sampling approach was anticipated to be higher than that for the 30-point incremental sampling approach. However, if acceptable decision rates can be achieved for the 5-point composite approach despite the higher variability, it may be acceptable to use the less invasive 5-point composite approach. Variability is discussed in the next section.

### 6.5.1 Variability

Variability was compared qualitatively and statistically using a WSR test. A total of 20 DU/depth combinations were used for this comparison. These included eight DUs with two depth intervals collected and one DU with all four depth intervals collected.

Table 6-3 summarizes the variability results for the two sampling methods. The results show qualitatively that the mean and median RSD for both arsenic and lead are higher for the 5-point composite approach than the 30-point incremental approach. The table also shows the calculated paired differences for each analyte.

The paired differences were imported into ProUCL 5.0, where WSR tests were conducted for arsenic, lead, and arsenic and lead combined. Because the RSDs were clearly larger for the 5-point composite approach, a one-sided test at a 95% confidence level was used for all tests. The null hypothesis was that the difference between the paired RSDs was statistically less than or equivalent to zero. The alternative hypothesis was that the difference between the paired RSDs was not less than or equivalent to zero. Tables 6-4, 6-5, and 6-6 show the ProUCL outputs for the WSR tests.

The WSR test for arsenic showed that the null hypothesis was not rejected at 5% significance ( $p\text{-value} \leq 0.05$ ), although it was very close to statistical significance with a  $p\text{-value}$  of 0.08. Nonetheless, the WSR test for arsenic alone mean that the arsenic variability (as RSD) for the 5-point composite approach is not significantly different from the variability for 30-point incremental approach. However, for lead alone, and for lead and arsenic combined, the results of the test were that the null hypothesis was rejected at 5% significance (the actual  $p\text{-values}$  were 0.001 for lead alone and 0.002 for lead and arsenic combined). These test results mean that the variability (as RSD) in the 5-point composite approach is was significantly higher than the variability for the 30-point incremental approach.

Because it was noted that there could be some influence of larger-sized DUs on the results, the tests were repeated with the results from the largest DU sampled during the DMA, SYE-0423, excluded. This DU had an area of over 12,000 square feet, while the other DUs in the DMA study were all less than 2,000 square feet. The conclusions from the statistical tests were the same as the conclusions when the large DU was included; however, the  $p\text{-values}$  became slightly less significant when the large DU was removed. The  $p\text{-value}$  increased from 0.08 to 0.23 for arsenic alone, from 0.001 to 0.02 for lead alone, and from 0.002 to 0.036 for the combined data set. The ProUCL outputs for these tests are also shown on Tables 6-4, 6-5, and 6-6.6.5.2.

### **6.5.2 Decision Error**

To determine whether the increased variability of the 5-point composite approach adversely affects decision-making at the DMA SLs for arsenic and lead, decision error rates were computed for the 5-point composite data sets. Acceptable error rates were chosen to be 5% false negatives and 20% false positives. Because the number of DU/depth interval combinations with both 5-point composite and 30-point incremental data ( $n=20$ ) is relatively small for assessing decision error, rates were also computed for the DUs having only 5-point composite samples. This provides a data set of 154 DU/depth combinations with 462 different individual 5-point composite triplicate results for each analyte.

To absolutely define false positives and false negatives, knowledge of the true analyte concentration would be necessary. Since it is impossible to know the actual analyte concentration, a best estimate must be used as a reference value. For this comparison, the reference value was chosen to be the triplicate mean. In other words, the mean of the three – point composite samples from each DU/depth combination was taken to be the “true” concentration for that DU and depth. For the discussion that follows, the following definitions are used to define “positive” and “negative” results, both “true” and “false”:

- Positive results are individual 5-point composite samples for which the result exceeds the DMA SL, and are split into the following subgroups:

- A true positive is a positive result for which the mean of the triplicate 5-point composite samples exceeds the DMA SL.
- A false positive is a positive result for which the mean of the triplicate 5-point composite samples is below the DMA SL.
- The false positive rate is the ratio of the number of false positive results to the total number of positive results.
- Negative results are individual 5-point composite samples for which the result is below the DMA SL, and are split into the following subgroups:
  - A true negative is a negative result for which the mean of the triplicate 5-point composite samples is below the DMA SL.
  - A false negative is a negative result for which the mean of the triplicate 5-point composite samples exceeds the DMA SL..
  - The false negative rate is the ratio of the number of false negative results to the total number of negative results.

Figure 6-9 shows the data sets for arsenic and lead visually, with the four corners of each chart representing one of the above four defined types of negative and positive results.

In addition to the above analysis, false positive rates and false negative rates were modified by removing certain results for which samples from a deeper layer within the DU, or results for the other analyte, would have resulted in a decision that the DU was above the DMA SL. Those cases included:

- Sample results for which all three results at the same DU and from the same depth layer (or a deeper layer) were above the DMA SL for the other analyte.
- Sample results for which all three results at the same DU and from a deeper layer were above the DMA SL for the same analyte.

Both of these cases would result in the DU and depth being considered above the DMA SL regardless of the individual result obtained from each layer. The modified false positive and false negative rates are therefore defined as the “effective false positive rate” and the “effective false negative rate”.

Table 6-7 shows a summary of the negative and positive results, and includes calculated false positive rates and false negative rates. It also shows effective false positive and effective false negatives results and rates.

The results indicate that the raw false positive rates for both analytes and for the combined data set are all well below the targeted decision error rate for false positives of 20%, and are all also below 10%. In addition, the effective false positive rates are below 5% for both analytes and the combined data set. These decision error rates meet EPA goals for the project.

The false negative rates for both analytes are below the targeted decision error rate for false negatives of 5%. In addition, the effective false negative rates are below 2% for both analytes,

and below 1% for arsenic alone and in the combined data set. These decision error rates meet EPA goals for the project.

Based on the decision error analysis of 154 DU/depth intervals and 462 5-point composite samples, it is concluded that the collection of 5-point composite triplicate samples is not necessary to provide defensible data for a given DU. Triplicate samples may be advisable for a subset of DUs sampled in the RI to provide an ongoing check that the findings of the DMA continue to hold across the range of residential property locations and soil types.

## **6.6 DEPTH VERSUS CONCENTRATION PROFILES**

The DMA also was designed to assess whether the collection of soil samples from all four depth ranges to 18 inches below ground surface (bgs) will be necessary to fully investigate contamination from the Colorado Smelter site. Table 6-8 summarizes DMA findings for depth versus concentration by showing the average result for each property, DU, and depth.

In summary, contamination above DMA SLs is present at all four depth ranges investigated in the study. The DMA data indicate that all four depths should continue to be investigated in the full sampling effort that will be implemented with the RI.

**TABLE 6-1**

**COMPARISON OF ICP-MS RESULTS TO DMA SCREENING LEVELS**

<b>Metal</b>	<b>DMA SL</b>	<b>DMA SL source</b>	<b>Detection Frequency</b>	<b>Range of Detected Concentrations (mg/kg)</b>	<b>Maximum Concentration &gt; DMA SL?</b>
Antimony	31	DMA QAPP PAL	34 / 36	0.27 - 4.5	No
Arsenic	0.39	DMA QAPP PAL	36 / 36	4.9 - 282	<b>Yes</b>
Barium	15,000	EPA RSL	36 / 36	105 - 322	No
Beryllium	160	EPA RSL	36 / 36	0.39 - 0.9	No
Cadmium	70	DMA QAPP PAL	36 / 36	0.83 - 10.4	No
Chromium	120,000	EPA RSL	36 / 36	8.3 - 162	No
Cobalt	23	EPA RSL	36 / 36	4.1 - 7.6	No
Copper	3,100	DMA QAPP PAL	36 / 36	13.8 - 182	No
Lead	400	DMA QAPP PAL	36 / 36	37.4 - 918	<b>Yes</b>
Manganese	1,800	EPA RSL	36 / 36	198 - 1,980	<b>Yes</b>
Nickel	1,500	EPA RSL	36 / 36	13.8 - 76.8	No
Selenium	390	EPA RSL	5 / 36	0.4 - 3.0	No
Silver	390	EPA RSL	30 / 36	0.081 - 5.0	No
Thallium	0.78	EPA RSL	9 / 36	0.14 - 0.36	No
Vanadium	390	EPA RSL	36 / 36	20.4 - 43.5	No
Zinc	23,000	DMA QAPP PAL	36 / 36	71.5 - 1,330	No

**Notes:**

DMA QAPP

PAL

Demonstration of Methods Applicability Project Action Level (PWT 2015)

DMA SL

Demonstration of Methods Applicability Screening Level (PWT 2015)

EPA RSL

EPA Regional Screening Level (EPA 2015)

ICP-MS

Inductively Coupled Plasma-Mass Spectrometry

mg/kg

Milligrams per kilogram

**TABLE 6-2**

**SUMMARY OF XRF LINEARITY RESULTS FOR ARSENIC AND LEAD**

Analyte	SRM	Certified Concentration (mg/kg)	Instrument 82347		Instrument 92959	
			Mean Measured Concentration (mg/kg)	Measured/ Certified Concentration	Mean Measured Concentration (mg/kg)	Measured/ Certified Concentration
Arsenic	NIST 2709a	10.5	10.2	0.97	10.7	1.02
Arsenic	JSAC 0461	21.53	21.1	0.98	21.1	0.98
Arsenic	USGS	78	79.6	1.02	76.5	0.98
Arsenic	RCRA	500	445	0.89	453	0.91
Arsenic	JSAC 0466	1,093	1,060	0.97	1,097	1.00
Lead	NIST 2709a	17.3	5.88	0.34	15.3	0.89
Lead	JSAC 0461	24.4	13.0	0.53	21.3	0.87
Lead	RCRA	500	464	0.93	481	0.96
Lead	USGS	761	781	1.03	811	1.07
Lead	JSAC 0466	1214	1,108	0.91	1,190	0.98

**Notes:**

- mg/kg      Milligrams per kilogram
- JSAC      Japanese Society of Analytical Chemistry
- National Institute for Standards and Technology
- NIST      National Institute for Standards and Technology
- RCRA      Resource Conservation and Recovery Act
- USGS      United States Geological Service



**TABLE 6-3**

**COMPARISON OF VARIABILITY FOR 5-POINT COMPOSITE SAMPLES TO 30-POINT INCREMENTAL SAMPLES**

DU ID	RSD						DU Size (square feet)
	Arsenic			Lead			
	5-point	30-point	Difference	5-point	30-point	Difference	
SY-0269	17.2%	3.7%	13.5%	1.3%	3.6%	-2.3%	1,025
SY-0269	9.3%	2.4%	6.9%	9.8%	3.6%	6.2%	1,025
BY-0389	19.4%	11.6%	7.9%	5.4%	2.6%	2.7%	1,780
BY-0389	12.1%	14.2%	-2.1%	8.2%	8.1%	0.1%	1,780
BY-0423	9.4%	6.6%	2.9%	3.7%	2.9%	0.8%	1,623
BY-0423	3.5%	4.9%	-1.5%	5.7%	10.5%	-4.8%	1,623
SYE-0423	5.0%	8.9%	-3.9%	12.3%	4.5%	7.8%	12,626
SYE-0423	28.6%	16.8%	11.8%	80.4%	14.2%	66.1%	12,626
SYE-0423	21.9%	10.7%	11.2%	102.7%	59.5%	43.3%	12,626
SYE-0423	22.5%	8.4%	14.1%	83.9%	69.6%	14.3%	12,626
BY-1076	17.1%	15.6%	1.5%	7.8%	3.7%	4.2%	1,115
BY-1076	3.4%	8.2%	-4.8%	6.4%	1.4%	5.0%	1,115
BY-1504	14.3%	1.9%	12.4%	5.3%	1.8%	3.5%	1,896
BY-1504	4.4%	7.2%	-2.8%	20.5%	5.3%	15.2%	1,896
FY-1504	11.5%	24.3%	-12.7%	4.0%	1.9%	2.1%	1,738
FY-1504	17.0%	23.0%	-6.0%	7.4%	9.0%	-1.5%	1,738
BY-1615	8.0%	8.9%	-0.9%	3.9%	2.5%	1.4%	990
BY-1615	15.7%	19.0%	-3.3%	5.0%	5.5%	-0.5%	990
FY-1654	22.3%	14.9%	7.4%	29.0%	9.1%	19.9%	1,197
FY-1654	20.2%	15.9%	4.3%	18.0%	17.0%	1.0%	1,197
Mean	14.1%	11.4%	2.8%	21.0%	11.8%	9.2%	NC
Median	15.0%	9.8%	2.2%	7.6%	4.9%	3.1%	NC
Standard Deviation	7.3%	6.5%	NC	30.3%	18.6%	NC	NC

**Notes:**

- DU        Decision Unit
- NC        Not calculated
- RSD      Relative Standard Deviation

**TABLE 6-4**

**PROUCL WSR TEST OUTPUT FOR ARSENIC**

**All Decision Units**

**Decision Unit SYE-0423 Excluded**

One Sample Wilcoxon Signed Rank Test for Uncensored Full Data Sets without NDs	One Sample Wilcoxon Signed Rank Test for Uncensored Full Data Sets without NDs
<p>User Selected Options</p> <p>Date/Time of Computation 7/31/2015 3:44:47 PM</p> <p>From File WorkSheet.xls</p> <p>Full Precision OFF</p> <p>Confidence Coefficient 95%</p> <p>Substantial Difference 0.000</p> <p>Action Level 0.000</p> <p>Selected Null Hypothesis Mean/Median &lt;= Action Level (Form 1)</p> <p>Alternative Hypothesis Mean/Median &gt; the Action Level</p>	<p>User Selected Options</p> <p>Date/Time of Computation 7/31/2015 3:47:00 PM</p> <p>From File WorkSheet.xls</p> <p>Full Precision OFF</p> <p>Confidence Coefficient 95%</p> <p>Substantial Difference 0.000</p> <p>Action Level 0.000</p> <p>Selected Null Hypothesis Mean/Median &lt;= Action Level (Form 1)</p> <p>Alternative Hypothesis Mean/Median &gt; the Action Level</p>
<p><b>Diff</b></p>	<p><b>Diff</b></p>
<p><b>One Sample Wilcoxon Signed Rank Test</b></p>	<p><b>One Sample Wilcoxon Signed Rank Test</b></p>
<p><b>Raw Statistics</b></p> <p>Number of Valid Observations 20</p> <p>Number of Distinct Observations 20</p> <p>Minimum -0.127</p> <p>Maximum 0.141</p> <p>Mean 0.028</p> <p>Median 0.022</p> <p>SD 0.0761</p> <p>SE of Mean 0.017</p> <p>Number Above Action Level 11</p> <p>Number Equal Action Level 0</p> <p>Number Below Action Level 9</p> <p>T-plus 143.5</p> <p>T-minus 66.5</p>	<p><b>Raw Statistics</b></p> <p>Number of Valid Observations 16</p> <p>Number of Distinct Observations 16</p> <p>Minimum -0.127</p> <p>Maximum 0.135</p> <p>Mean 0.0142</p> <p>Median 0.003</p> <p>SD 0.0704</p> <p>SE of Mean 0.0176</p> <p>Number Above Action Level 8</p> <p>Number Equal Action Level 0</p> <p>Number Below Action Level 8</p> <p>T-plus 82.5</p> <p>T-minus 53.5</p>
<p><b>H0: Sample Mean/Median &lt;= 0 (Form 1)</b></p>	<p><b>H0: Sample Mean/Median &lt;= 0 (Form 1)</b></p>
<p>Exact Test Statistic 143.5</p> <p>Critical Value (0.05) 150</p> <p>P-Value 0.0768</p>	<p>Exact Test Statistic 82.5</p> <p>Critical Value (0.05) 101</p> <p>P-Value 0.232</p>
<p><b>Conclusion with Alpha = 0.05</b></p> <p><b>Do Not Reject H0, Conclude Mean/Median &lt;= 0</b></p> <p><b>P-Value &gt; Alpha (0.05)</b></p>	<p><b>Conclusion with Alpha = 0.05</b></p> <p><b>Do Not Reject H0, Conclude Mean/Median &lt;= 0</b></p> <p><b>P-Value &gt; Alpha (0.05)</b></p>

**TABLE 6-5**

**PROUCL WSR TEST OUTPUT FOR LEAD**

**All Decision Units**

**Decision Unit SYE-0423 Excluded**

One Sample Wilcoxon Signed Rank Test for Uncensored Full Data Sets without NDs	One Sample Wilcoxon Signed Rank Test for Uncensored Full Data Sets without NDs
<p>User Selected Options</p> <p>Date/Time of Computation 7/31/2015 3:10:41 PM</p> <p>From File WorkSheet.xls</p> <p>Full Precision OFF</p> <p>Confidence Coefficient 95%</p> <p>Substantial Difference 0.000</p> <p>Action Level 0.000</p> <p>Selected Null Hypothesis Mean/Median &lt;= Action Level (Form 1)</p> <p>Alternative Hypothesis Mean/Median &gt; the Action Level</p>	<p>User Selected Options</p> <p>Date/Time of Computation 7/31/2015 3:33:04 PM</p> <p>From File WorkSheet.xls</p> <p>Full Precision OFF</p> <p>Confidence Coefficient 95%</p> <p>Substantial Difference 0.000</p> <p>Action Level 0.000</p> <p>Selected Null Hypothesis Mean/Median &lt;= Action Level (Form 1)</p> <p>Alternative Hypothesis Mean/Median &gt; the Action Level</p>
<p><b>Diff</b></p>	<p><b>Diff</b></p>
<p><b>One Sample Wilcoxon Signed Rank Test</b></p>	<p><b>One Sample Wilcoxon Signed Rank Test</b></p>
<p><b>Raw Statistics</b></p> <p>Number of Valid Observations 20</p> <p>Number of Distinct Observations 20</p> <p>Minimum -0.048</p> <p>Maximum 0.661</p> <p>Mean 0.0923</p> <p>Median 0.031</p> <p>SD 0.171</p> <p>SE of Mean 0.0383</p> <p>Number Above Action Level 16</p> <p>Number Equal Action Level 0</p> <p>Number Below Action Level 4</p> <p>T-plus 182</p> <p>T-minus 28</p>	<p><b>Raw Statistics</b></p> <p>Number of Valid Observations 16</p> <p>Number of Distinct Observations 16</p> <p>Minimum -0.048</p> <p>Maximum 0.199</p> <p>Mean 0.0331</p> <p>Median 0.0175</p> <p>SD 0.0628</p> <p>SE of Mean 0.0157</p> <p>Number Above Action Level 12</p> <p>Number Equal Action Level 0</p> <p>Number Below Action Level 4</p> <p>T-plus 108</p> <p>T-minus 28</p>
<p><b>H0: Sample Mean/Median &lt;= 0 (Form 1)</b></p>	<p><b>H0: Sample Mean/Median &lt;= 0 (Form 1)</b></p>
<p>Exact Test Statistic 182</p> <p>Critical Value (0.05) 150</p> <p>P-Value 0.0014</p>	<p>Exact Test Statistic 108</p> <p>Critical Value (0.05) 101</p> <p>P-Value 0.0193</p>
<p><b>Conclusion with Alpha = 0.05</b></p> <p><b>Reject H0, Conclude Mean/Median &gt; 0</b></p> <p><b>P-Value &lt; Alpha (0.05)</b></p>	<p><b>Conclusion with Alpha = 0.05</b></p> <p><b>Reject H0, Conclude Mean/Median &gt; 0</b></p> <p><b>P-Value &lt; Alpha (0.05)</b></p>

**TABLE 6-6**

**PROUCL WSR TEST OUTPUT FOR LEAD AND ARSENIC COMBINED**

**All Decision Units**

**Decision Unit SYE-0423 Excluded**

One Sample Wilcoxon Signed Rank Test for Uncensored Full Data Sets without NDs	One Sample Wilcoxon Signed Rank Test for Uncensored Full Data Sets without NDs
<p>User Selected Options</p> <p>Date/Time of Computation 7/31/2015 3:48:24 PM</p> <p>From File WorkSheet.xls</p> <p>Full Precision OFF</p> <p>Confidence Coefficient 95%</p> <p>Substantial Difference 0.000</p> <p>Action Level 0.000</p> <p>Selected Null Hypothesis Mean/Median &lt;= Action Level (Form 1)</p> <p>Alternative Hypothesis Mean/Median &gt; the Action Level</p>	<p>User Selected Options</p> <p>Date/Time of Computation 7/31/2015 3:51:34 PM</p> <p>From File WorkSheet.xls</p> <p>Full Precision OFF</p> <p>Confidence Coefficient 95%</p> <p>Substantial Difference 0.000</p> <p>Action Level 0.000</p> <p>Selected Null Hypothesis Mean/Median &lt;= Action Level (Form 1)</p> <p>Alternative Hypothesis Mean/Median &gt; the Action Level</p>
<b>Diff</b>	<b>Diff</b>
<b>One Sample Wilcoxon Signed Rank Test</b>	<b>One Sample Wilcoxon Signed Rank Test</b>
<p style="text-align: center;"><b>Raw Statistics</b></p> <p>Number of Valid Observations 40</p> <p>Number of Distinct Observations 38</p> <p>Minimum -0.127</p> <p>Maximum 0.661</p> <p>Mean 0.0601</p> <p>Median 0.028</p> <p>SD 0.135</p> <p>SE of Mean 0.0213</p> <p>Number Above Action Level 27</p> <p>Number Equal Action Level 0</p> <p>Number Below Action Level 13</p> <p>T-plus 627.5</p> <p>T-minus 192.5</p>	<p style="text-align: center;"><b>Raw Statistics</b></p> <p>Number of Valid Observations 32</p> <p>Number of Distinct Observations 30</p> <p>Minimum -0.127</p> <p>Maximum 0.199</p> <p>Mean 0.0237</p> <p>Median 0.0145</p> <p>SD 0.0663</p> <p>SE of Mean 0.0117</p> <p>Number Above Action Level 20</p> <p>Number Equal Action Level 0</p> <p>Number Below Action Level 12</p> <p>T-plus 360.5</p> <p>T-minus 167.5</p>
<b>H0: Sample Mean/Median &lt;= 0 (Form 1)</b>	<b>H0: Sample Mean/Median &lt;= 0 (Form 1)</b>
<p>Large Sample z-Test Statistic 2.917</p> <p>Critical Value (0.05) 1.645</p> <p>P-Value 0.00177</p>	<p>Large Sample z-Test Statistic 1.795</p> <p>Critical Value (0.05) 1.645</p> <p>P-Value 0.0363</p>
<p><b>Conclusion with Alpha = 0.05</b></p> <p><b>Reject H0, Conclude Mean/Median &gt; 0</b></p> <p><b>P-Value &lt; Alpha (0.05)</b></p>	<p><b>Conclusion with Alpha = 0.05</b></p> <p><b>Reject H0, Conclude Mean/Median &gt; 0</b></p> <p><b>P-Value &lt; Alpha (0.05)</b></p>

**TABLE 6-7**  
**DECISION ERROR SUMMARY**

	<b>Arsenic</b>	<b>Lead</b>	<b>Combined</b>
Total samples	462	462	924
Positive results	82	157	239
True positives	75	149	224
False positives (results suggest dirty when actually clean)	7	8	15
<b>False positive rate</b>	<b>8.5%</b>	<b>5.1%</b>	<b>6.3%</b>
Effective false positives	4	5	9
<b>Effective false positive rate</b>	<b>4.9%</b>	<b>3.2%</b>	<b>3.8%</b>

	<b>Arsenic</b>	<b>Lead</b>	<b>Combined</b>
Total samples	462	462	924
Negative results	380	305	685
True negatives	377	292	669
False negatives (results suggest clean when actually dirty)	3	13	16
<b>False negative rate</b>	<b>0.8%</b>	<b>4.3%</b>	<b>2.3%</b>
Effective false negatives	1	4	5
<b>Effective false negative rate</b>	<b>0.3%</b>	<b>1.3%</b>	<b>0.7%</b>

Notes:

Positive results are individual 5-point composite samples for which the result exceeds the DMA SL.

A true positive is a positive result for which the mean of the triplicate 5-point composite samples exceeds the DMA SL

A false positive is a positive sample for which the mean of the triplicate 5-point composite samples is below the DMA SL.

Negative results are individual 5-point composite samples for which the result is below the DMA SL.

A true negative is a negative sample in which the mean of the triplicate 5-point composite samples is below the DMA SL

A false negative is a negative sample in which the mean of the triplicate 5-point composite samples exceeds the DMA SL.

The false positive rate is the ratio of false positive results to total positive results.

The false negative rate is the ratio of false negative results to total negative results.

Effective false positives are false positives modified by removing results that were true positives for all three individual 5-point composite samples for the other analyte at the depth being considered, or deeper depths.

Effective false negatives are false negatives modified by removing results that were true positives for all three individual 5-point composite sample results for the other analyte at the depth being considered, or deeper depths.

**TABLE 6-8**

**DEPTH PROFILE OF ARSENIC AND LEAD AT COLORADO SMELTER DMA PROPERTIES**

DU	Notes	Mean arsenic concentration (mg/kg) by depth interval (inches bgs)							
		Arsenic				Lead			
		0-1 (or 0-2)	1-6 (or 2-6)	6-12	12-18	0-1 (or 0-2)	1-6 (or 2-6)	6-12	12-18
BY-0181		14.4	15.1	15.4	27.3	432	457	452	786
FY-0181		9.19	13.7	12.3	7.99	245	344	234	68.8
GA-0181	a	17.7	14.6	20.4	24.9	489	494	600	782
SY-0181		15.5	22.8	28.8	12.6	410	619	701	217
AP-0269		8.49	7.06	4.23	3.31	178	77.9	24.8	16.4
BY-0269		11.4	12.5	11.3	8.15	336	345	233	106
DZ-0269	b	12.0	NS	NS	NS	459	NS	NS	NS
SY-0269		10.6	9.90	10.1	8.23	284	245	161	87.9
AP-0389		113	55.9	23.4	6.00	433	141	26.2	11.9
BY-0389		12.0	27.6	16.6	10.9	273	356	232	101
DZ-0389	b	57.4	NS	NS	NS	514	NS	NS	NS
FY-0389		29.4	15.6	8.22	4.54	400	265	73.4	33.6
SY-0389		41.4	59.5	55.5	24.9	525	633	658	383
BY-0423		7.25	8.38	7.45	7.69	180	215	102	118
DZ-0423	c	12.2	13.4	NS	NS	351	537	NS	NS
ED-0423	b	7.06	NS	NS	NS	189	NS	NS	NS
GA-0423	a	8.50	8.02	9.74	13.1	199	178	198	303
SYE-0423		7.03	6.92	4.08	3.96	110	79.5	31.3	17.6
SYW-0423		8.57	10.0	12.7	14.8	207	213	415	487
BY-0496		7.90	7.55	8.37	6.40	257	287	304	168
FY-0496		3.66	4.23	7.04	4.28	87.2	124	202	90.9
SY-0496		10.6	11.3	7.67	5.55	497	537	261	78.9
FY-0724		12.1	15.2	14.8	12.5	174	181	121	52.0
SYE-0724		9.41	10.4	9.69	9.39	175	215	225	372
SYW-0724		7.63	9.55	7.23	7.92	146	184	137	143
AP-1076		9.70	7.76	6.37	4.89	250	206	103	78.4
BY-1076		14.7	15.5	10.6	4.08	514	524	287	35.7
DZ-1076	b	11.0	NS	NS	NS	410	NS	NS	NS
ED-1076		14.3	16.1	13.5	9.18	554	546	363	232
FY-1076		10.3	9.62	7.59	6.61	277	239	210	280
BY-1504		9.67	10.2	16.3	11.0	372	376	518	213
DZ-1504	b	13.7	NS	NS	NS	444	NS	NS	NS
FY-1504		12.6	11.4	8.85	7.75	334	348	231	166

DU	Notes	Mean arsenic concentration (mg/kg) by depth interval (inches bgs)							
		Arsenic				Lead			
		0-1 (or 0-2)	1-6 (or 2-6)	6-12	12-18	0-1 (or 0-2)	1-6 (or 2-6)	6-12	12-18
BY-1592		53.1	65.8	113	143	370	425	477	579
FY-1592		43.4	63.0	91.6	61.2	317	435	627	374
GA-1592	a	62.0	83.6	150	93.8	491	517	554	448
PA-1592		80.4	150	131	113	476	637	419	366
AP-1615		19.8	26.9	31.1	25.0	427	551	568	461
BY-1615		27.9	30.8	18.2	15.7	459	475	320	283
ED-1615	a	12.0	15.1	16.1	18.0	297	382	357	256
FY-1615		23.7	28.2	20.8	8.91	592	794	580	83.2
GA-1615	a	19.3	19.2	14.1	14.3	440	425	360	357
SY-1615	b	15.1	NS	NS	NS	446	NS	NS	NS
BY-1654		76.2	203	116	32.2	1031	2650	1647	225
DZ-1654	b	22.1	NS	NS	NS	530	NS	NS	NS
FY-1654		68.1	66.5	28.6	18.9	623	998	175	43.6
GA-1654		25.0	17.8	50.0	49.0	361	349	779	815
AP-1835		12.1	13.5	8.94	4.93	355	362	195	32.0
BY-1835		14.3	14.5	14.0	8.96	410	455	438	201
DZ-1835	b	20.3	NS	NS	NS	717	NS	NS	NS
FY-1835		11.0	11.5	6.79	4.49	352	337	124	25.5

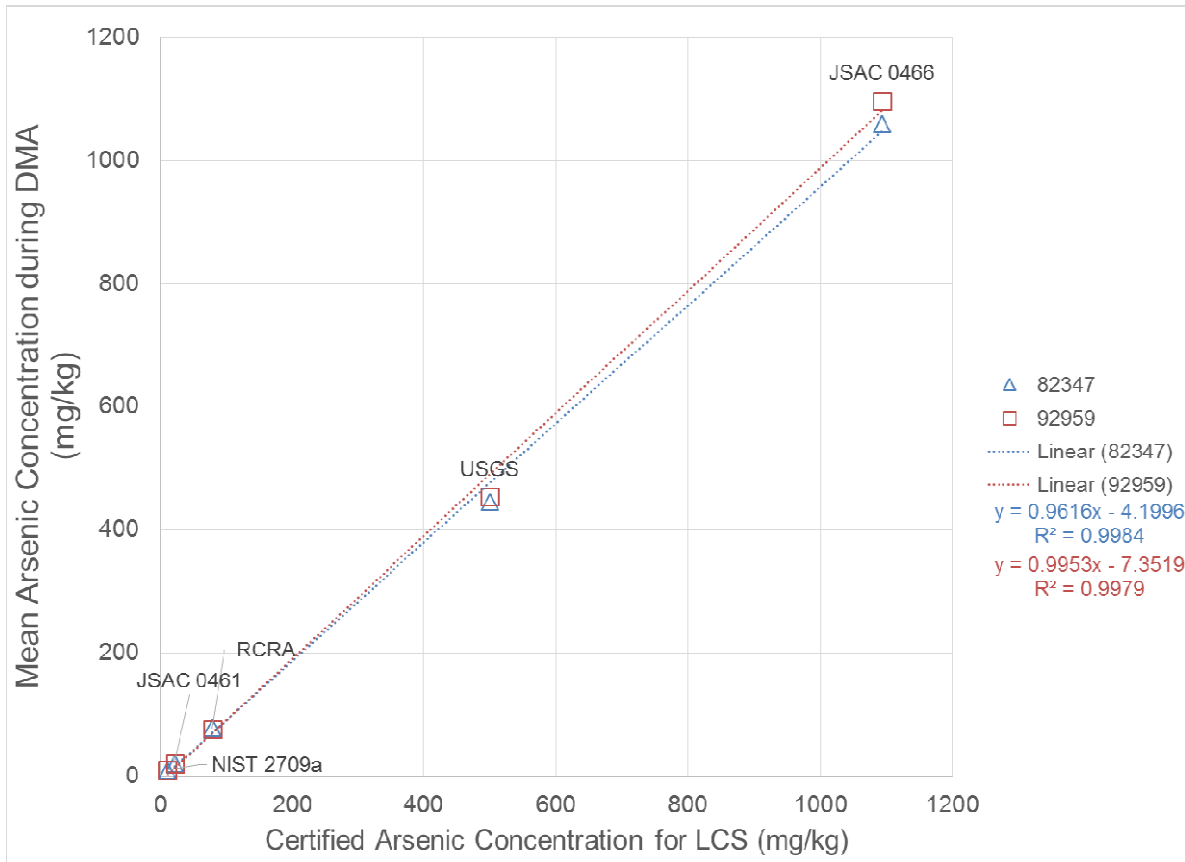
**Notes:**

All concentrations in mg/kg (milligrams per kilogram).

- a Triplicate sample not collected due to DU size
- b Sample collected only at surface layer
- c Sample collected only at top two depth layers
- AP Apron
- bgs Below ground surface
- BY Back yard
- DU Decision unit
- DZ Drip zone
- FY Front yard
- GA Garden
- NS Not sampled
- PA Play area
- SY Side yard
- SYE Side yard east
- SYW Side yard west

FIGURE 6-1

MEAN LCS RESULTS FOR ARSENIC DURING THE DMA

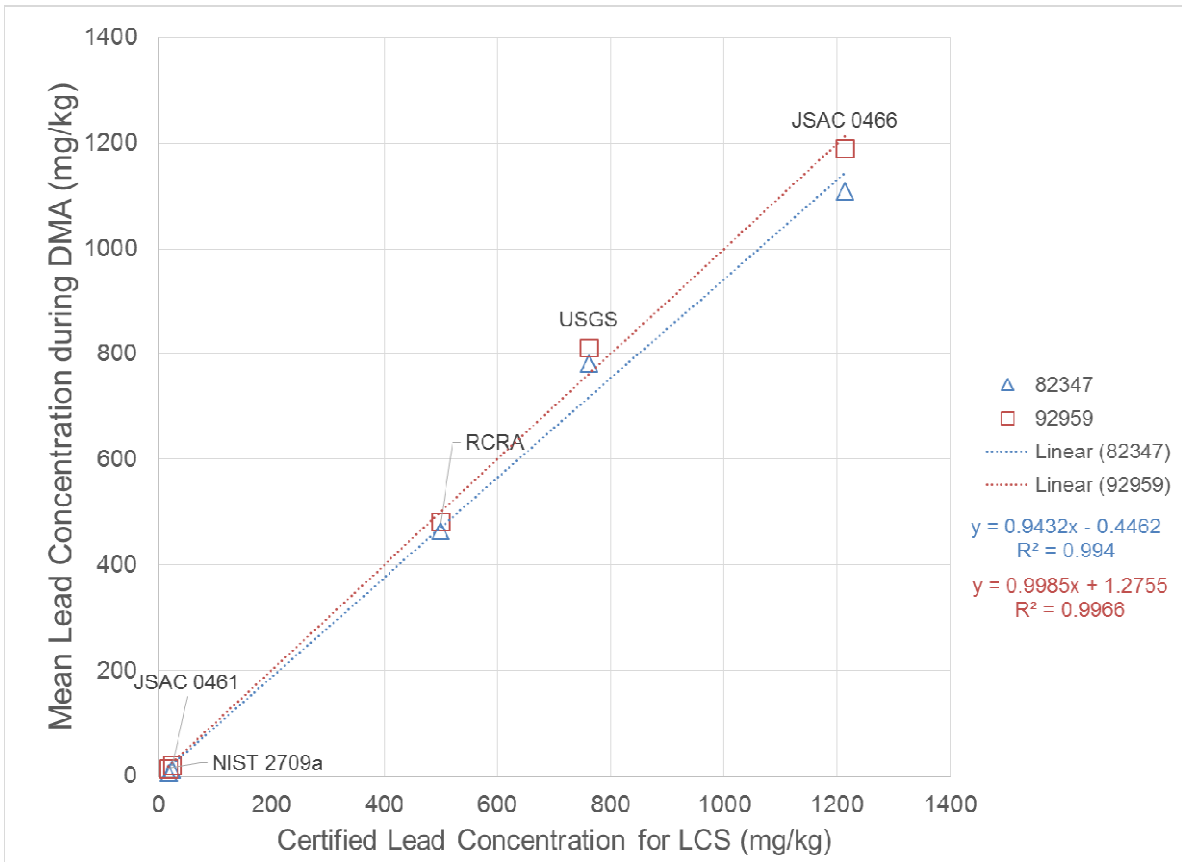


Notes: mg/kg = milligram/kilogram  
LCS = Laboratory control sample  
DMA = Demonstration of Methods Analysis



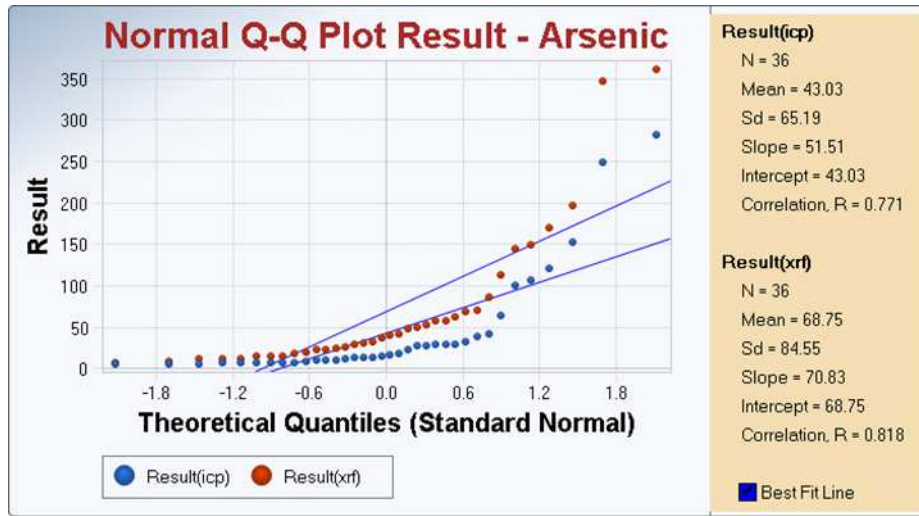
FIGURE 6-2

MEAN LCS RESULTS FOR LEAD DURING THE DMA



Notes: mg/kg = milligram/kilogram  
LCS = XXX  
DMA = Demonstration of Methods Analysis

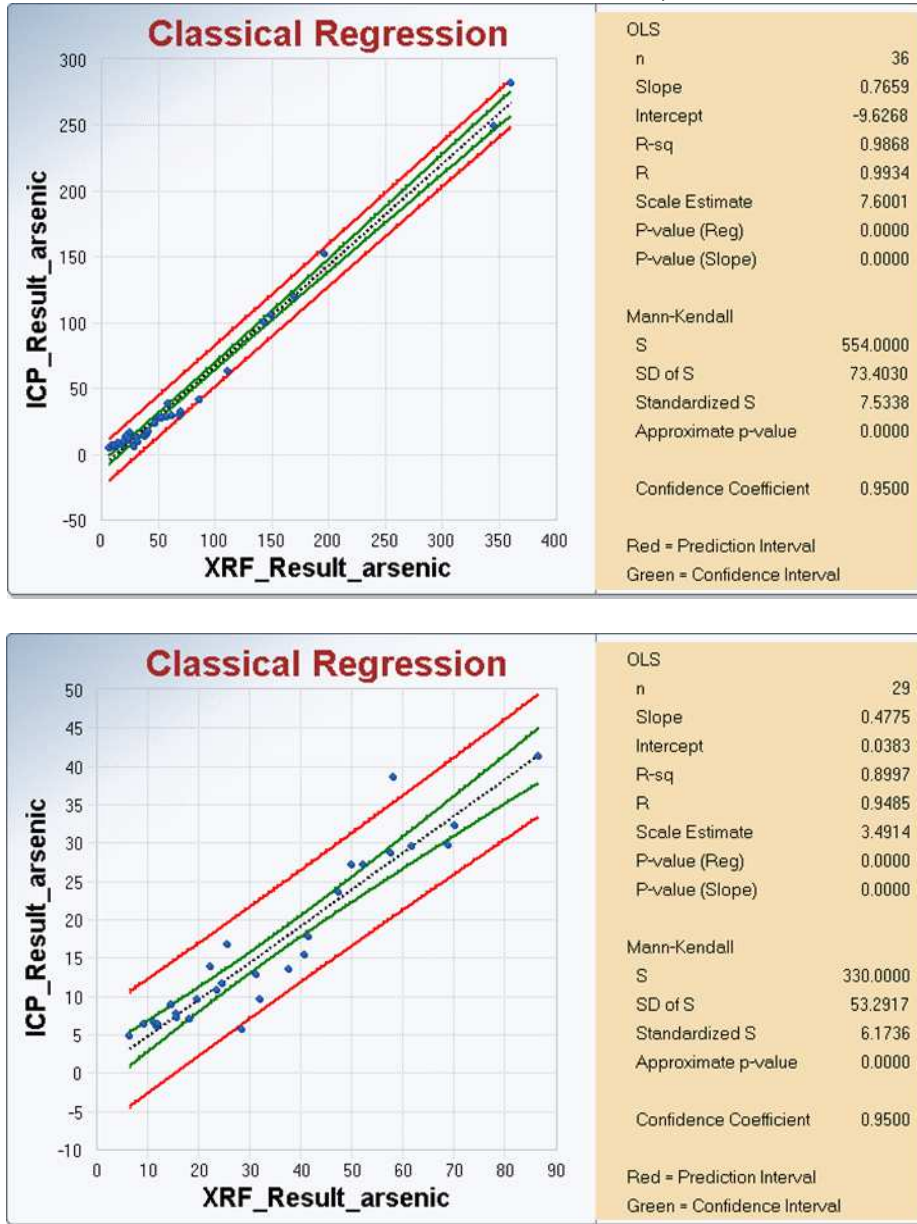
**FIGURE 6-3**  
**NORMAL Q-Q PLOT AND WSR TEST RESULTS FOR ARSENIC, FROM PROUCL 5.0**



XRF-ICP (arsenic)	
<b>One Sample Wilcoxon Signed Rank Test</b>	
<b>Raw Statistics</b>	
Number of Valid Observations	36
Number of Distinct Observations	36
Minimum	147
Maximum	97
Mean	25.72
Median	22.8
SD	2117
SE of Mean	3.528
Number Above Action Level	36
Number Equal Action Level	0
Number Below Action Level	0
T-plus	666
T-minus	0
<b>H0: Sample Mean/Median = 0</b>	
Large Sample z-Test Statistic	5.224
Lower Critical Value (0.025)	-1.96
Upper Critical Value (0.975)	1.96
P-Value	1.75E-07
<b>Conclusion with Alpha = 0.05</b>	
<b>Reject H0, Conclude Mean/Median &lt;&gt; 0</b>	
<b>P-Value &lt; Alpha (0.05)</b>	

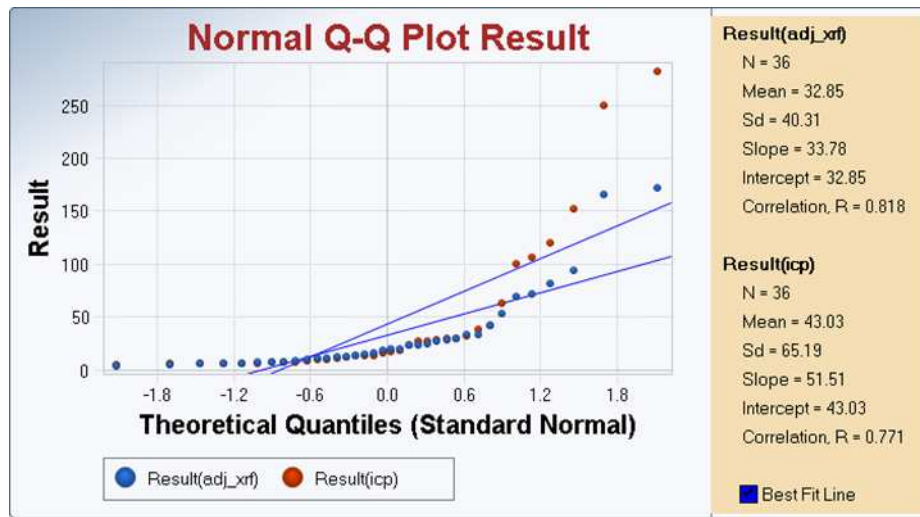
FIGURE 6-4

LINEAR REGRESSION RESULTS FOR ARSENIC, FROM PROUCL 5.0



(Top, all data; Bottom, data below 90 mg/kg)

**FIGURE 6-5**  
**NORMAL Q-Q PLOTS AND WSR TEST RESULTS FOR ADJUSTED ARSENIC, FROM PROUCL 5.0**



Adj_XRF-ICP (arsenic)	Adj_XRF-ICP (arsenic)
<b>One Sample Wilcoxon Signed Rank Test</b>	<b>One Sample Wilcoxon Signed Rank Test</b>
<b>Raw Statistics</b>	<b>Raw Statistics</b>
Number of Valid Observations: 29	Number of Valid Observations: 36
Number of Distinct Observations: 29	Number of Distinct Observations: 36
Minimum: -10.6	Minimum: -110
Maximum: 7.9	Maximum: 7.9
Mean: -0.00172	Mean: -10.18
Median: -0.15	Median: -0.715
SD: 3.424	SD: 25.57
SE of Mean: 0.636	SE of Mean: 4.262
Number Above Action Level: 13	Number Above Action Level: 13
Number Equal Action Level: 1	Number Equal Action Level: 1
Number Below Action Level: 15	Number Below Action Level: 22
T-plus: 196	T-plus: 196
T-minus: 210	T-minus: 434
<b>H0: Sample Mean/Median = 0</b>	<b>H0: Sample Mean/Median = 0</b>
Large Sample z-Test Statistic: 0.478	Large Sample z-Test Statistic: 2.226
Lower Critical Value(0.025): -1.96	Lower Critical Value(0.025): -1.96
Upper Critical Value(0.975): 1.96	Upper Critical Value(0.975): 1.96
P-Value: 0.633	P-Value: 0.0254
<b>Conclusion with Alpha = 0.05</b>	<b>Conclusion with Alpha = 0.05</b>
<b>Do Not Reject H0, Conclude Mean/Median = 0</b>	<b>Reject H0, Conclude Mean/Median &lt;&gt; 0</b>
<b>P-Value &gt; Alpha (0.05)</b>	<b>P-Value &lt; Alpha (0.05)</b>

FIGURE 6-6

LINEAR REGRESSION RESULTS FOR ADJUSTED ARSENIC, FROM PROUCL 5.0

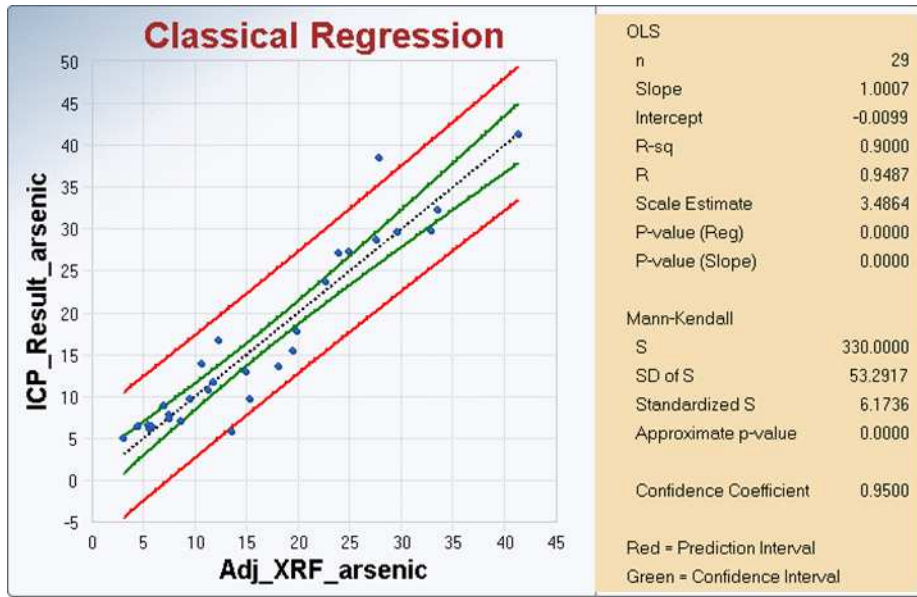
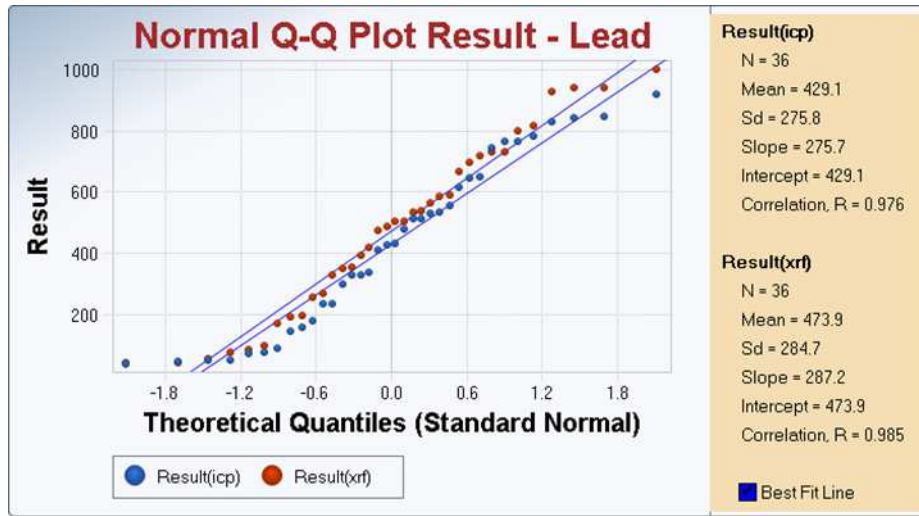


FIGURE 6-7

NORMAL Q-Q PLOT AND WSR TEST RESULTS FOR LEAD, FROM PROUCL 5.0



XRF-ICP (lead)	
<b>One Sample Wilcoxon Signed Rank Test</b>	
<b>Raw Statistics</b>	
Number of Valid Observations	36
Number of Distinct Observations	33
Minimum	-69
Maximum	429.3
Mean	44.79
Median	29.5
SD	75.91
SE of Mean	12.65
Number Above Action Level	31
Number Equal Action Level	0
Number Below Action Level	5
T-plus	613.5
T-minus	52.5
<b>H0: Sample Mean/Median = 0</b>	
Large Sample z-Test Statistic	4.399
Lower Critical Value (0.025)	-1.96
Upper Critical Value (0.975)	1.96
P-Value	1.09E-05
<b>Conclusion with Alpha = 0.05</b>	
<b>Reject H0, Conclude Mean/Median &lt;&gt; 0</b>	
<b>P-Value &lt; Alpha (0.05)</b>	

FIGURE 6-8

LINEAR REGRESSION RESULTS FOR LEAD, FROM PROUCL 5.0

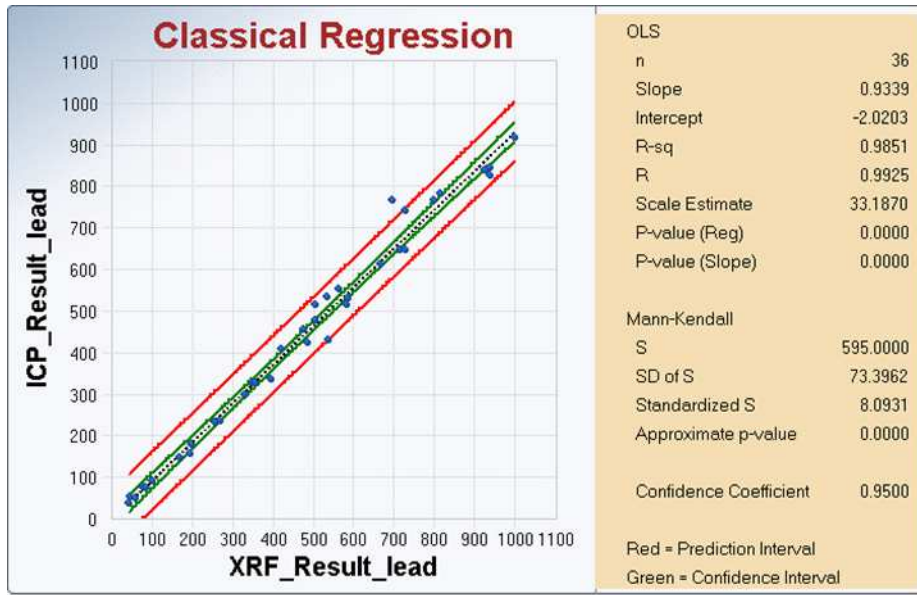
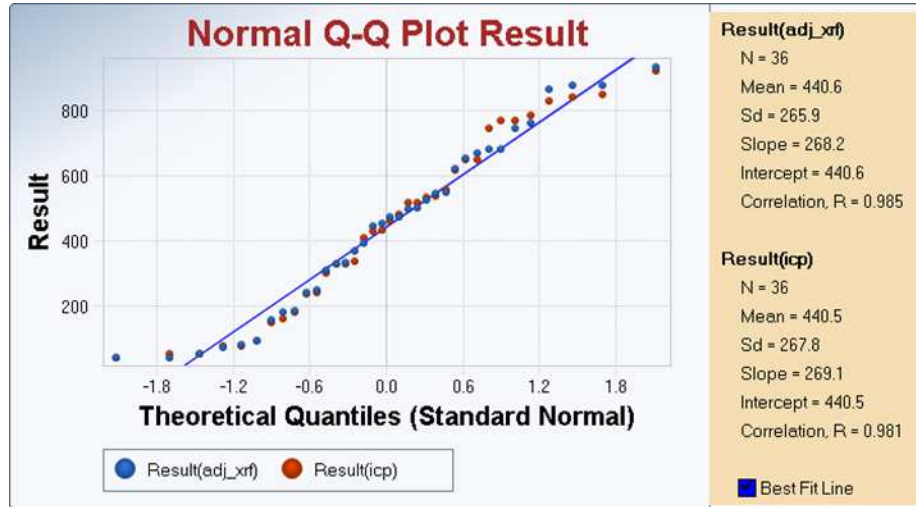


FIGURE 6-9

NORMAL Q-Q PLOTS AND WSR TEST RESULTS FOR ADJUSTED LEAD, FROM PROUCL 5.0



Adj_XRF-ICP (lead)	
<b>One Sample Wilcoxon Signed Rank Test</b>	
<b>Raw Statistics</b>	
Number of Valid Observations	36
Number of Distinct Observations	34
Minimum	-17
Maximum	69
Mean	0.0528
Median	3
SD	32.64
SE of Mean	5.44
Number Above Action Level	23
Number Equal Action Level	0
Number Below Action Level	13
T-plus	384.5
T-minus	2815
<b>H0: Sample Mean/Median = 0</b>	
Large Sample z-Test Statistic	0.801
Lower Critical Value (0.025)	-1.96
Upper Critical Value (0.975)	1.96
P-Value	0.423
<b>Conclusion with Alpha = 0.05</b>	
Do Not Reject H0, Conclude Mean/Median = 0	
P-Value > Alpha (0.05)	



FIGURE 6-10

LINEAR REGRESSION RESULTS FOR ADJUSTED LEAD, FROM PROUCL 5.0

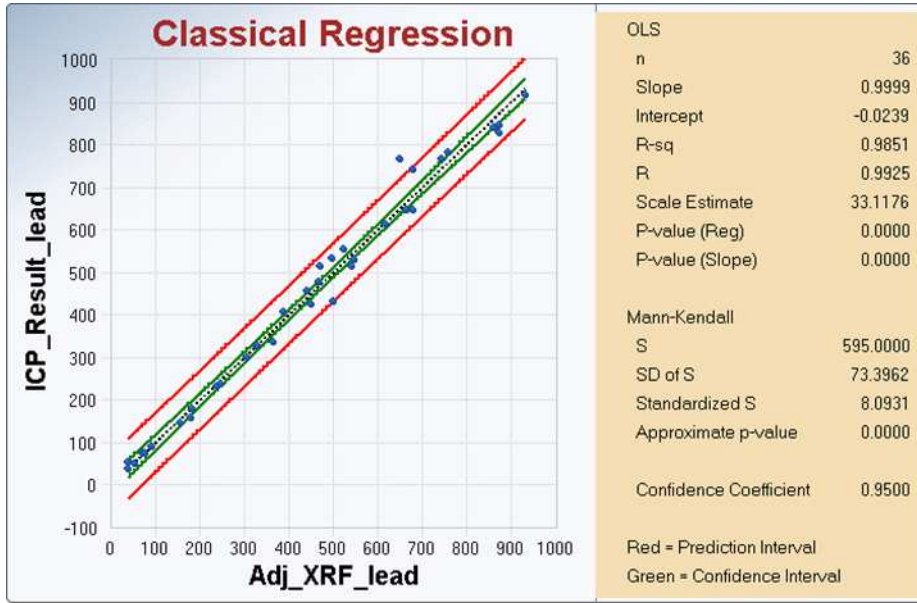
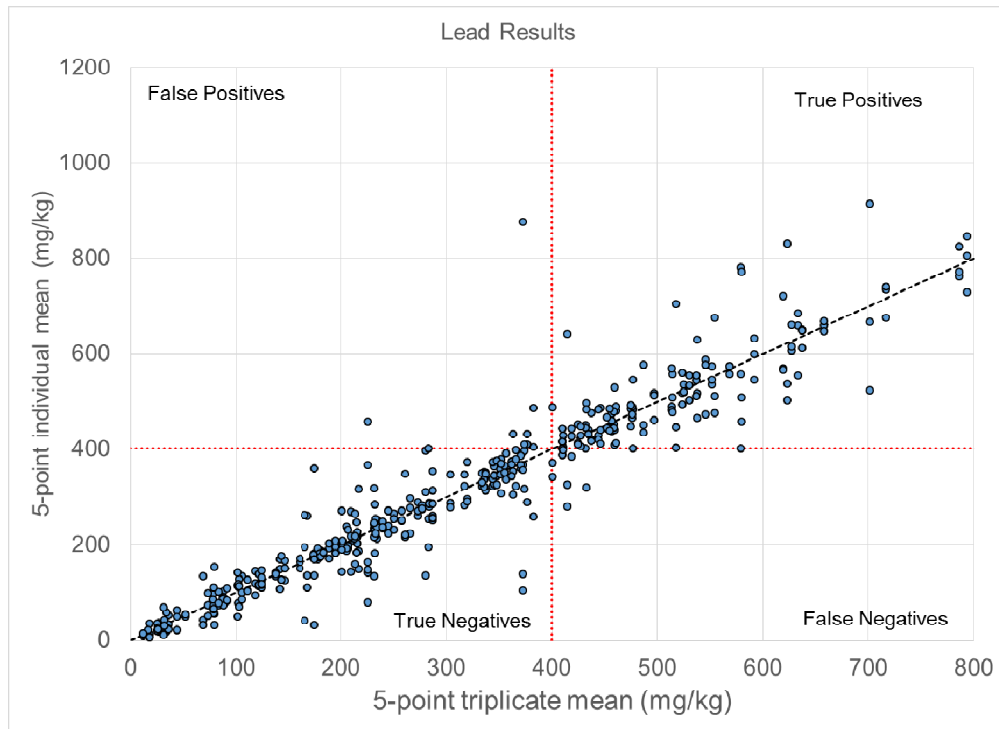
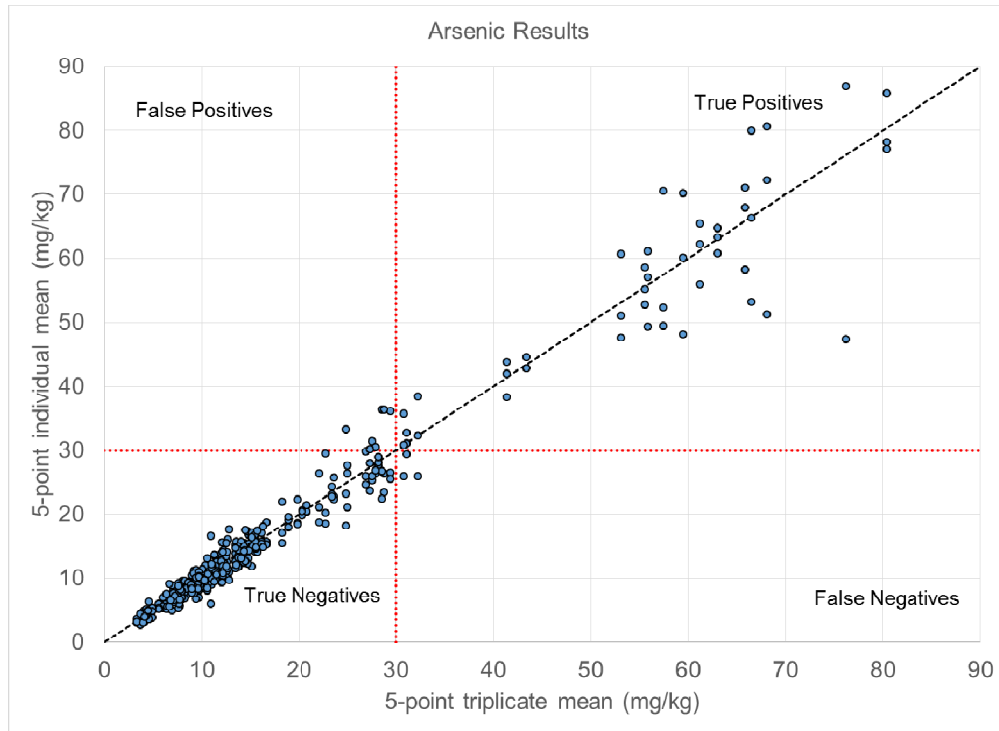


FIGURE 6-11

ARSENIC AND LEAD NEGATIVE AND POSITIVE RESULT CHARTS



## 7.0 SUMMARY AND CONCLUSIONS

Based on the discussion presented in this DMA DSR, the following conclusions can be identified and used to implement the RI project for OU1 for Colorado Smelter:

- The field sampling equipment and sampling methodologies identified in the DMA QAPP and employed during the DMA are adequate to provide samples of sufficient quality for proper characterization of DUs on the residential properties and the slag/contaminated soil areas.
- The laboratory preparation and analysis equipment and XRF analysis methodologies identified in the DMA QAPP and employed during the DMA are adequate to provide data of sufficient quality for decision making.
- Third party verification and validation of both XRF results and ICP laboratory results indicate that all data collected for the DMA project are valid and useable for decision making purposes.
- Statistical evaluation of the XRF results and laboratory ICP results evaluated for the DMA indicates that the XRF appears to provide defensible data for arsenic and lead for soil samples from the Colorado Smelter site. However, a subset of the samples analyzed by XRF will also be analyzed by a commercial laboratory to continue to monitor the comparability of XRF and ICP results, for quality assurance and data comparability purposes and to provide data for other metals for the HHRA.
- Statistical evaluation of the 30-point incremental data verses the 5-point composite data indicates that the 5-point composite sampling methodology provides adequate information to support project decisions for a particular DU.
- Statistical evaluation of the triplicate results has concluded that it is not necessary to collect triplicate samples to provide defensible data for a particular DU and to meet RI goals for decision error rates. Triplicate samples are planned to be collected at 5% of DUs sampled during the RI to provide a quantitative measure of variability and to continue to monitor decision error rates and the performance of the sampling design .
- Evaluation of the soil results from the various depth intervals indicates that contamination above DMA screening levels is present at all four depth ranges investigated in the DMA study. Therefore, all four depth intervals should continue to be investigated in the RI sampling project.

## 8.0 REFERENCES

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