PNNL-23868

100-OL-1 Operable Unit Pilot Study:

XRF Evaluation of Select Pre-Hanford Orchards

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Prior to the acquisition of land by the U.S. Department of War in February 1943 and the creation of the Hanford Site, the land along the Columbia River was home to over 1000 people. Farming and orchard operations by both homesteaders and commercial organizations were prevalent. Orchard activities and the associated application of lead arsenate pesticide ceased in 1943, when residents were moved from the Hanford Site at the beginning of the Manhattan Project. Today, the residues from historical application of lead arsenate pesticide persist in some locations on the Hanford Site.

In 2012, the U.S. Department of Energy, U.S. Environmental Protection Agency, and Washington State Department of Ecology established the 100-OL-1 Operable Unit (OU) through the Hanford Federal Facility Agreement and Consent Order, known as the Tri-Party Agreement. 100-OL-1 OU addresses the lead and arsenic contamination from pesticide use in the orchard areas prior to the Manhattan Project. The pre-Hanford orchard lands identified as the 100-OL-1 OU are located south of the Columbia River and east of the present-day Vernita Bridge, and extend southeast to the former Hanford townsite. The discontinuous orchard lands within 100-OL-1 OU are approximately 20 km^2 (5000 ac).

A pilot study was conducted to support the approval of the remedial investigation/feasibility study work plan to evaluate the 100-OL-1 OU. This pilot study evaluated the use of a field portable X-ray fluorescence (XRF) analyzer for evaluating lead and arsenic concentrations on the soil surface as an indicator of lead arsenate pesticide residues in the OU. The objectives of the pilot study included evaluating a field portable XRF analyzer as the analytical method for decision making, estimating the nature and extent of lead and arsenic in surface soils in four decision units, evaluating the results for the purpose of optimizing the sampling approach implemented in the remedial investigation, collecting information to improve the cost estimate, and planning the cultural resources review for sampling activities in the remedial investigation.

The results of the pilot study demonstrated that the field portable XRF analyzer performed to the quality assurance criteria for comparability to laboratory-based methods. Additional advantages of the XRF analyzer are minimal disturbance to the soil and little turn-around time for the results, which allows for additional investigation in a timely fashion and little additional cost. Based on the results of the pilot study, the recommendations for the revision of the work plan are to

- characterize the surface soil using field portable XRF measurements with confirmatory inductively coupled plasma mass spectroscopy sampling for the remedial investigation
- establish decision units of similar defined areas
- establish a process for field investigation of soil concentrations exceeding the screening criteria at the border of the 100-OL-1 OU
- define data quality objectives for the work plan using the results of the pilot study and refining the sampling approach for the remedial investigation.

Acknowledgments

The authors would like to thank those who contributed to the plans and execution of this study. We appreciate the support and guidance from many organizations: from the U.S. Department of Energy, John Sands, James Hansen, Douglas Hildebrand, John Neath, and Briant Charboneau; from the U.S. Environmental Protection Agency, Christopher Guzzetti and Dennis Faulk; from the Washington State Department of Ecology, Kim Welsch, Arthur Kapell, Nina Menard, Beth Rochette, Alicia Boyd, Damon Delistraty, and Jerel Yokel; from Hanford Site contractors, Jason Capron, Joan Kessner, Richard Weiss, Mary Hartman, Landon Collom, Douglas Fenske, Wendy Thompson, Jeffrey Lerch, David St. John, David Shea, April Johnson, Jennifer Mendez, Keith Mendez, James Sharpe, Aaron Fergusson, and Justin Wilde.

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Acronyms and Abbreviations

ASTM	American Society for Testing and Materials
DOE	U.S. Department of Energy
DQA	data quality assurance
DQO	data quality objective
DVZ-AFRI	Deep Vadose Zone Applied Field Research Initiative
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
FS	feasibility study
GPS	Global Positioning System
HASQARD	Hanford Analytical Services Quality Assurance Requirements Document
HEIS	Hanford Environmental Information System
ICP-MS	inductively coupled plasma mass spectroscopy
LCS	laboratory control samples
MB	method blank
MDL	method detection limit
MS	matrix spikes
MTCA	Model Toxics Control Act
ND	not detected
NHPA	National Historic Preservation Act
OU	operable unit
PD	percent difference
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
RI	remedial investigation
RL	U.S. Department of Energy, Richland Operations Office
RPD	relative percent deviation
RSD	relative standard deviation
SAP	sampling and analysis plan
SRM	standard reference material
TPA	Tri-Party Agreement
VSP	Visual Sample Plan
WIDS	Waste Information Data System
XRF	X-ray fluorescence

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1.0 Introduction

Prior to the acquisition of land by the U.S. Department of War in February 1943 and the creation of the Hanford Site, the land along the Columbia River was home to over 1000 people. Farming and orchard operations by both homesteaders and commercial organizations were prevalent. Orchard activities and the associated application of lead arsenate pesticide ceased in 1943, when residents were moved from the Hanford Site at the beginning of the Manhattan Project. Today, the residues from historical application of lead arsenate pesticide persist in some locations on the Hanford Site.

In 2012, the U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (EPA), and the Washington State Department of Ecology (Ecology) established the 100-OL-1 Operable Unit (OU) through the Hanford Federal Facility Agreement and Consent Order, known as the Tri-Party Agreement (TPA 2012). The pre-Hanford orchard lands identified as the 100-OL-1 OU are located south of the Columbia River and east of the present-day Vernita Bridge, and extend southeast to the former Hanford townsite (Figure 1.1). The discontinuous orchard lands within 100-OL-1 OU are approximately 20 km^2 (5000 ac).

A pilot study was conducted to support the approval of the remedial investigation/feasibility study (RI/FS) work plan to evaluate the 100-OL-1 OU. This pilot study evaluated the use of a field portable X-ray fluorescence (XRF) analyzer for evaluating lead and arsenic concentrations on the soil surface as an indicator of lead arsenate pesticide residues in the OU. The objectives of the pilot study included:

- evaluating field portable XRF analyzer as an analytical method for decision making
- determining the nature and extent of lead and arsenic in surface soils in selected decision units within 100-OL-1 OU
- evaluating the results for the purpose of optimizing the sampling approach implemented in the remedial investigation:
  - estimating the spatial variability
  - evaluating the appropriate size for decision units within the OU
  - optimizing decision unit boundaries for characterization
- improving the cost estimate and planning the cultural resources review for sampling activities in the remedial investigation.

For the pilot study, the soil surface of four decision units was analyzed in situ for lead and arsenic concentrations (DOE-RL 2014). The screening criteria for the surface soil were 250 mg/kg lead and 20 mg/kg arsenic. The decision units varied in size, previous agriculture activities, and level of soil disturbances since 1943. The in situ analysis was conducted using a hand-held XRF, with confirmatory results obtained via inductively coupled plasma mass spectroscopy (ICP-MS) analyses of soils collected at two of the decision units. Results from this study will be used to revise the initial conceptual site model and provide recommendations for sampling approaches. The RI/FS work plan for the 100-OL-1 OU will include the results and recommendations from this pilot study.

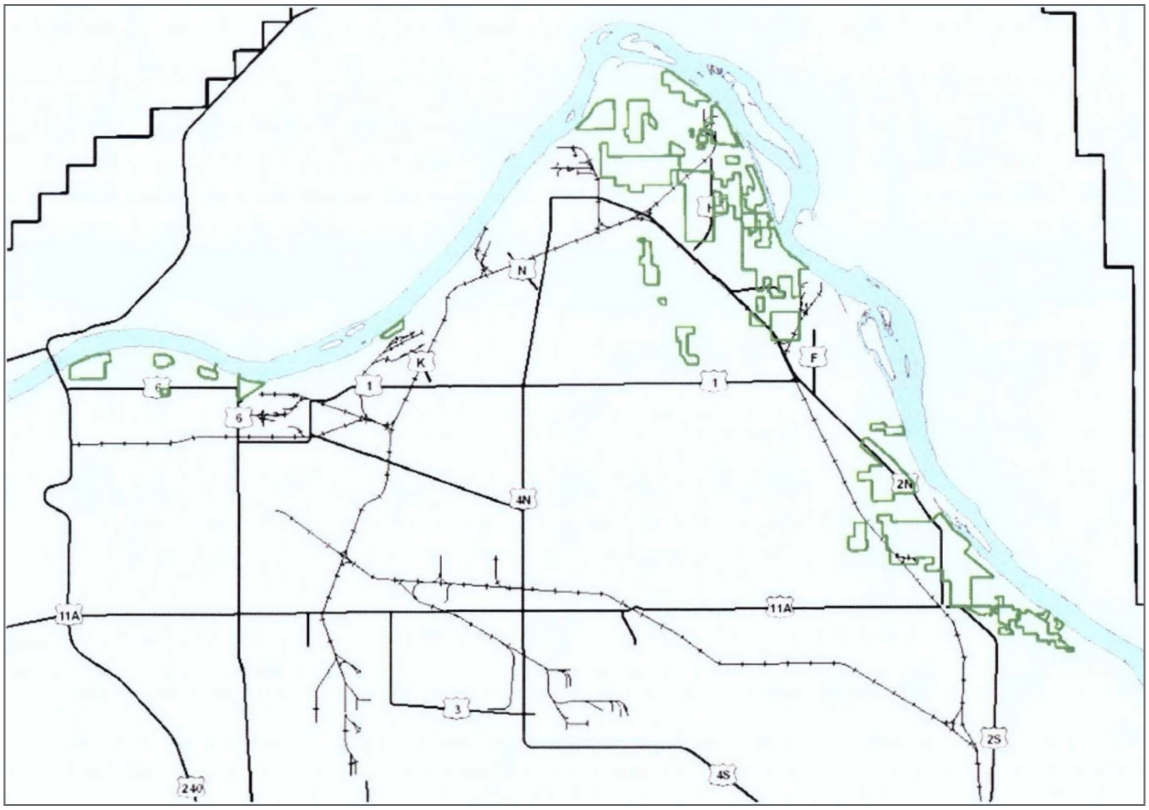


Figure 1.1. Section of the Hanford Site showing former orchard lands within the green boundaries (TPA 2012)

2.0 Methods

This section discusses the methods used in the pilot study. The data needs for this project were reported in the *100-OL-1 Operable Unit Field Portable X-Ray Fluorescence (XRF) Analyzer Pilot Study Plan* (DOE-RL 2014). The operation of the field-portable XRF analyzer, collection of soil, and confirmatory analyses by ICP-MS are discussed. In addition, this section describes the sampling approach and special study to address spatial variability in the field. Appendix A provides the detailed sampling and analysis plan and quality assurance project plan (QAPP).

2.1 Decision Unit Selection

Four decision units within the 100-OL-1 OU were selected for inclusion in the pilot study, as described in the *100-OL-1 Operable Unit Field Portable X-Ray Fluorescence (XRF) Analyzer Pilot Study Plan* (DOE-RL 2014). Several criteria were used to identify the decision units selected for analysis. Decision units were identified where previous Hanford activities had resulted in a portion of the decision unit being cleared by the Hanford Site Cultural Resources Program. Areas that had previously been cleared for soil sampling through the Section 106 review were identified in the process for decision units OL-14 and IU6-4. Decision unit size was also considered; at least two needed to be of similar size, while at least one needed to be substantially larger. Additional considerations were the visible presence of trees in 1943 aerial photography and known soil disturbances at the site (either pre- or post-1943). Finally, decision units with previously measured lead and/or arsenic concentrations in surface soil were preferable. Ultimately, the four decision units chosen were OL-14, a portion of OL-32, a portion of FR2-1, and IU6-4 (DOE-RL 2014). Table 2.1 summarizes the characteristics of the four decision units. Figure 2.1 shows the four decision units across the 100-OL-1 OU.

Table 2.1. Summary of characteristics of four decision units

Decision Unit ID	Area of Decision Unit km^2	Area of Decision Unit Acres	Presence of Trees in 1943 Aerial Imagery?	Evidence of Soil Disturbance Since 1943?	WIDS[a] Site within Decision Unit Boundaries?	Previously Sampled?
OL-14	0.19	46.4	Yes	Yes	Yes	Yes
OL-32[b]	0.12	28.7	Yes	No	No	Yes[c]
FR2-1[b]	0.19	48.0	No	Yes	Yes	Yes
IU6-4	1.01	250.6	Yes	Yes	Yes	Yes

(a) Waste Information Data System
(b) Decision unit is a portion of the area defined with the same name in the draft work plan.
(c) Yokel and Delistraty 2003; Delistraty and Yokel 2011

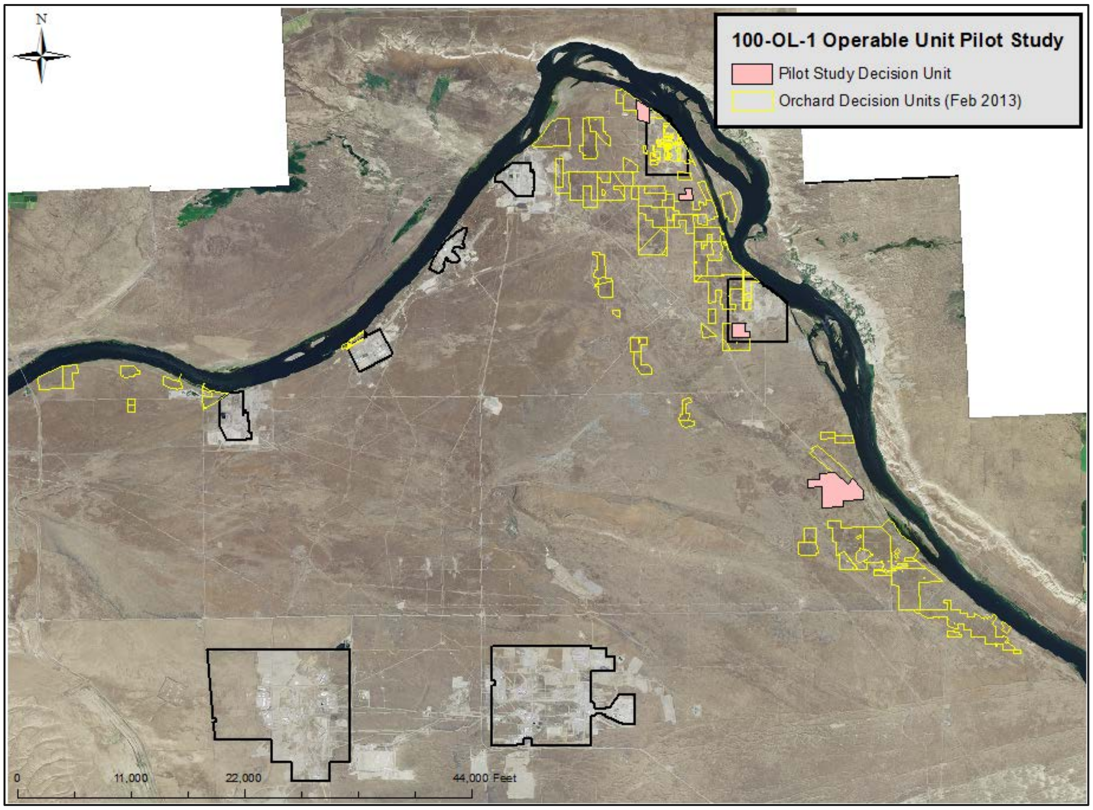


Figure 2.1. Pilot study decision units within the 100-OL-1 OU

2.2 Sampling Approach

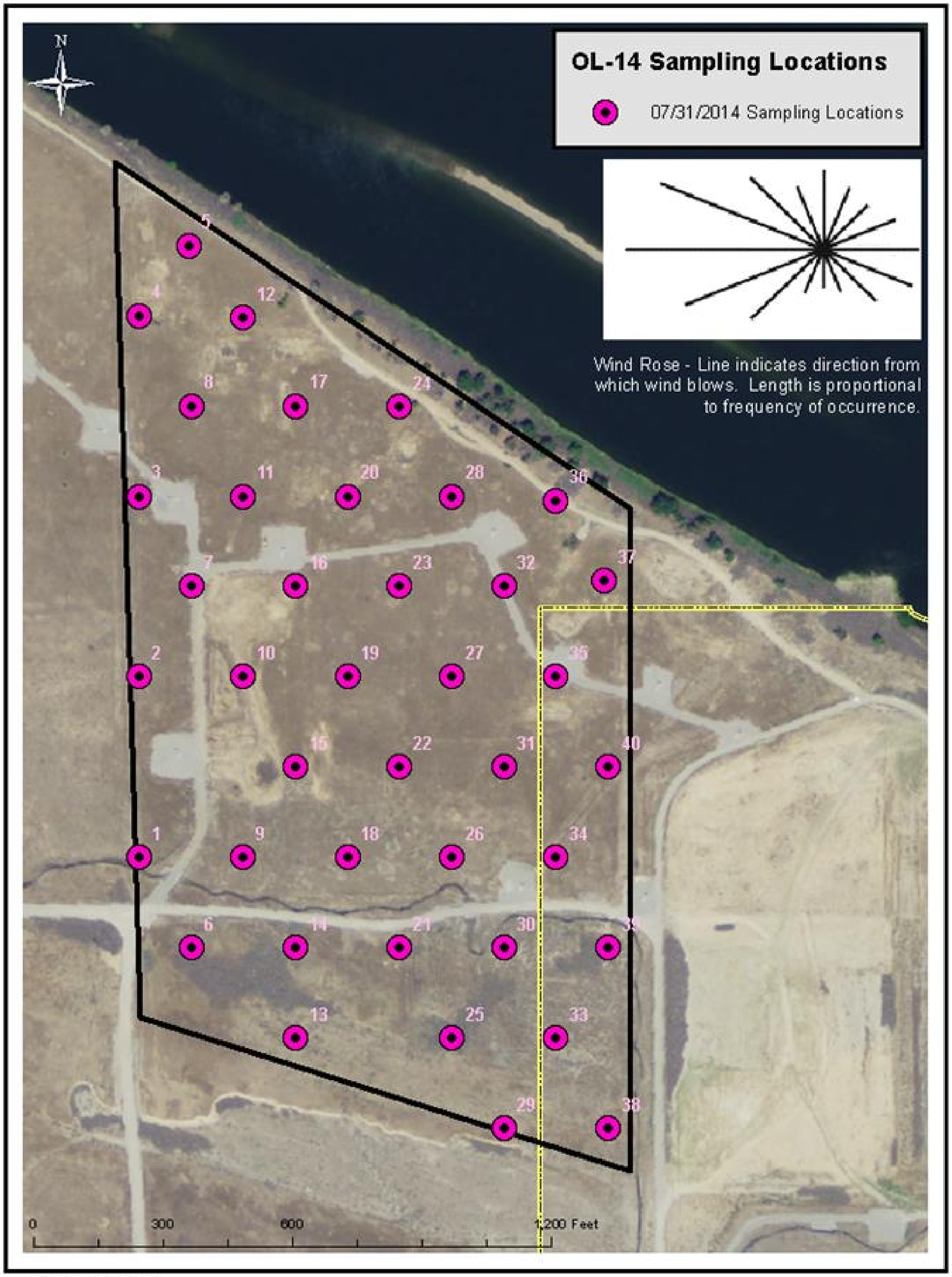
For sampling of each decision unit, 40 sample points were selected (DOE-RL 2014). These points were selected using a software package (Visual Sample Plan [VSP]; Matzke et al. 2010). The 40 locations were spread uniformly across each decision unit in a random-start, systematic-grid-sampling design pattern with a triangular grid. Some regions were excluded based on the location of soil-disturbing activities identified in the Waste Information Data System, e.g., in the northeastern quadrant of FR2-1.

Using a systematic grid with a random start ensures uniform spatial coverage while still meeting the requirements of random locations. While a fixed number of sampling locations were chosen for each decision unit, the number was not arbitrary. VSP was first used to estimate the number of sampling locations necessary to determine, with 99% confidence, that a decision unit is “dirty” if the true mean exceeds the screening criteria (250 and 20 mg/kg for lead and arsenic, respectively), with the assumptions that the data would not be normally distributed and the relative standard deviation (RSD) was 100%. With these parameters, VSP identified 28 samples as being necessary. To evaluate the objectives for the pilot study concerning field variability, the number of sample locations was increased to 40 samples per decision unit.

While it was important to have pre-determined sampling locations, it was recognized that moving the collection location would be necessary in the field to avoid roads, well pads, and any impediments that would make a sample not representative of former orchard soil (DOE-RL 2014). When a sample had to be relocated, the new coordinates were determined using a handheld Global Positioning System (GPS) device (Montana GPS, Garmin, Olathe, KS) and recorded on the field data sheet.

Figure 2.2 through Figure 2.5 show the sample locations for each decision unit in the pilot study. The coordinates for all samples collected are included in Appendix C. For each sample, the XRF was placed on the ground as close as possible to the pre-determined location, and three replicate measurements were taken without moving the analyzer using the in situ method for sample analysis.

Note: Hanford 2013 Imagery



1 inch = 300 feet

Figure 2.2. OL-14 decision unit sample locations for the pilot study

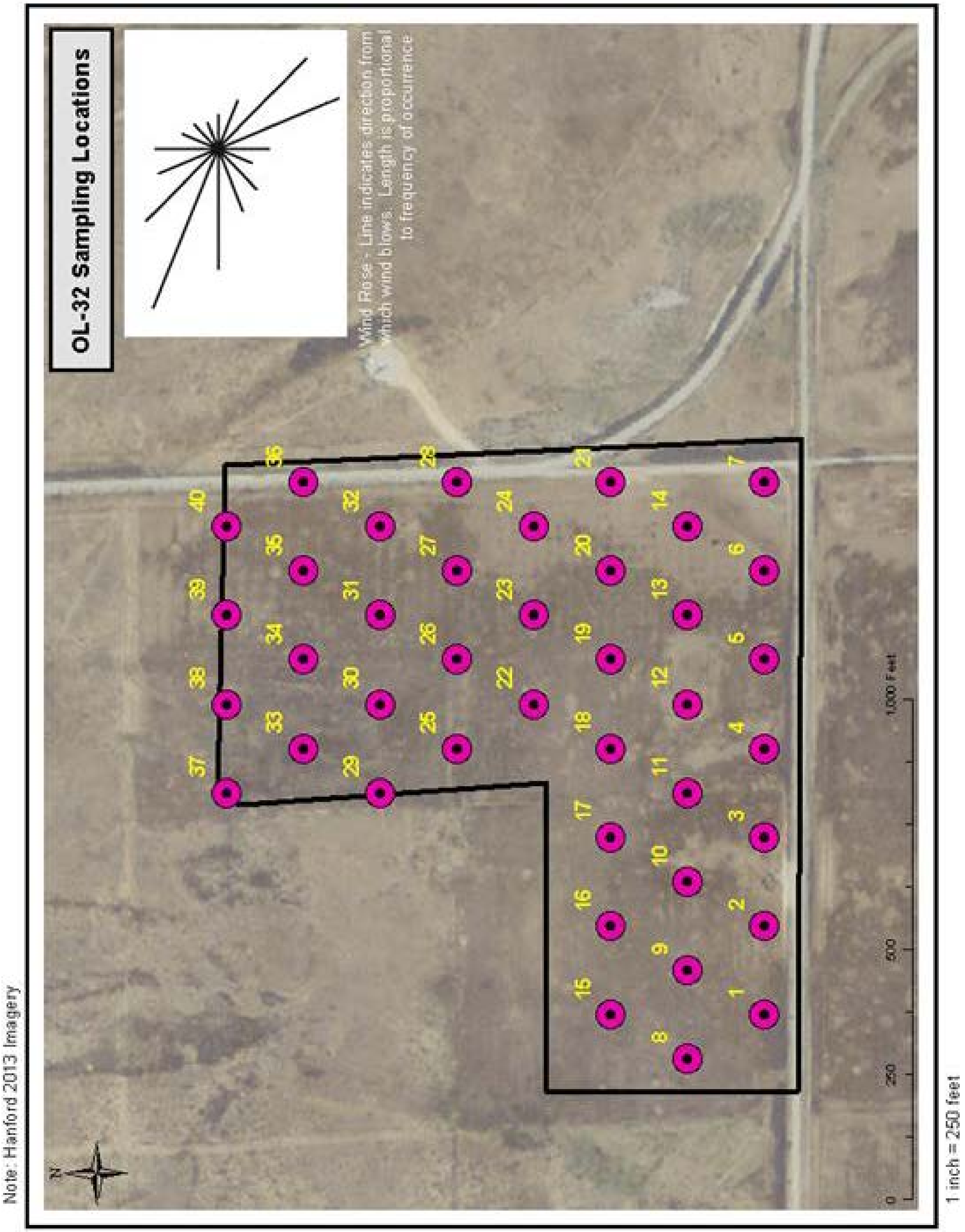


Figure 2.3. OL-32 decision unit sample locations for the pilot study

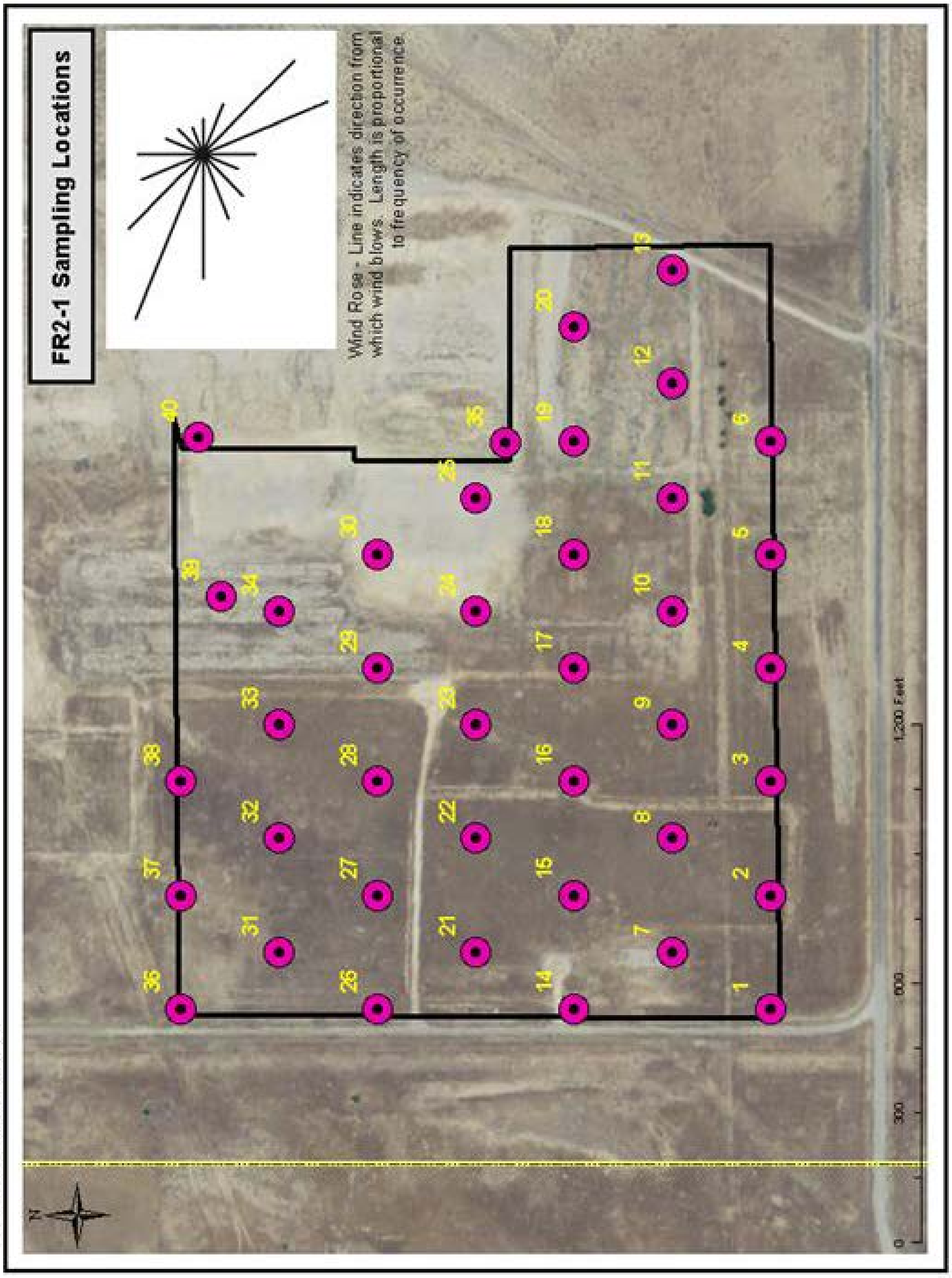
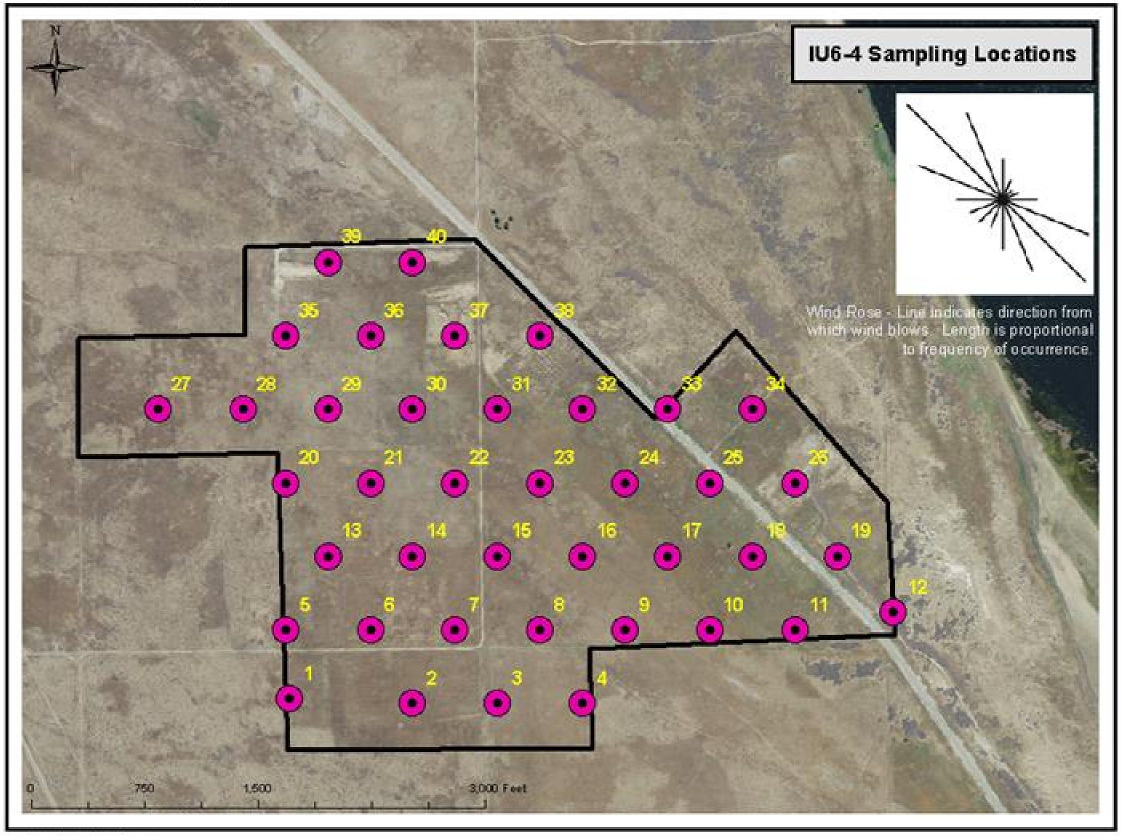


Figure 2.4. FR2-1 decision unit sample locations for the pilot study

Note: Hanford 2013 Imagery



1 inch = 750 feet

Figure 2.5. IU6-4 decision unit sample locations for the pilot study

2.3 XRF Operation

For this study, a handheld, field-portable XRF analyzer was the primary analytical tool (Figure 2.6). The XRF analyzer (Niton XL3t 950, Thermo Scientific, Tewksbury, MA) was selected based on improved software algorithms capable of accurately measuring arsenic concentrations in the presence of lead. The XRF was operated according to the manufacturer's procedures. According to the procedures, there are two ways to analyze a sample: by simply holding down the trigger on the instrument, or through a computer interface using manufacturer software (Thermo Scientific Niton XL3 Series Software, Version 8.4A). For in situ analysis, the hand-held option was used (Figure 2.6A). For intrusive analysis, there was the option to use a computer interface with the XRF. "Intrusive analysis" is termed by EPA as a soil sample collected from the field, placed in a sample cup, and then analyzed with the XRF (EPA 2007). The computer interface option allowed hands-free operation of the XRF, eliminating movement as a potential source of error (Figure 2.6B). Intrusive analyses were performed in a laboratory and in the field using previously collected samples packed into 33 mm (1.3 in.) sample cups (PN 187-466, Thermo Scientific, Tewksbury, MA) with polypropylene film (PN 187-461, Thermo Scientific, Tewksbury, MA). In both configurations, the XRF analyzer recorded the data in the same manner. Data were downloaded from the instrument as a Microsoft Excel file (Microsoft Excel 2010). Data files included sequential sample number, date/time stamp, count duration, and the measured concentrations plus 2σ counting errors for 18 metals (including lead and arsenic).

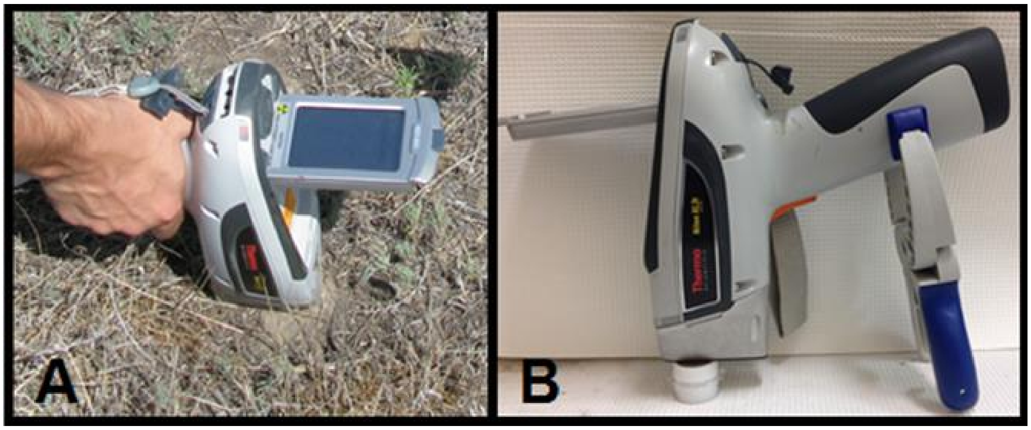


Figure 2.6. XRF instrument used (A) in the field for in situ analysis and (B) in the laboratory for intrusive analysis

For in situ analysis, a 60-second count time for the XRF analyzer was used. This count time was determined necessary for providing adequate detection and precision of arsenic concentrations (section 3.1.2). In the field, the manufacturer's procedure for in situ soil surface analysis was followed (Thermo Scientific XRF Resource Guide 8.2.0). This procedure stipulated that the measurement location be cleared of any significant vegetation, such as large clumps of grass, and scuffed or otherwise leveled to provide a flat surface on which to place the instrument window (EPA SESD Procedure 107-R2 [EPA 2011] and EPA Method 6200 [EPA 2007]). Individual acid washed (10% nitric acid wash) spatulas (24 cm (9.45 in.) long; McMaster-Carr, Sante Fe Springs, CA) were used to scrape and level the soil at each measurement location, as necessary.

Intrusive analysis required the collection of soil in the field, followed by preparation before the analysis. Sample preparation first involved the removal of large non-soil particles (e.g., rocks and vegetation). The sample was spread out on a clean sheet of paper (Whatman Benchkote 2300-594), and non-soil particles were removed manually. Sample homogenization was then done by placing 150 to 200 g of soil on parchment paper (45 by 45 cm [17 by 17 in.]), alternately lifting corners, and rolling the soil onto itself toward the opposite corner 20 times (EPA Method 6200). Each sample was returned to the original container once homogenization was complete. After homogenization, samples could be prepared for ICP-MS analysis (see section 2.4) or prepared for intrusive XRF analysis. Intrusive XRF analysis involved placing a soil sample into a plastic sample cup with a thin polypropylene film in the lid. Sample cups were prepared according to the manufacturer's procedure (Thermo Scientific XRF Resource Guide 8.2.0). It is important that the cups be filled completely and tightly packed, with no air gaps between the sample and the polypropylene window.

2.4 ICP-MS

EPA Method 6200 requires confirmatory analysis of samples measured by the XRF analyzer. Soil was collected on June 13 and July 17, 2014, during the pilot study, and analyzed using ICP-MS as well as intrusively with XRF. Aliquots of the homogenized soil (15 to 20 g) were placed in pre-cleaned, pre-tarred, 50 mL polypropylene sample bottles and sent to the Pacific Northwest National Laboratory (PNNL) Marine Sciences Laboratory (Sequim, Washington) for ICP-MS analyses.

The soil samples were digested using a procedure based on a modification of EPA Method 3050B (EPA 1996a). An approximately 400 mg (dry weight) aliquot of each sample was combined with a 3:1 ratio of hydrochloric and nitric acids (aqua regia) in a Teflon digestion vessel and heated in an oven at 130°C (±10°C) for a minimum of 8 hours. After heating and cooling, deionized water was added to the sediment digestate to achieve analysis volume. Digested samples were analyzed for arsenic and lead using ICP-MS. This procedure is based on two methods modified and adapted for analysis of low-level sediment and tissue samples: EPA Methods 1638 and 200.8 (EPA 1996b and 1994, respectively).

The samples were analyzed within 10 days of receipt. Analytical results were reported with respect to the annual sediment method detection limit (MDL) study derived using seven replicates of quartz sand (0.006 mg/kg dry weight lead; 0.3 mg/kg dry weight arsenic). Two method blanks were analyzed with this batch of samples. Metal concentrations above the reporting limits (0.02 mg/kg dry weight lead; 1.0 mg/kg dry weight arsenic) were not detected in the method blank. Two laboratory control samples (LCS) were analyzed with the batches of samples. The LCS recoveries were within the quality control (QC) acceptance criterion of ±25% recovery for all metals. Two soil samples were selected for matrix spikes (MS). The MS recoveries were within the QC acceptance criterion of ±25% recovery for all metals. Precision for this set of samples was evaluated by the analysis of laboratory duplicates and expressed as the relative percent deviation (RPD) of replicate results. The RPD values for the duplicate samples were within the QC criterion of ≤25% RSD for all metals. The standard reference material (SRM) accuracy was expressed as the percent difference (PD) between the measured and certified or reference value for the SRM. Recovery of a particular analyte exceeded the QC criterion if the PD exceeded 20%. The SRM PACS-3 *Marine Sediment Certified Reference Material for Trace Metals and Other Constituents* was analyzed with these samples (National Research Council Canada, Ottawa, Ontario, Canada). The percent differences were within the QC acceptance criterion of PD ± 20%.

2.5 Site-Specific Reference Material

Prior to using the XRF instrument for in situ soil analysis, it was necessary to conduct confirmation studies with site-specific soil. Prior to soil collection, Mission Support Alliance performed cultural and ecological resources clearance (Appendix B). The XRF instrument was used in a screening capacity to select locations for soil collection within two separate decision units. In total, seven soil samples were collected on June 13, 2014: four from decision unit OL-14 and three from decision unit IU6-4. The targeted concentrations were soils with lead and arsenic concentrations close to the screening criteria (250 mg/kg and 20 mg/kg, respectively), and then soils with concentrations both above and below the screening criteria. Samples were collected using a cleaned (10% nitric acid washed) 1.9 L polyethylene scoop. Several kilograms of surface soil (top 10 cm) were collected and placed into a pre-cleaned 2 L polyethylene jar. Each jar was labeled with a sample ID and the approximate soil concentrations. Additionally, the latitude and longitude of each sample collection location was measured (Montana GPS, Garmin, Olathe KS) and recorded on each sample jar.

The site-specific reference material was brought to the laboratory and prepared for analysis (section 2.3). Subsamples of each site-specific sample were packed into XRF sample cups for intrusive XRF analysis, and packed into pre-cleaned polypropylene bottles for ICP-MS analysis (section 2.4). The results of the site-specific reference analysis and XRF comparison are presented in the quality assurance (QA) section (section 3.1.4). Additionally, some of these site-specific reference samples were used in the daily precision checks conducted prior to in situ analysis (section 3.1.3).

2.6 Spatial Variability

One issue with the XRF is that the volume of soil actually analyzed is on the order of a few milliliters. However, the result for that small volume is assumed to represent a much large volume of soil. Therefore, it was necessary to determine if the volume of soil analyzed by the XRF would be sufficiently representative of a larger area. To accomplish this, XRF was used to measure the lead and arsenic concentration along four transects normal to each other with measurements made at varying distances from a center point (0, 0.15, 0.3, 0.6, 1.2, 2.4, 3.8, and 4.9 m). Spatial variability was evaluated at two locations in OL-14 and one location in IU6-4. The central point at each location was selected to cover the range of anticipated lead and arsenic results in the region.

3.0 Quality Assurance

The PNNL QA Program is based on the requirements as defined in DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A, Quality Assurance Requirements (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.

- ASME NQA-1-2000, Part II, Subpart 2.7, Quality Assurance Requirements for Computer Software for Nuclear Facility Applications, including problem reporting and corrective action.

- ASME NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The procedures necessary to implement the requirements are documented through PNNL's "How Do I…? (HDI), a system for managing the delivery of laboratory-level policies, requirements, and procedures.

The *DVZ-AFRI Quality Assurance Plan* is the minimum applicable QA document for all Deep Vadose Zone Applied Field Research Initiative (DVZ-AFRI) projects. This QA plan also conforms to the QA requirements of DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, Subpart A, Quality Assurance Requirements. The DVZ-AFRI is subject to the *Price Anderson Amendments Act*.

The implementation of the DVZ-AFRI QA program is graded in accordance with NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The work for this report was performed under the technology level of Applied Research. Basic Research consists of research tasks that are conducted to acquire and disseminate new scientific knowledge. During basic research, maximum flexibility is desired in order to allow the researcher the necessary latitude to conduct the research.

Applied Research consists of research tasks that acquire data and documentation necessary to ensure satisfactory reproducibility of results. The emphasis during this stage of a research task is on achieving adequate documentation and controls necessary to reproduce results.

Development Work consists of research tasks moving toward technology commercialization. These tasks still require a degree of flexibility, and a degree of uncertainty still exists in many cases. The role of quality on development work is to make sure that adequate controls exist to support movement into commercialization.

Research and Development Support Activities are those that are conventional and secondary to the advancement of knowledge or development of technology, but allow the primary purpose of the work to be accomplished credibly. An example of a support activity is controlling and maintaining documents and records. The level of quality for these activities is the same as for developmental work.

Within each technology level, the application process for QA controls is graded such that the level of analysis, extent of documentation, and degree of rigor of process control are applied commensurate with their significance, importance to safety, life-cycle state of a facility or work, or programmatic mission.

A QAPP was developed for the pilot study (Appendix A). This plan outlined the requirements necessary for ensuring that meaningful data was collected to meet the pilot study's objectives. The plan addressed instrument accuracy and precision, data documentation requirements, and other standard quality practices followed by project staff. The QA and QC needs for this project are reported in the *100-OL-1 Operable Unit Field Portable X-Ray Fluorescence (XRF) Analyzer Pilot Study Plan* (DOE-RL 2014). While XRF analyses are not specifically addressed in the *Hanford Analytical Services Quality Assurance Requirements Document* (HASQARD), the QAPP incorporated the relevant guidance for field analyses at the Hanford Site (DOE-RL 2007). This section presents results relevant to the discussions about the results and recommendations.

3.1 Instrument Quality Assurance Results

Guidelines for determining the accuracy and precision of the XRF instrument were developed prior to conducting the pilot study (DOE-RL 2014). Appendix C includes the raw data used to support the determination of the quality of the data for pilot study. This section summarizes results for the MDL, count time for XRF analyses, daily instrument checks, and confirmatory samples analyzed with XRF and ICP-MS.

3.1.1 Determination of XRF Method Detection Limit

The MDL for the XRF analyzer was determined using site-specific reference material soil collected at OL-14. EPA Method 6200 calls for determining the lower limits of detection with spike recoveries of site-specific soil material or with certified reference material (EPA 2007), both of which are not representative of the soil at Hanford or weathered lead arsenate residues. EPA's procedure for determination of the MDL described in 40 CFR 136, Appendix B, was selected since site-specific reference material could be used.

A single sample (OL-14-L) was hand sieved and homogenized according to EPA Method 6200 (EPA 2007). The homogenized soil was then separated into seven sample cups, providing the necessary number of replicates to calculate the MDL according to 40 CFR 136, Appendix B. Following the procedure, the average concentration of the replicate analyses, the standard deviation of the replicates, and the Student's T-value for seven samples were determined. The MDL is the product of the Student's T-value and the standard deviation. It was recognized that the MDL calculated for lead would likely be biased high because this sample had lead concentrations slightly above the recommended range (1 to 5 times the MDL). However, Hanford background lead concentrations are more than 5 times the estimated MDL (10.2 mg/kg lead [DOE-RL 1993]), making it nearly impossible to use site-specific material and still meet this requirement. The results of the MDL study indicate that under ideal conditions, the lead and arsenic MDLs for the XRF analyzer are 2.6 and 3.9 mg/kg, respectively (Table 3.1).

Table 3.1. Results from seven replicates analyzed for determination of the XRF MDL

Sample	Lead (mg/kg)	Arsenic (mg/kg)
OL-14-L-1	19.3	4.9
OL-14-L-2	17.8	7.9
OL-14-L-3	19.1	5.0
OL-14-L-4	18.5	6.0
OL-14-L-5	18.0	6.9
OL-14-L-6	20.1	4.4
OL-14-L-7	18.1	6.1
Average	18.7	5.9
Standard Deviation	0.84	1.23
Student's T-value (*n*=7)	3.143	3.143
MDL	2.6	3.9

The MDLs are substantially less than the screening criteria concentrations (250 mg/kg lead and 20 mg/kg arsenic [DOE-RL 2014]) and background concentrations (10.2 mg/kg lead and 6.47 mg/kg arsenic [DOE-RL 1993]) for both lead and arsenic. However, it should be noted that while the MDL is less than the arsenic background, this does not mean that all samples will have detectable concentrations of arsenic. The MDL was determined under ideal laboratory conditions; actual in situ measurements of soil with arsenic concentrations just slightly above the MDL could still result in a non-detected sample result, recorded as "<LOD" ("less than level of detection") by the XRF analyzer.

3.1.2 Determination of Appropriate XRF Counting Duration

Prior to operating the XRF in the field, the optimum duration for the count time of the XRF analyzer was determined. A balance between minimizing time spent in the field and improving instrument accuracy with longer counting duration was necessary. To determine the minimally acceptable count duration, a site-specific reference sample (OL-14-M) with concentrations close to the lead and arsenic screening criteria was placed in a dish with a depth of ~4 cm. The soil was analyzed by the XRF using variable count durations. The RSD of five replicate analyses was calculated using count durations of 15, 30, 45, 60, 90, 120, and 180 seconds. This analysis indicated that the concentration for lead in a soil sample stabilized faster than the concentration for arsenic with the XRF analyzer. A count duration of 60 seconds was chosen for the in situ analyses. For arsenic concentrations near the screening criteria, the variability attributable to the counting duration is expected to be less than 10% with a 60-second count (Figure 3.1). EPA Method 6200 states that XRF data is adequately precise if the RSD is less than 20% (EPA 2007).

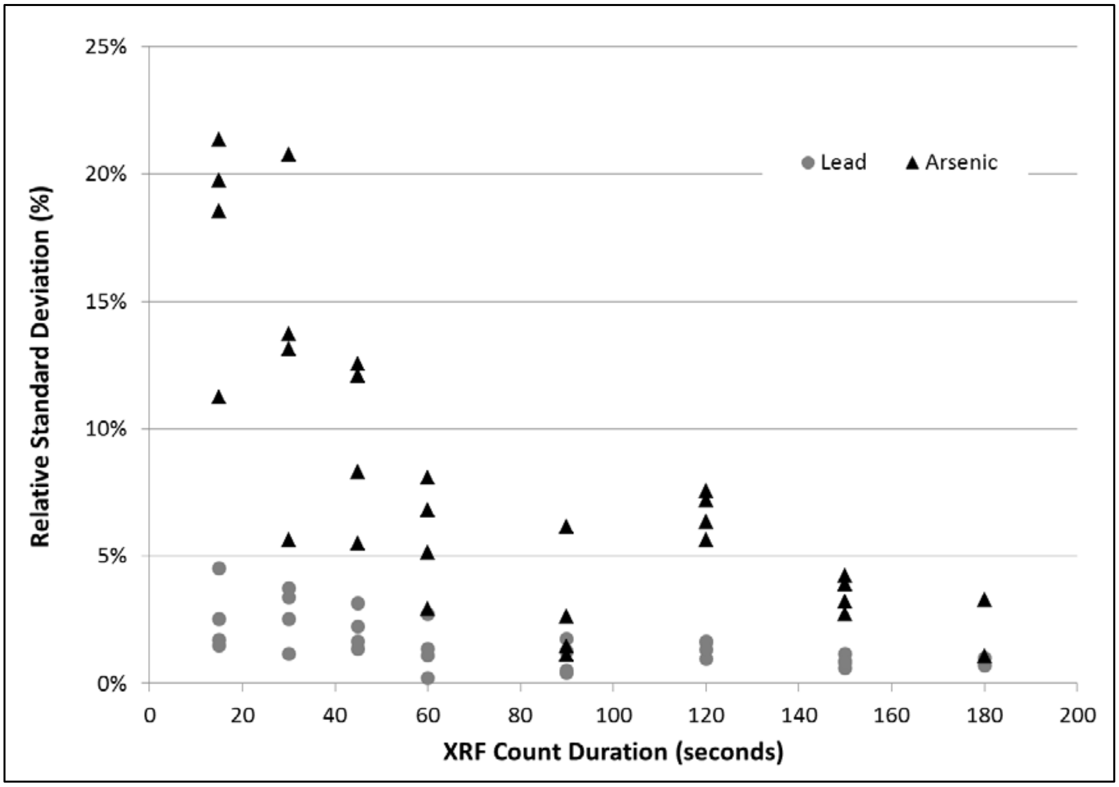


Figure 3.1. RSD in measured XRF concentrations as a function of count duration

3.1.3 Daily Instrument Checks

Each day that in situ analyses were conducted, the performance of the XRF analyzer was evaluated at the field location. This evaluation consisted of precision tests, an SRM check, and a blank check. The precision test consisted of three site-specific reference samples representing low, medium, and high concentrations of lead and arsenic. Seven replicate measurements of each sample were made. The performance criteria required that the RSD for the seven replicate measurements be less than 20% (EPA 2007).

Once the precision test was completed, the SRM and blank were measured by the XRF analyzer three times each. The SRM and blank replicate analyses were completed at the beginning of each day and after every 20 field analyses. The performance criteria for the SRM and blank check required the SRM to report a value within 10% of the SRM concentration as reported by ICP-MS analysis. The blank check required two of the three replicates to be reported as non-detectable, with any detectable results being less than two times the MDL. The XRF met all required metrics prior to conducting sampling each day. The results of all daily checks are included in Appendix C.

3.1.4 Confirmatory Samples with ICP-MS Results

The performance of the XRF analyzer was also compared against results obtained using ICP-MS. ICP-MS analyses were performed as discussed in section 2.4. A total of 15 soil samples were analyzed for lead and arsenic with ICP-MS and XRF, and each sample was analyzed in triplicate. This resulted in 45 comparable results, and met the requirement for in situ analysis in the field of a minimum of one sample for each 20 locations (DOE-RL 2014). Soil was collected at locations within OL-14 or IU6-4 that were cleared of sensitive cultural and ecological resources (Appendix B), and the collection location was determined qualitatively in situ with the XRF analyzer. The soil samples were returned to the laboratory for homogenization (section 2.3). Aliquots for ICP-MS analysis were packaged and sent to the Marine Sciences Laboratory for ICP-MS analysis. Subsamples for intrusive XRF analysis were then packaged and counted 14 times with the XRF instrument.

The results of these split sample analyses indicate that the XRF analyzer and ICP-MS report concentrations of lead and arsenic that are nominally the same. There was no difference observed in the correlation between XRF and ICP-MS for samples collected at the OL-14 and IU6-4 decision units (Appendix C). Therefore, the results for samples collected from both decision units are combined for comparison. The range of concentrations of lead and arsenic for the confirmatory samples was over three orders of magnitude. Figure 3.2 shows the results of the samples throughout the entire concentration range (left graphs) and the results in an expanded view of the lowest concentration range (right graphs).

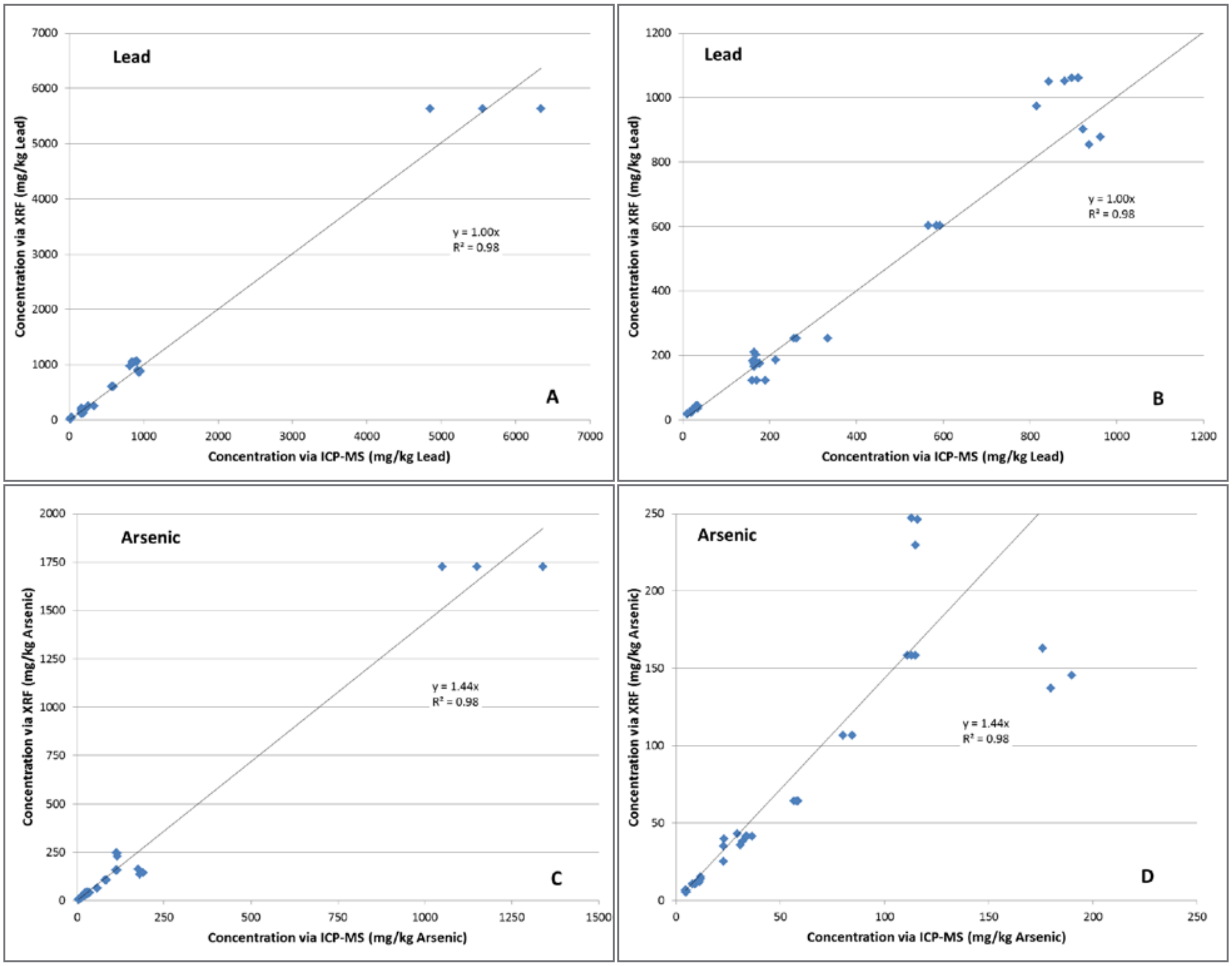


Figure 3.2. Comparison of XRF analyses and ICP-MS results for confirmatory soil samples for lead (A, B) and arsenic (C, D). Plots on the right (B, D) are enlarged to provide better detail of the results at lower concentrations.

The percent difference between confirmatory sample results obtained with XRF and ICP-MS for any one split sample ranged from -27% to 74% for arsenic, and -43% to 58% for lead (Appendix C). When the results are compared graphically, there is a very strong correlation between the XRF and ICP-MS results for both lead and arsenic (r^2 = 0 .98) between the concentrations measured with the two methods (Figure 3.2). The RSD between replicates analyzed with ICP-MS averaged 4%, but was as high as 15%. Similarly, the RSD of replicate analyses via XRF averaged 8%, but was as high as 30%. Therefore, most of the variability between results obtained with ICP-MS and XRF could be explained by the combined variability of each method.

According to EPA Method 6200, the soil samples for confirmatory analyses between the two methods should have a correlation coefficient (r) of 0.7 or greater for the results to be considered “screening level data” (EPA 2007). Figure 3.3 shows the log-transformed data since the concentrations of the confirmatory soil samples span more than one order of magnitude. The correlation coefficient for the lead as well as for the arsenic concentrations as measured by XRF and ICP-MS is greater than 0.9. According to EPA Method 6200, the XRF data “could potentially meet definitive level data criteria” (EPA 2007).

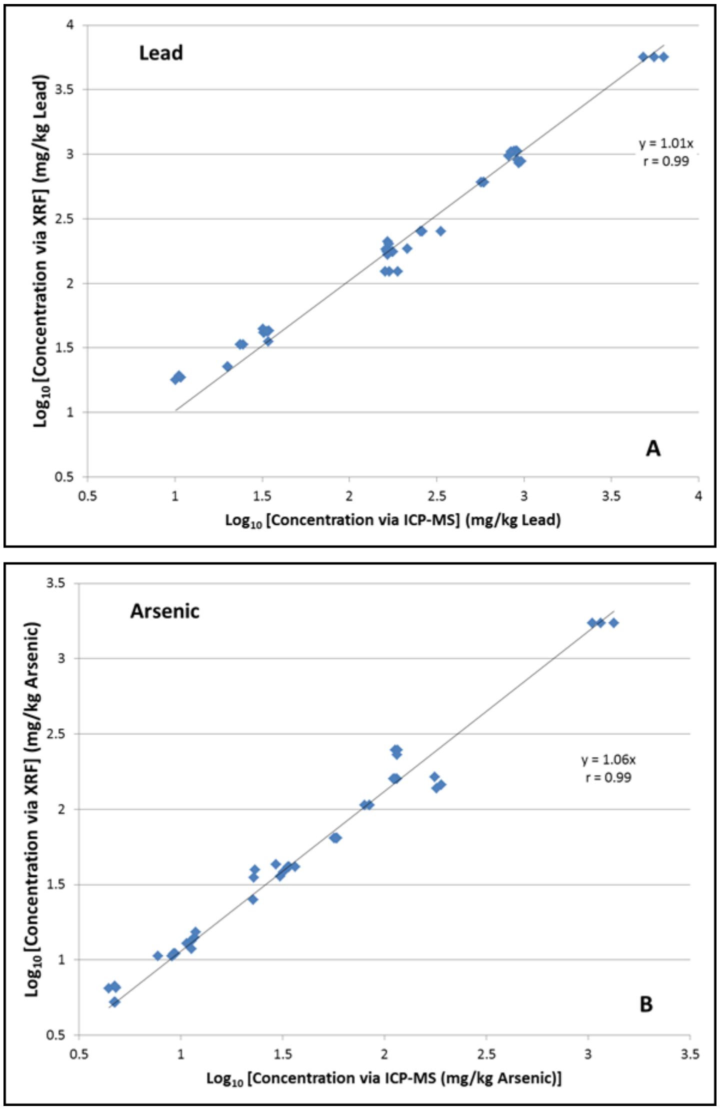


Figure 3.3. Log-transformed data for confirmatory soil samples analyzed for lead and arsenic by XRF and ICP-MS

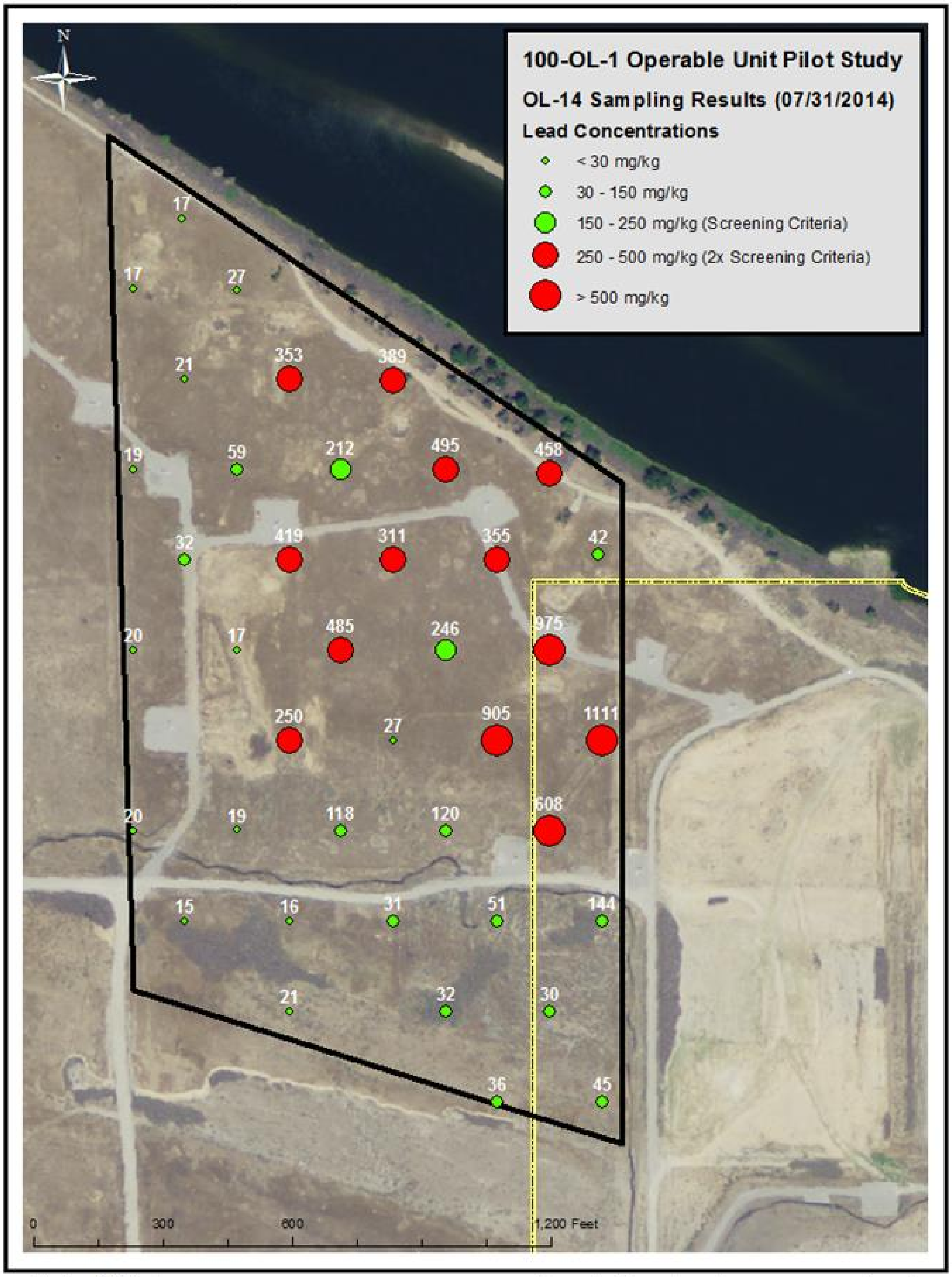
3.2 Quality Assurance Conclusions

When all of the results of the QA evaluations are considered, the field portable XRF can be considered an adequate analytical tool for in situ characterization of surface soil concentrations of lead and arsenic. The MDL is less than the screening criteria concentrations for both lead and arsenic. The accuracy of the XRF is demonstrated by the good correlation with measured concentrations of split, confirmatory samples analyzed by both XRF and ICP-MS. The precision of the XRF instrument was demonstrated daily and was shown to have an RSD of less than 20%. The ability of the XRF to repeatedly provide consistent results was verified through the repeated checks of the SRM. Since the QA results indicate that the XRF is an adequate analytical tool, the remainder of this report only includes the average of the three replicate analyses conducted at each sampling location (all the data is included in Appendix C).

4.0 Results of Pilot Study

The discussion of the results from the evaluation of lead and arsenic concentrations in the decision units is organized based on the objectives of the pilot study. The nature and extent of lead and arsenic in surface soils of the pilot study decision units is covered in section 4.1. Analyses of the data to support the optimization of the remedial investigation and feasibility study are discussed in section 4.2. Section 4.3 provides information related to the cost estimate for sampling activities and the evaluation of cultural resources review in the remedial investigation. The results are displayed for each decision unit, for arsenic and lead, and with 2013 satellite and 1943 aerial imagery in Figure 4.1 through Figure 4.16. The value of the soil sample is shown as not detected (ND) in the figures if all three replicate analyses at a location were recorded by the XRF analyzer as less than level of detection.

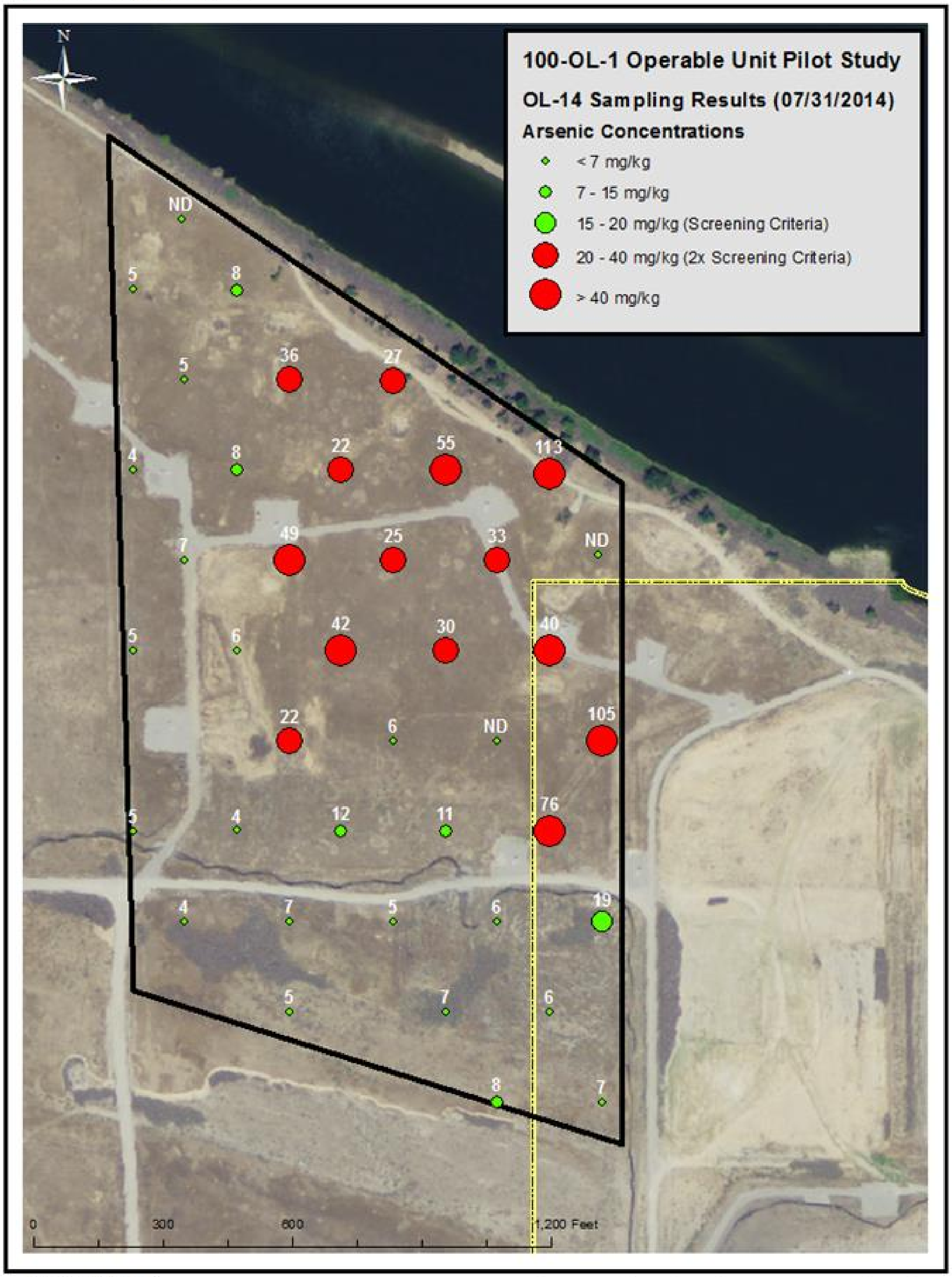
Note: Hanford 2013 Imagery



1 inch = 300 feet

Concentration values shown on map are in mg/kg.
Values that were non-detected are marked ND.

Figure 4.1. Results for lead concentrations in OL-14 decision unit with 2013 satellite imagery



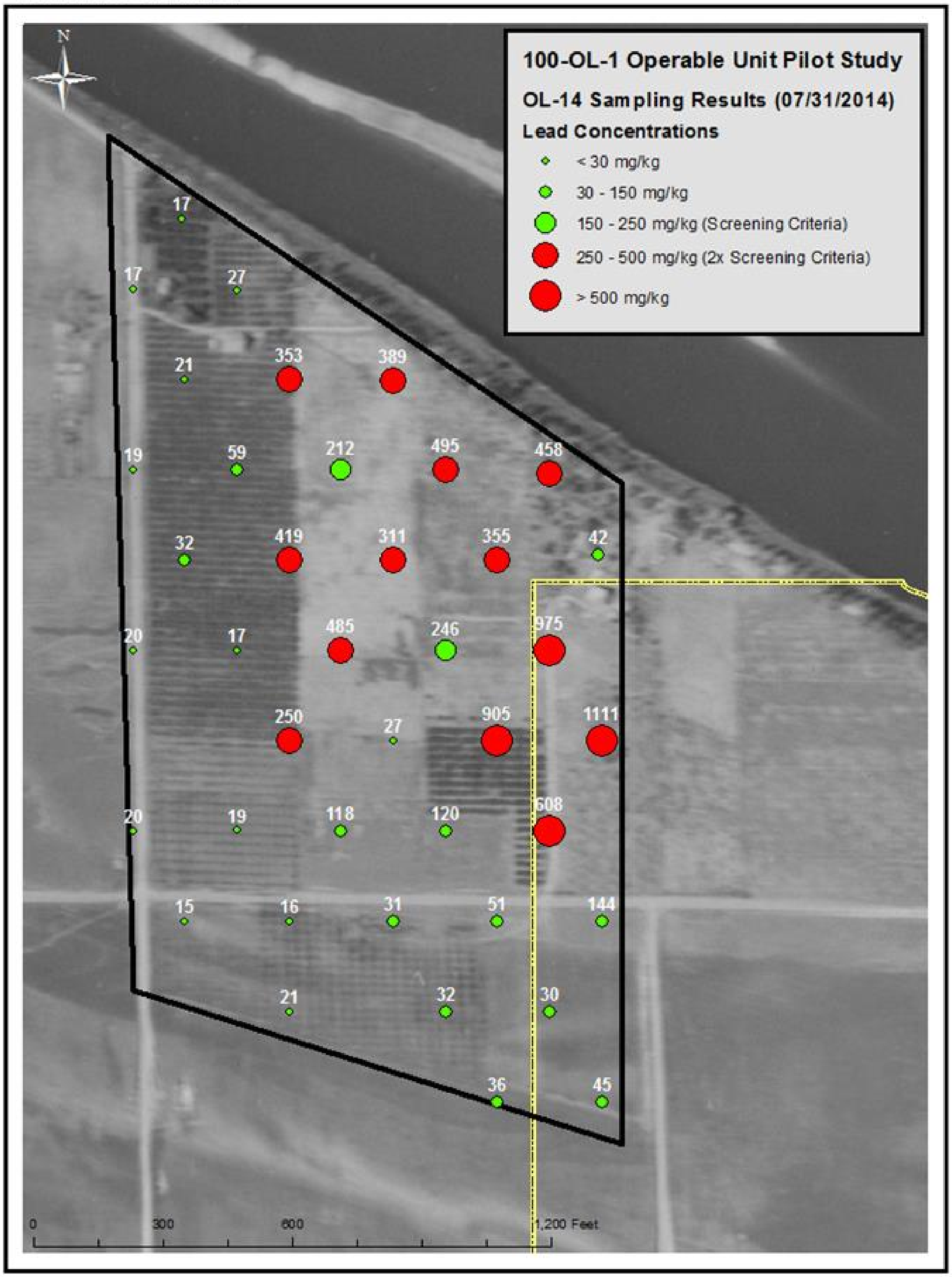
Note: Hanford 2013 Imagery

1 inch = 300 feet

Concentration values shown on map are in mg/kg.
Values that were non-detected are marked ND.

Figure 4.2. Results for arsenic concentrations in OL-14 decision unit with 2013 satellite imagery

Note: Hanford 1943 Imagery

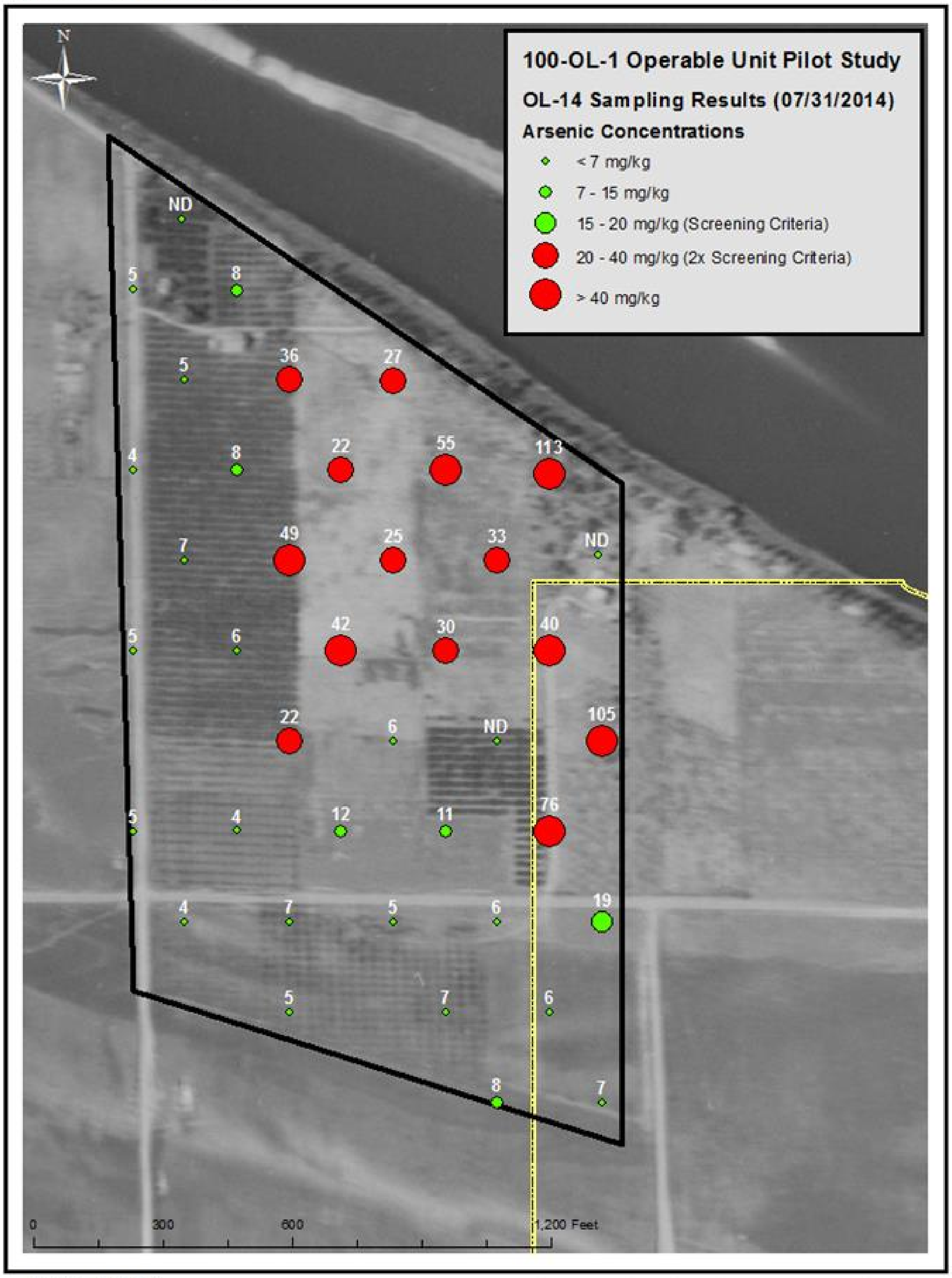


1 inch = 300 feet

Concentration values shown on map are in mg/kg.
Values that were non-detected are marked ND.

Figure 4.3. Results for lead concentrations in OL-14 decision unit with 1943 aerial imagery

Note: Hanford 1943 Imagery



1 inch = 300 feet

Concentration values shown on map are in mg/kg.
Values that were non-detected are marked ND.

Figure 4.4. Results for arsenic concentrations in OL-14 decision unit with 1943 aerial imagery

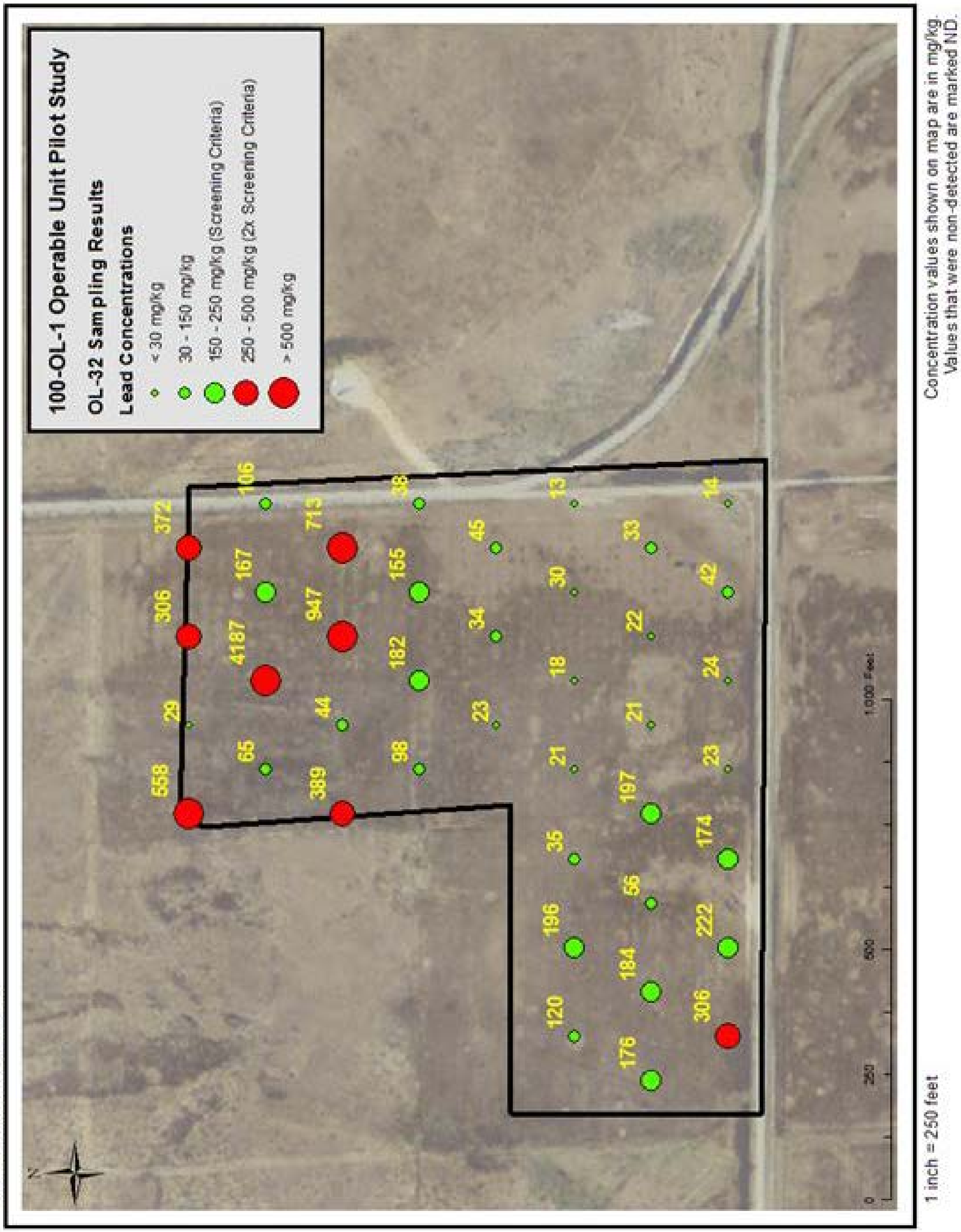


Figure 4.5. Results for lead concentrations in OL-32 decision unit with 2013 satellite imagery

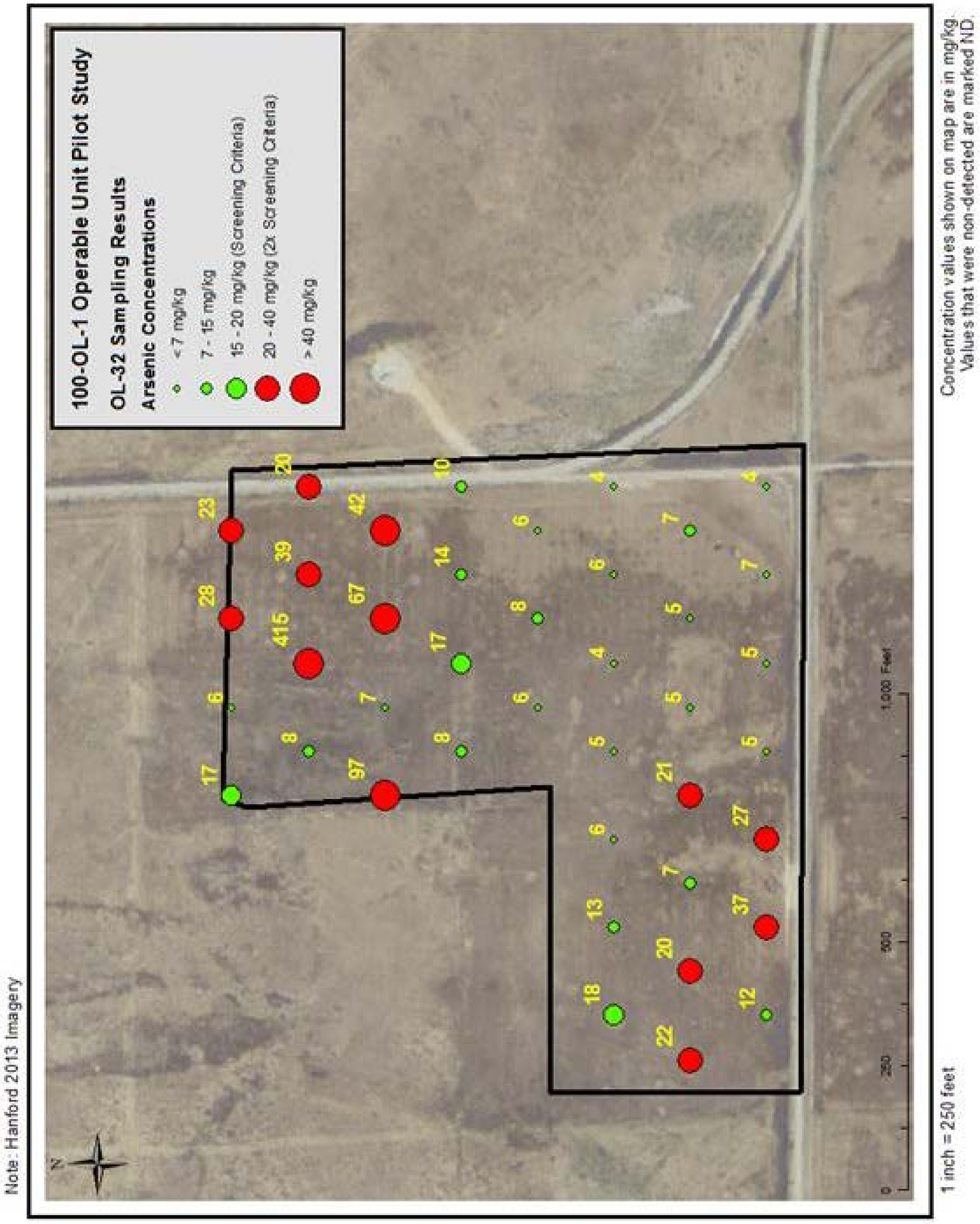
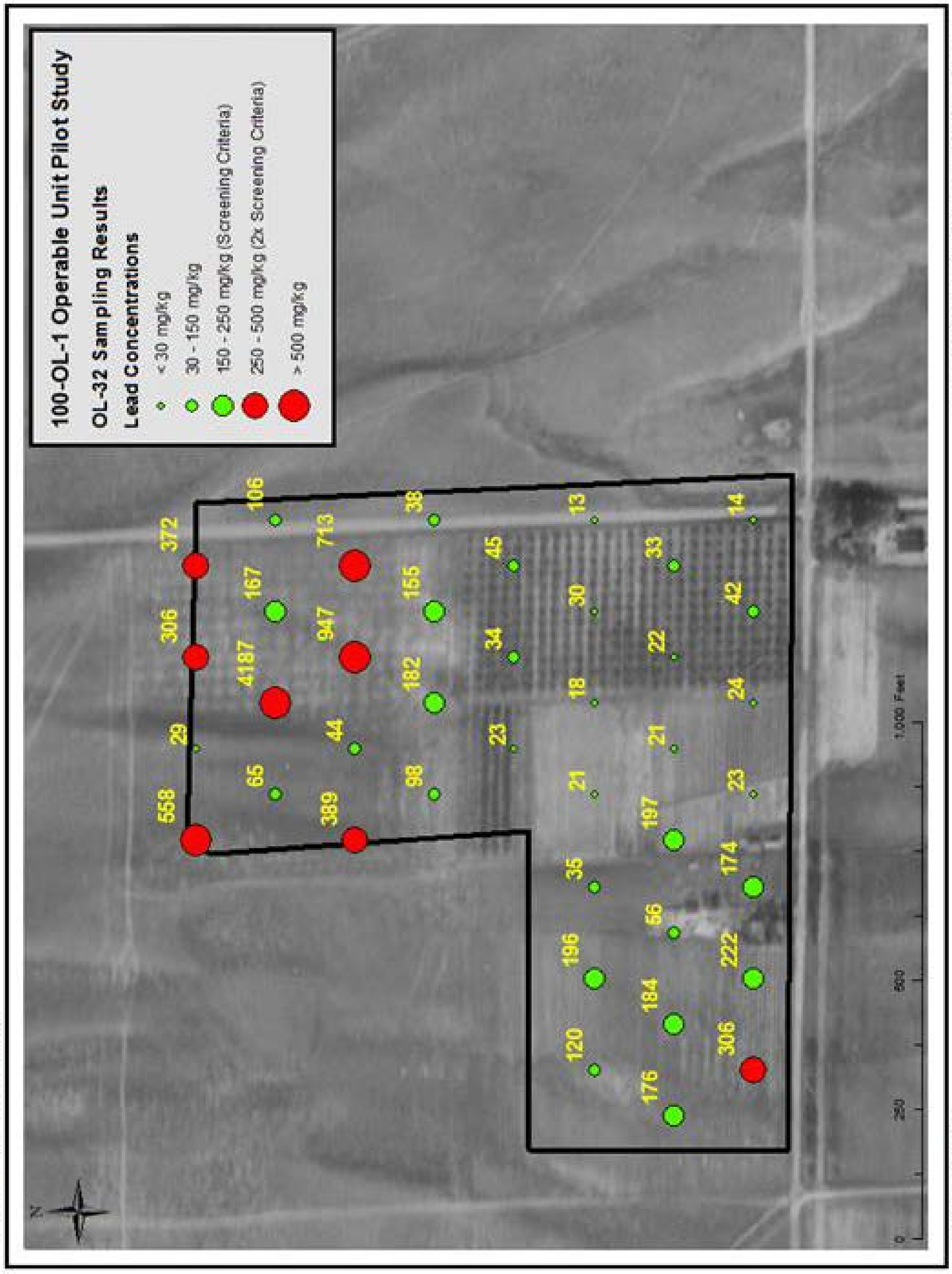


Figure 4.6. Results for arsenic concentrations in OL-32 decision unit with 2013 satellite imagery



Note: Hanford 1943 Imagery

1 inch = 250 feet

Concentration values shown on map are in mg/kg.
Values that were non-detected are marked ND.

Figure 4.7. Results for lead concentrations in OL-32 decision unit with 1943 aerial imagery

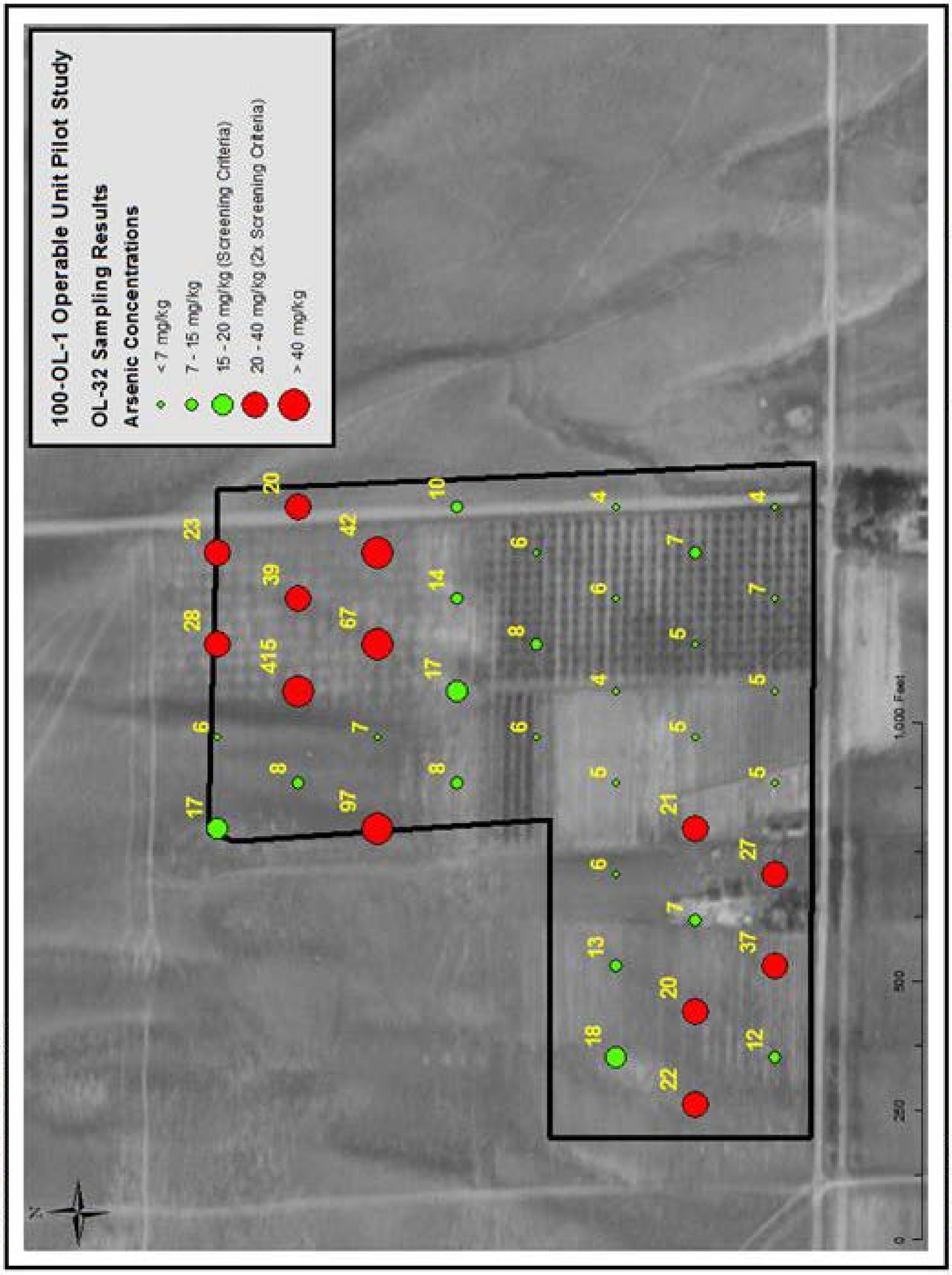
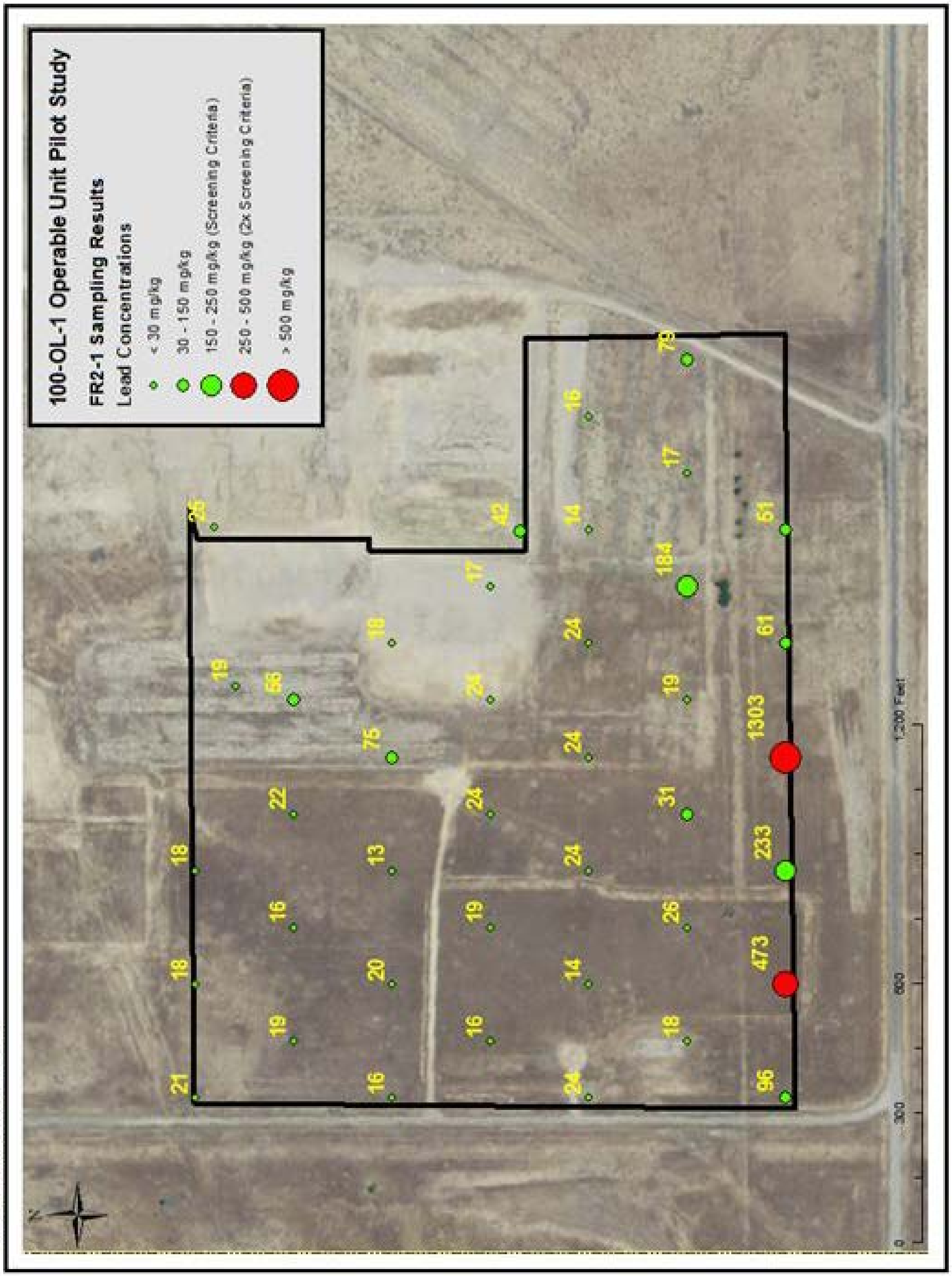


Figure 4.8. Results for arsenic concentrations in OL-32 decision unit with 1943 aerial imagery



Note: Hanford 2013 Imagery

Concentration values shown on map are in mg/kg.
Values that were non-detected are marked ND.

Figure 4.9. Results for lead concentrations in FR2-1 decision unit with 2013 satellite imagery

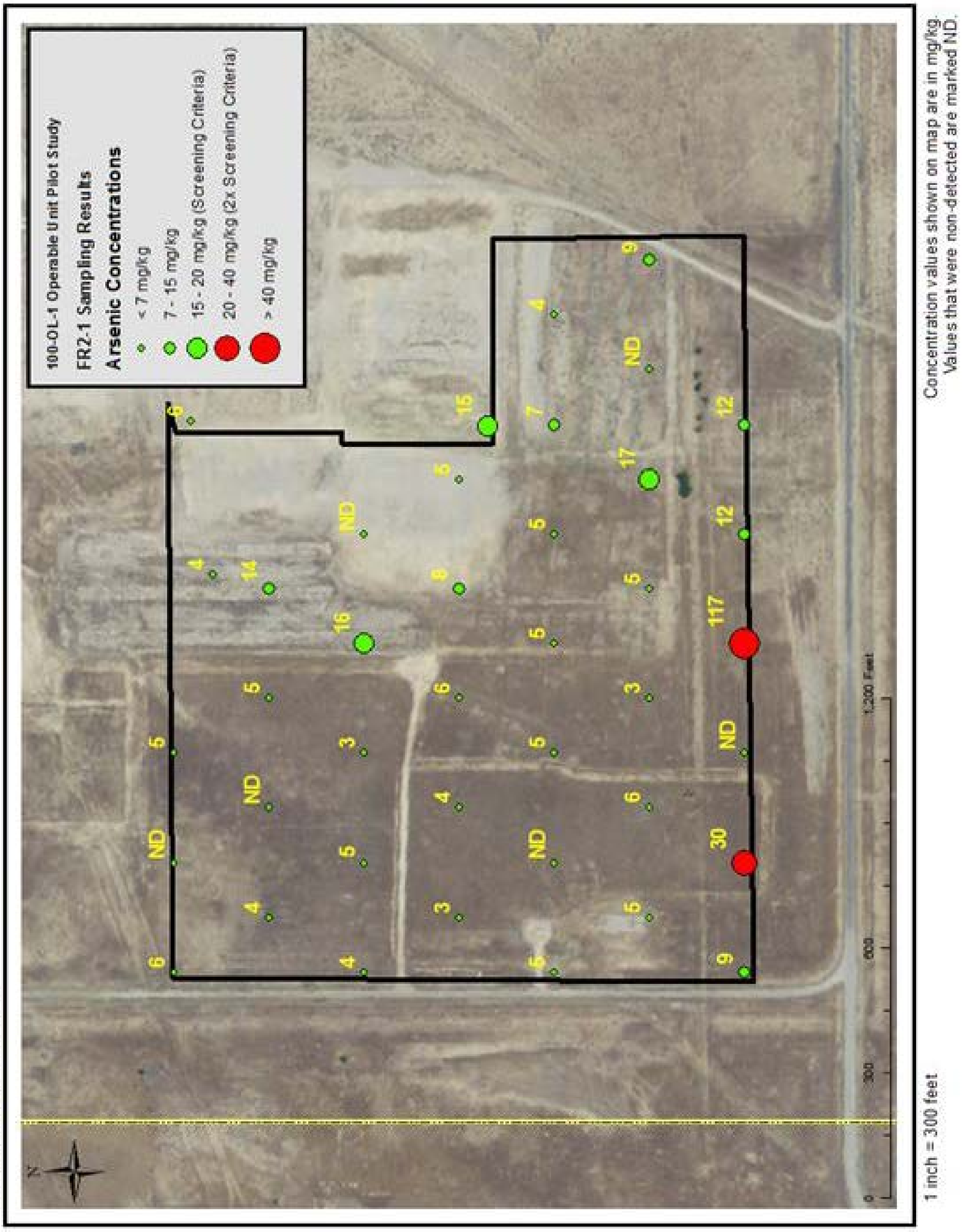


Figure 4.10. Results for arsenic concentrations in FR2-1 decision unit with 2013 satellite imagery

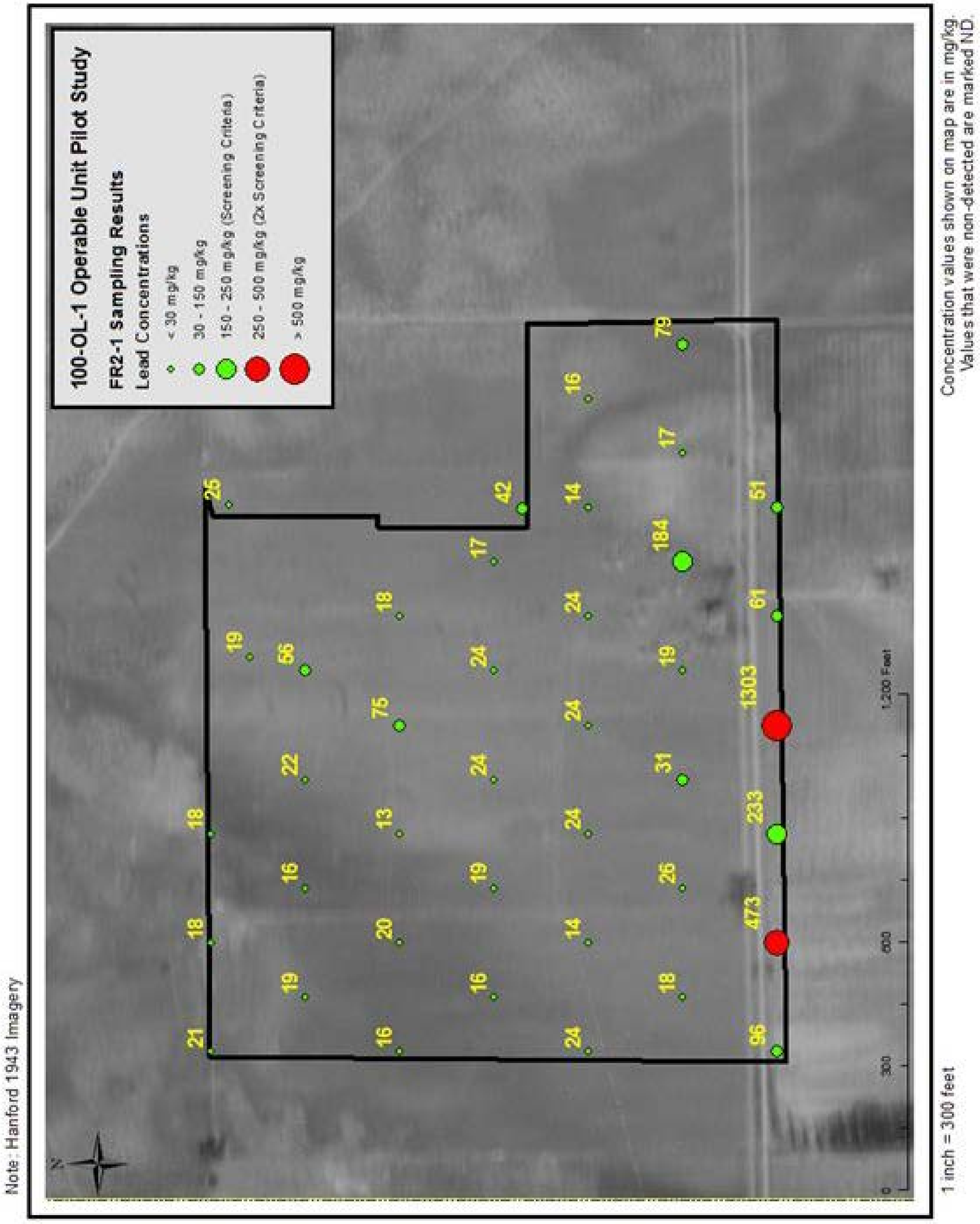


Figure 4.11. Results for lead concentrations in FR2-1 decision unit with 1943 aerial imagery

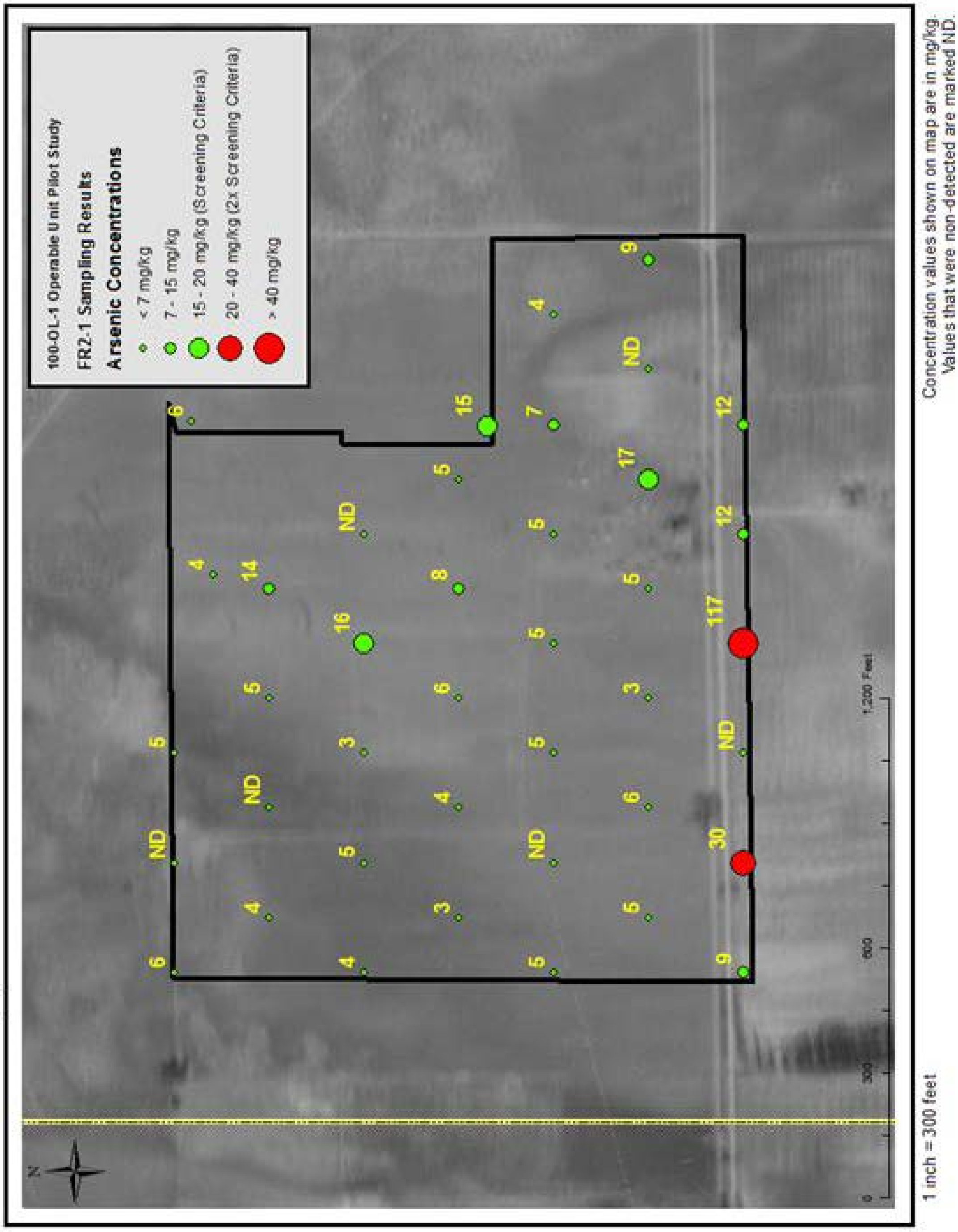


Figure 4.12. Results for arsenic concentrations in FR2-1 decision unit with 1943 aerial imagery

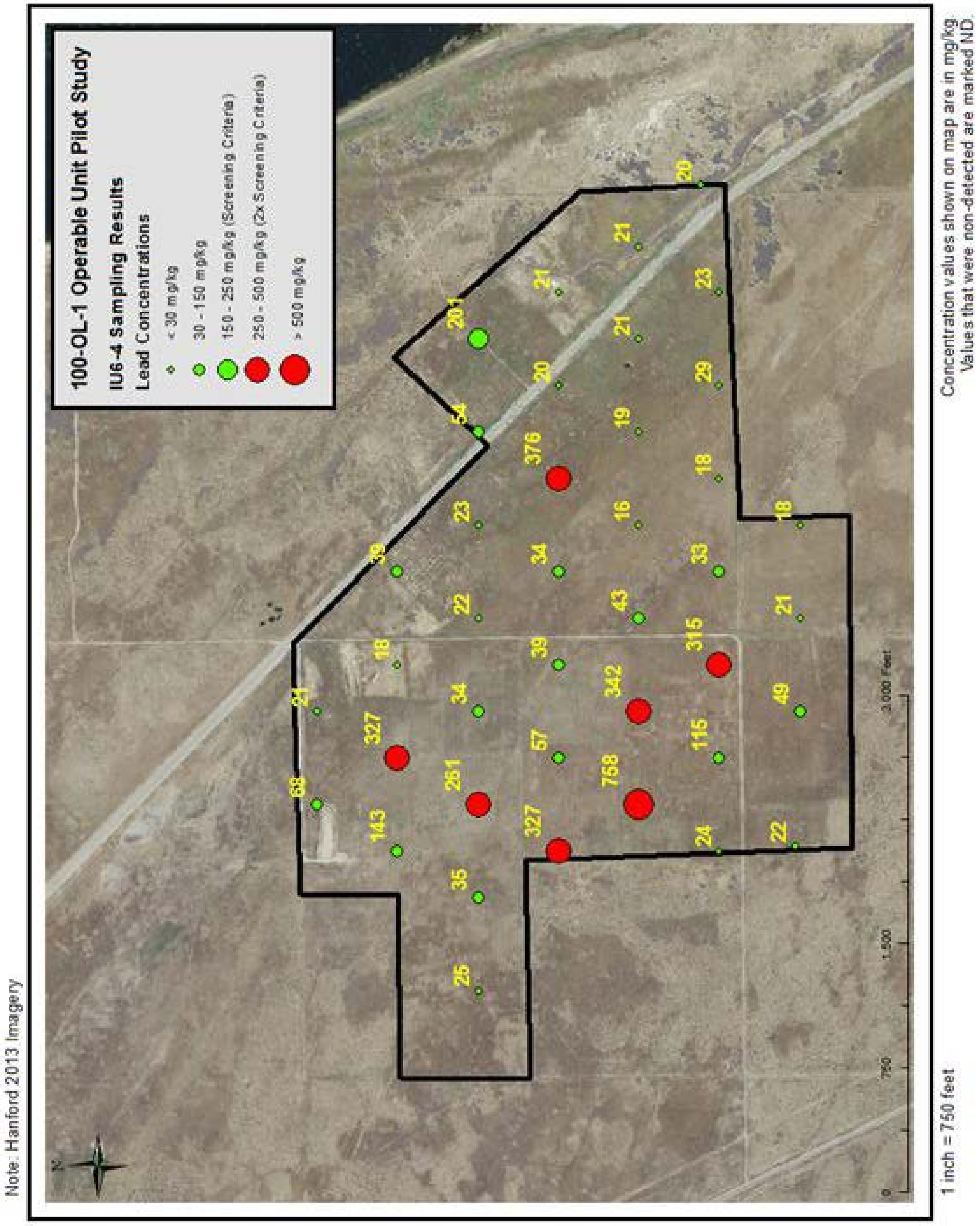


Figure 4.13. Results for lead concentrations in IU6-4 decision unit with 2013 satellite imagery

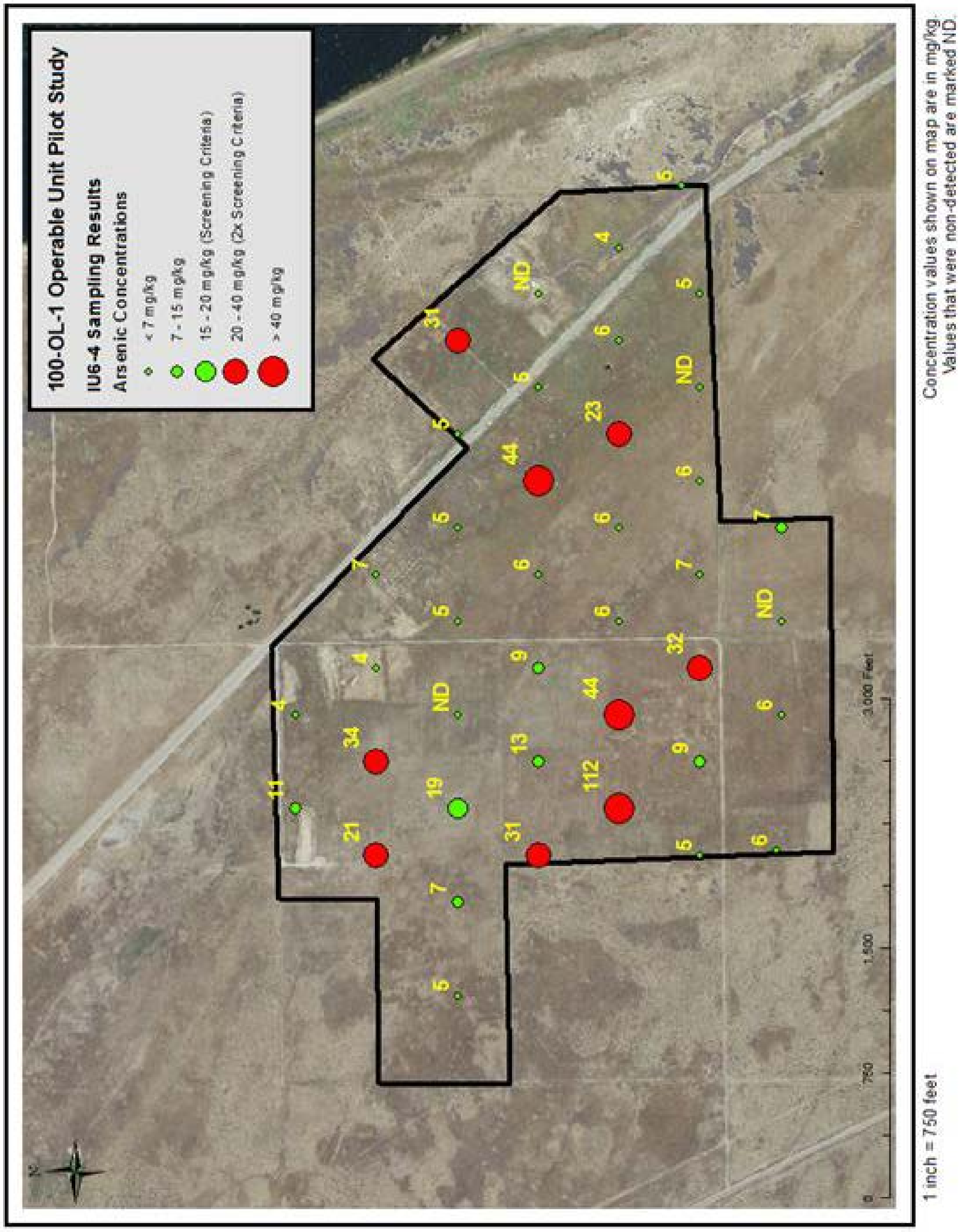
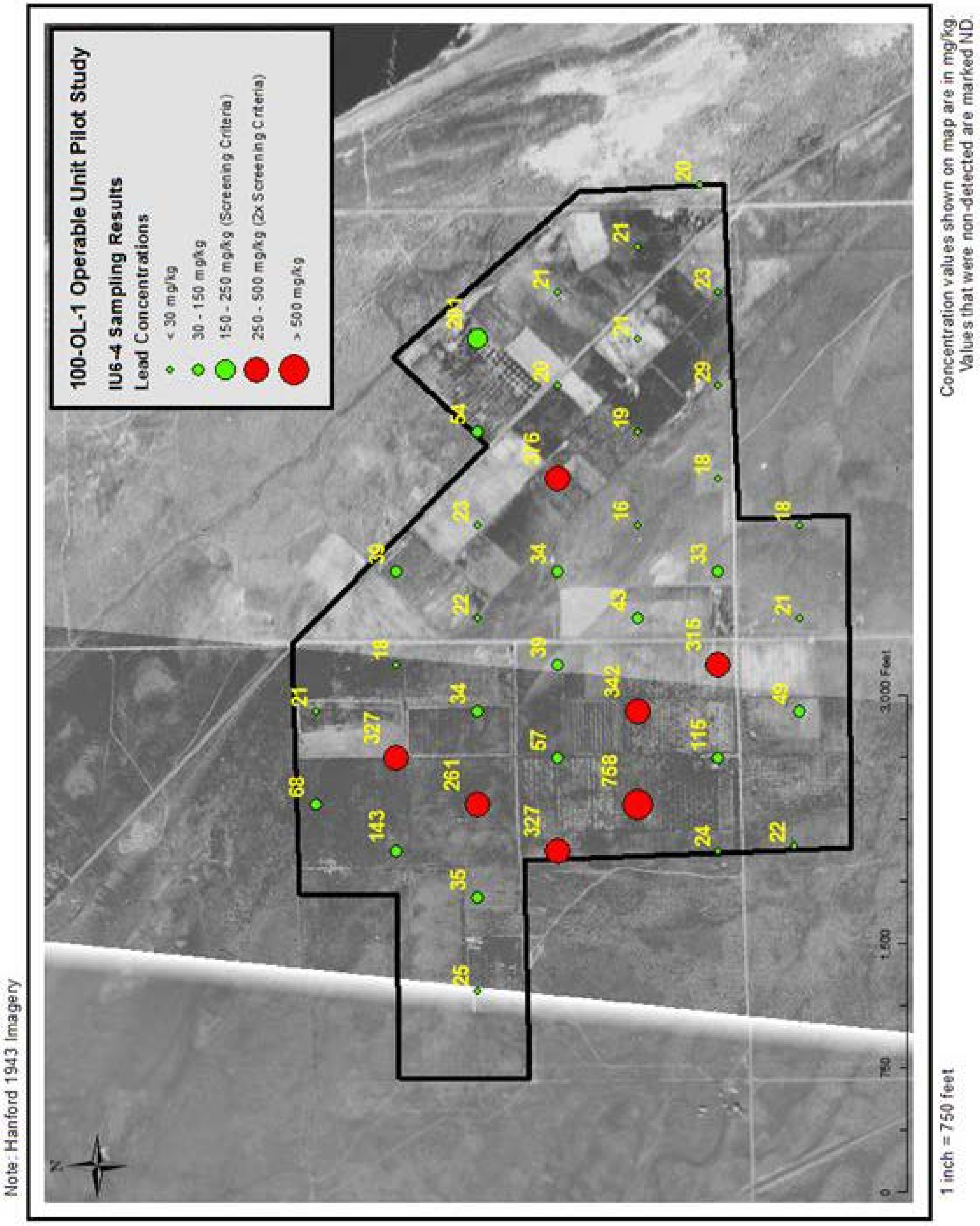


Figure 4.14. Results for arsenic concentrations in IU6-4 decision unit with 2013 satellite imagery



Note: Hanford 1943 Imagery

Concentration values shown on map are in mg/kg.
Values that were non-detected are marked ND.

Figure 4.15. Results for lead concentrations in IU6-4 decision unit with 1943 aerial imagery

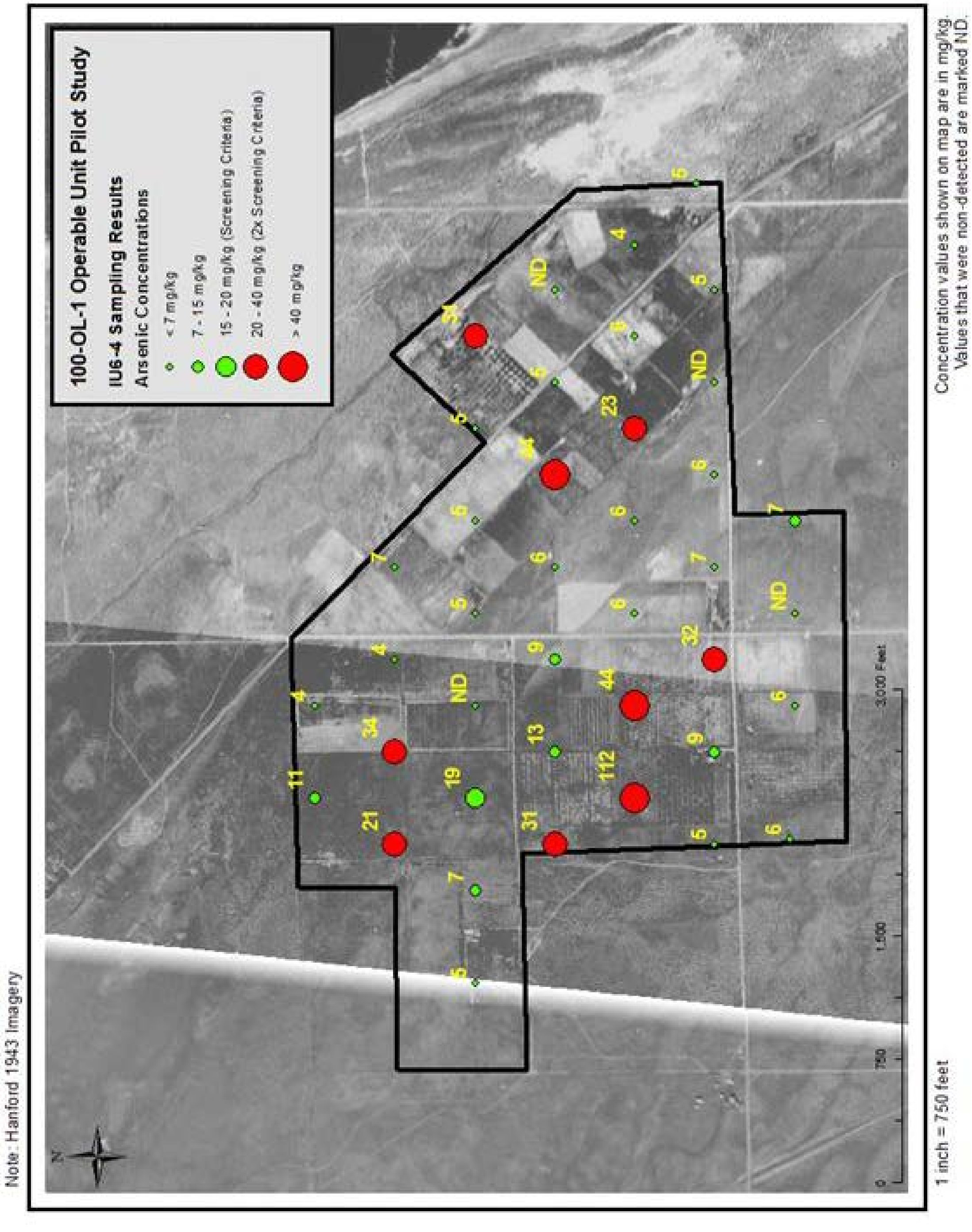


Figure 4.16. Results for arsenic concentrations in IU6-4 decision unit with 1943 aerial imagery

4.1 Nature and Extent of Lead and Arsenic

Table 4.1 summarizes the results in each decision unit evaluated during the pilot study, and demonstrates further the variable results. Summary statistics for each decision unit indicate that the RSD of the four decision units, for both lead and arsenic, varied between 125% and 266%. The difference between the maximum and minimum concentrations within a decision unit was as much as two orders of magnitude.

Table 4.1. Summary statistics for the evaluation of 40 surface soil locations in each pilot study decision unit

Decision Unit	OL-14		OL-32		FR2-1		IU6-4	
Result[a]	Lead	Arsenic	Lead	Arsenic	Lead	Arsenic	Lead	Arsenic
Average (mg/kg)[b]	214	21	260	27	81	9.8	101	14
Standard Deviation (mg/kg)[b]	284	26	668	66	214	18	153	20
Relative Standard Deviation (%)	132%	125%	257%	243%	266%	185%	151%	137%
Maximum Concentration (mg/kg)	1111	113	4187	415	1303	117	758	112
Minimum Concentration (mg/kg)[c]	13	3.7	13	3.9	13	3.2	16	4.0
# Non-detected samples[d]	0	3	0	0	0	7	0	4

(a) Results are based on the average of three replicate measurements at each location within a decision unit.

(b) Averages and standard deviations were calculated by replacing non-detected results with the MDL for calculation purposes.

(c) Minimum is the minimum detected concentration. Non-detected values not included.

(d) Non-detected samples are those measured by the XRF analyzer as “<LOD,” or less than level of detection.

The aerial imagery from March 1943 illustrates the state of the orchards at the time when the residents of the area left and the Manhattan Project began. Figure 4.17 shows examples of the stage of the fruit trees, non-orchard agricultural activities, and former areas that were probably orchards. Based on historical information about the orchards, the orchards were typically pruned in January and February (Sharpe 1999). Lead arsenate pesticide applications were usually applied around the time that the codling moths hatched, which was typically in June (Sharpe 1999). The 1943 imagery shows the orchards where the trees were leafing, with cherry trees (an early season crop) showing a higher density of leaves than apple trees (a late crop). The 1943 imagery also shows areas where trees had previously been cut down.

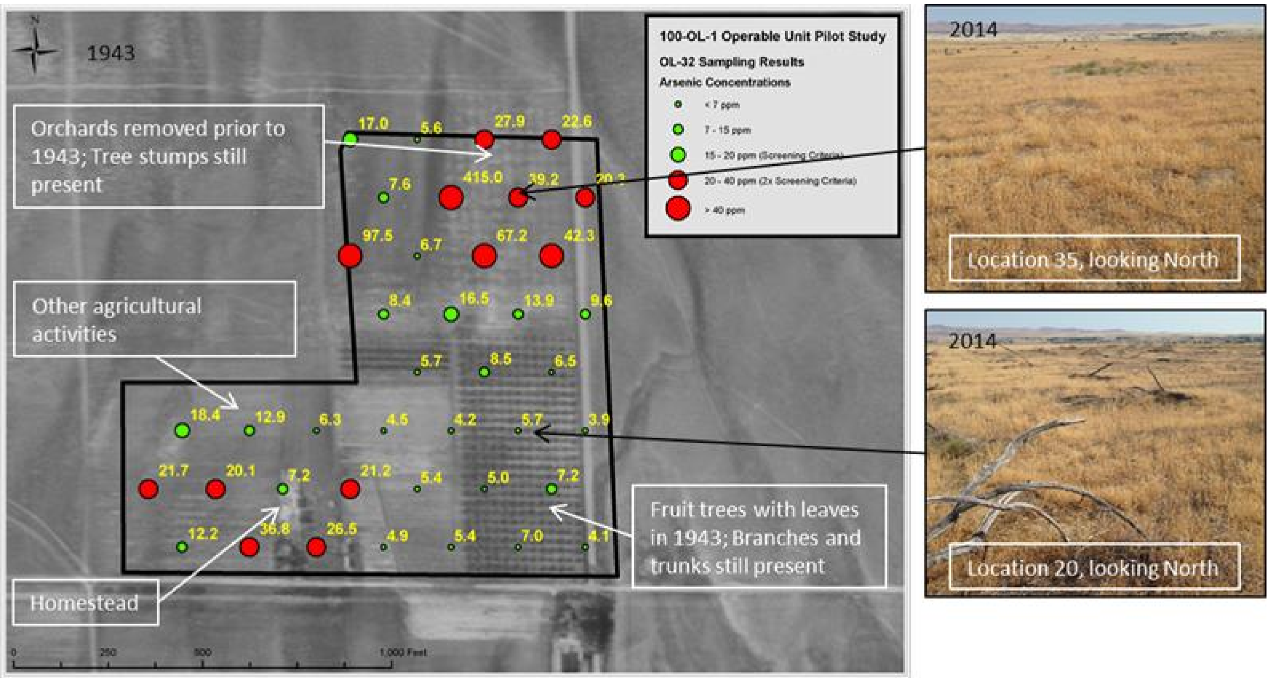


Figure 4.17. Aerial imagery from 1943 provides context for identifying areas where there were fruit trees and other agricultural activities. Inset pictures were taken during the pilot study.

The 2013 satellite imagery shows remnants of past agricultural activities as well as other disturbances since 1943. The soil disturbances include changes from the Cold War activities, direct remediation activities (Figure 4.18), and ancillary activities associated with remediation (e.g., laydown areas). All these activities could have redistributed soils within the decision unit.

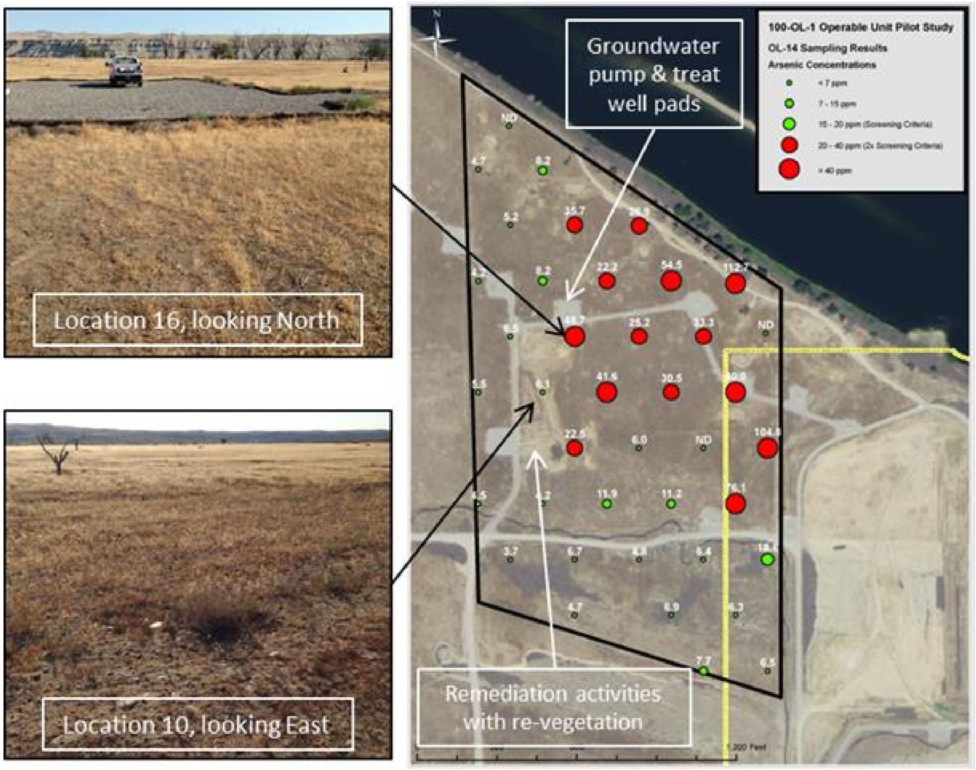


Figure 4.18. Satellite imagery from 2013 provides context for identifying areas where there have been soil disturbances since 1943. Inset pictures were taken during the pilot study.

Although only a limited amount (~7%) of 100-OL-1 OU was sampled as part of the pilot study, the results demonstrated that the distribution of the lead and arsenic in the surface soil could not be predicted based on historical data. There were no clear correlations between measured concentrations and the appearance of the land surface in 1943 (Figure 4.3, Figure 4.4, Figure 4.7, Figure 4.8, Figure 4.11, Figure 4.12, Figure 4.15, and Figure 4.16). In OL-14, where areas of trees and areas of no-trees were both present in 1943, the higher concentrations of lead and arsenic were located in areas where no trees are visible in the 1943 aerial imagery. This is not consistent with the initial conceptual site model developed prior to the pilot study. On the other hand, at OL-32 the measured concentrations of lead and arsenic were elevated significantly above background concentrations in only a couple of areas, despite there being tree remains (stumps and branches) spread across the entire decision unit (Figure 4.17). At FR2-1, despite no concrete evidence of orchards ever having been present in the 1943 aerial imagery, there was one location where lead and arsenic concentrations exceeded two times the screening criteria, and several samples where lead and arsenic concentrations were measured at concentrations several times higher than background (but below the screening criteria). The lead and arsenic concentrations measured in samples collected at IU6-4 also showed no distinct correlation with the presence of orchards in 1943. Some areas that appear to have had trees in 1943 had elevated concentrations; other areas with trees in 1943 did not have elevated concentrations. Some areas that look like non-orchard agriculture in the 1943 imagery had elevated concentrations; other areas that look like non-orchard agriculture in the 1943 imagery did not have elevated concentrations. Also, at IU6-4, some elevated concentrations of lead and arsenic were measured at locations where asparagus was still growing wild (presumably, the area was planted with asparagus prior to 1943).

Wind and water can redistribute soil in an area. Wind roses are included on Figure 2.2 through Figure 2.5 to show the direction and frequency of the wind, obtained from the closest meteorological monitoring station to the decision unit (Poston et al. 2010). While the wind over the 70 plus years since the last application of lead arsenate pesticide probably dispersed some contaminated soils, the very low concentration of lead and arsenic where trees are apparent in the 1943 aerial imagery is likely not due to wind scouring the contaminated soils away. For example, in OL-14 the western edge of the decision unit shows orchards in the 1943 imagery and the concentrations of lead and arsenic are close to background levels (Figure 4.3 and Figure 4.4). The flow of water from irrigation of the orchards or from overland flow due to precipitation events over the years might redistribute contaminated soil. However, OL-32 and FR2-1 are mostly flat, with no more than ~3 m elevation change across the decision unit. IU6-4 has several rolling areas across the 250 acres of the decision unit, with as much as a 6 m change in elevation. The southern portion of OL-14 is about 3 m above the area north of the road that bisects the lower portion of the decision unit, and the higher elevation areas are all regions below the screening criteria. The pattern of lead and arsenic concentrations exceeding the screening criteria does not seem to be explained by dispersion from wind and water.

There was a trend between the measured lead and arsenic concentrations for the locations in all the decision units (Figure 4.19A and B). However, the correlation of the lead and arsenic concentrations was not uniform, as some measured concentrations had lead concentrations above the screening criteria with arsenic concentrations below the screening criteria, and vice-versa. The lead concentration measured at a location was not a good indicator of the arsenic concentration from past pesticide residues. In particular, in the concentration ranges around the screening criteria, a number of samples were measured with concentrations that exceeded one of the criteria, but not both (Figure 4.19B). For example, there were 31 locations measured in the four decision units with arsenic concentrations between 10 and 30 mg/kg and lead concentrations measured between 0 and 500 mg/kg. Of these, 8 (or 26%) exceeded the 20 mg/kg screening criteria for arsenic, but did not exceed the 250 mg/kg screening criteria for lead. More frequently, the presence of elevated lead concentrations at a location indicates elevated arsenic concentrations. However, conversely, the presence of elevated arsenic at a location does not always indicate elevated lead.

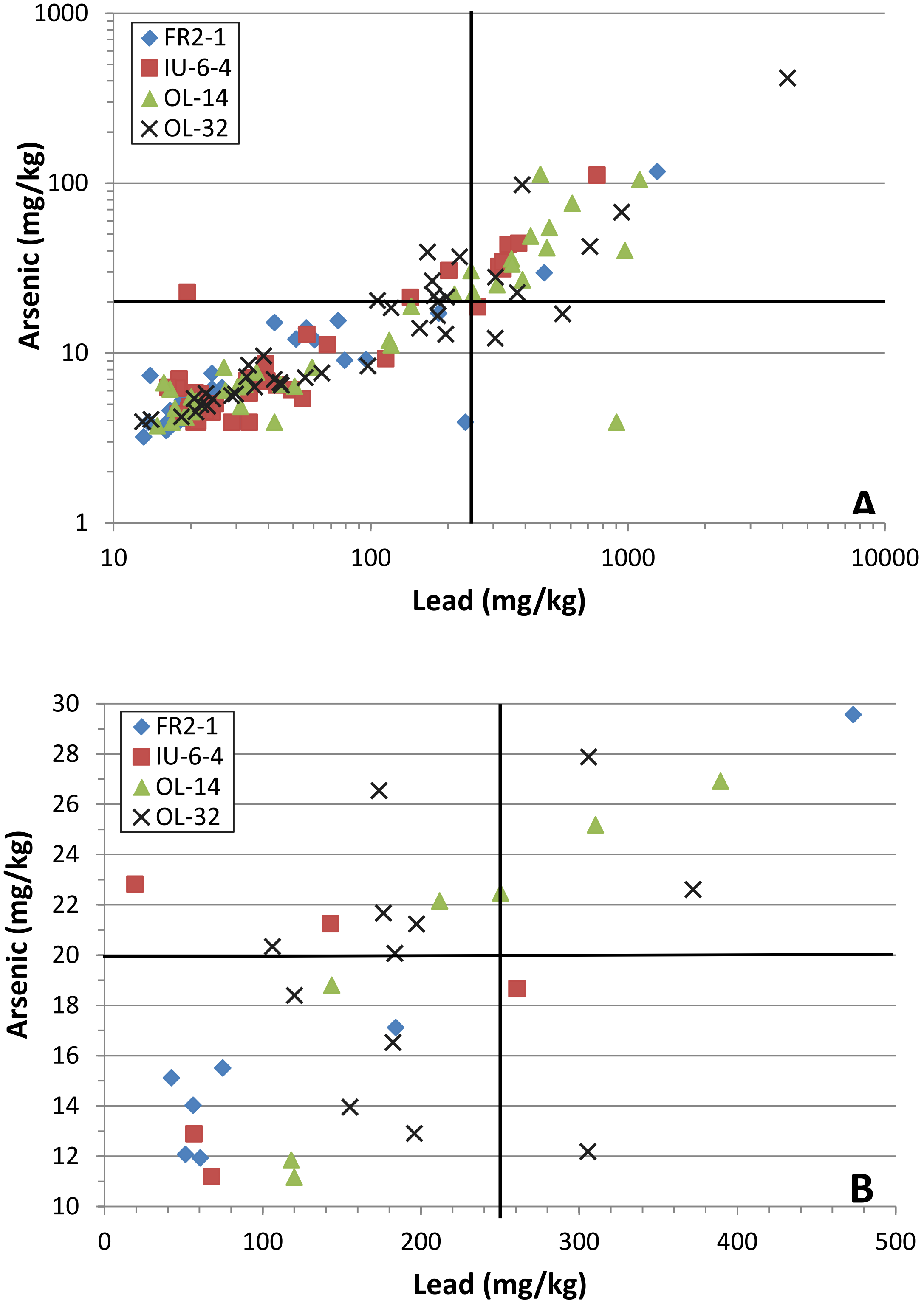


Figure 4.19. (A) Correlation between lead and arsenic concentrations measured at the four decision units on a log scale. (B) Enlarged area of the same data illustrating the intersection between the arsenic screening criteria (20 mg/kg) and the lead criteria (250 mg/kg), on a linear scale.

The lack of correlation between the lead and arsenic concentrations at a location is likely due to the difference in chemical behavior of the two elements in the subsurface. Other studies have shown that lead and arsenic transport in soils at different rates. Previous studies of the vertical transport of lead and arsenic through soil have indicated various depths of contamination below the surface. One consistent observation is that the arsenic is generally more mobile, moving to somewhat lower depths than lead. This finding would indicate that the lead and arsenic are no longer chemically associated and could be treated as two distinct contaminants (Renshaw et al. 2006). Figure 4.20 illustrates the vertical profile of lead and arsenic as reported by Peryea and Creger (1994) in six orchard soils from Washington State. The vertical migration of contaminants is a function of soil type, soil chemistry, and precipitation/irrigation (Veneman et al. 1983; Newton et al. 2006; Maclean and Langille 1981; Renshaw et al. 2006; Staed et al. 2009; Delistraty and Yokel 2011). The studies of vertical migration most relevant to the former orchard properties indicate that lead could be expected to have migrated down to 0.4 m (16 in.), and arsenic to 1 m (39 in.) (Peryea and Creger 1994; Yokel and Delistraty 2003).

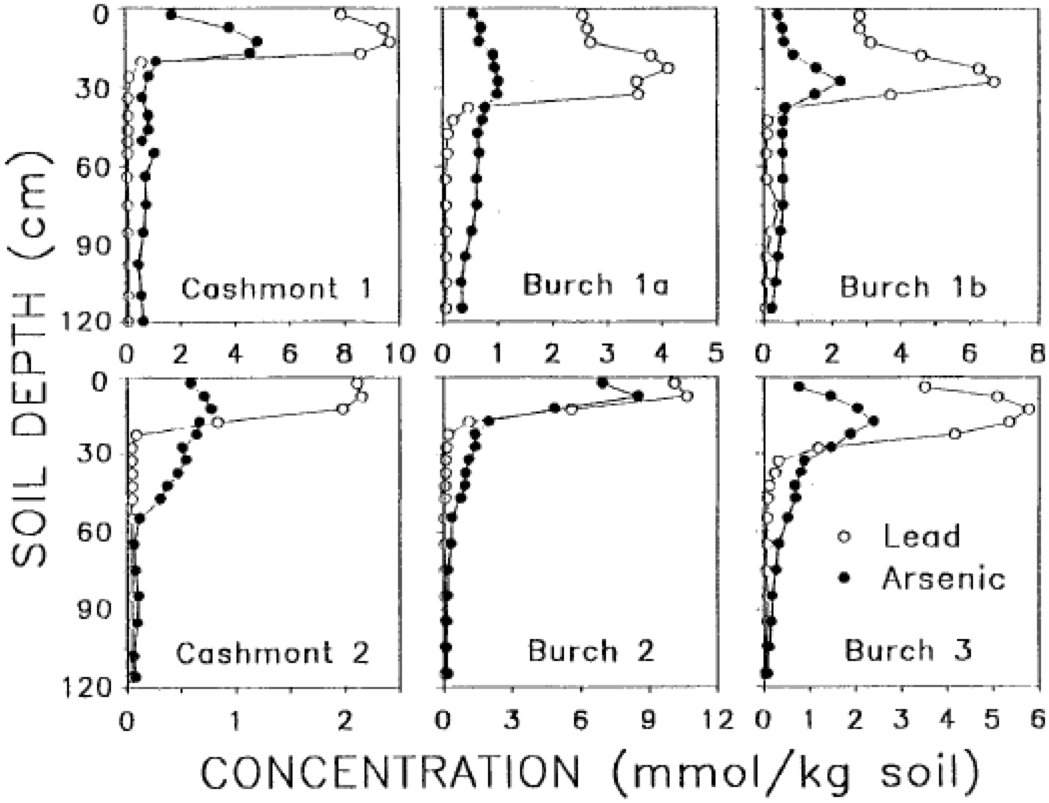


Figure 4.20. Vertical profile of lead and arsenic in six lead arsenate-contaminated orchard soils (Peryea and Creger 1994; reproduced with publisher's permission)

4.2 Evaluating the Sampling Approach to Optimize Sampling for the Remedial Investigation

The sampling approach for the pilot study was designed to provide information for improving the approach in the remedial investigation for the 100-OL-1 OU. This section discusses the results of the pilot study to address questions about the spatial variability of lead arsenate residues, evaluate the size for the decision units, and optimize the boundaries of the decision units for characterization.

4.2.1 Estimating the Spatial Variability

The XRF analyzer was used to survey the soil within the area identified for collection of the site-specific reference material. Note: This special study is provided for information only, and the quality assurance procedures for precision testing the XRF was not conducted prior to collection of information in the field. To understand the spatial variability, three separate locations were evaluated as a transect (section 2.6): one with concentrations well in excess of the screening criteria (OL-14), one with concentrations close to the screening criteria (OL-14), and one with concentrations less than the screening criteria (IU6-4). All the data is included in Appendix D. Figure 4.21 shows the results for lead and arsenic concentrations at the IU6-4 decision unit. These results indicated that the spatial variability was large and irregular. However, overall the RSD for both lead and arsenic was less than 100% (Table 4.2). The RSD of each transect was also less than the RSD of each decision unit in the pilot study (Table 4.1). The results of the transect studies support the need to evaluate the decision units, assuming a high degree of spatial variability, and support the need to select the number of locations to measure in a decision unit based on a determined statistical confidence.

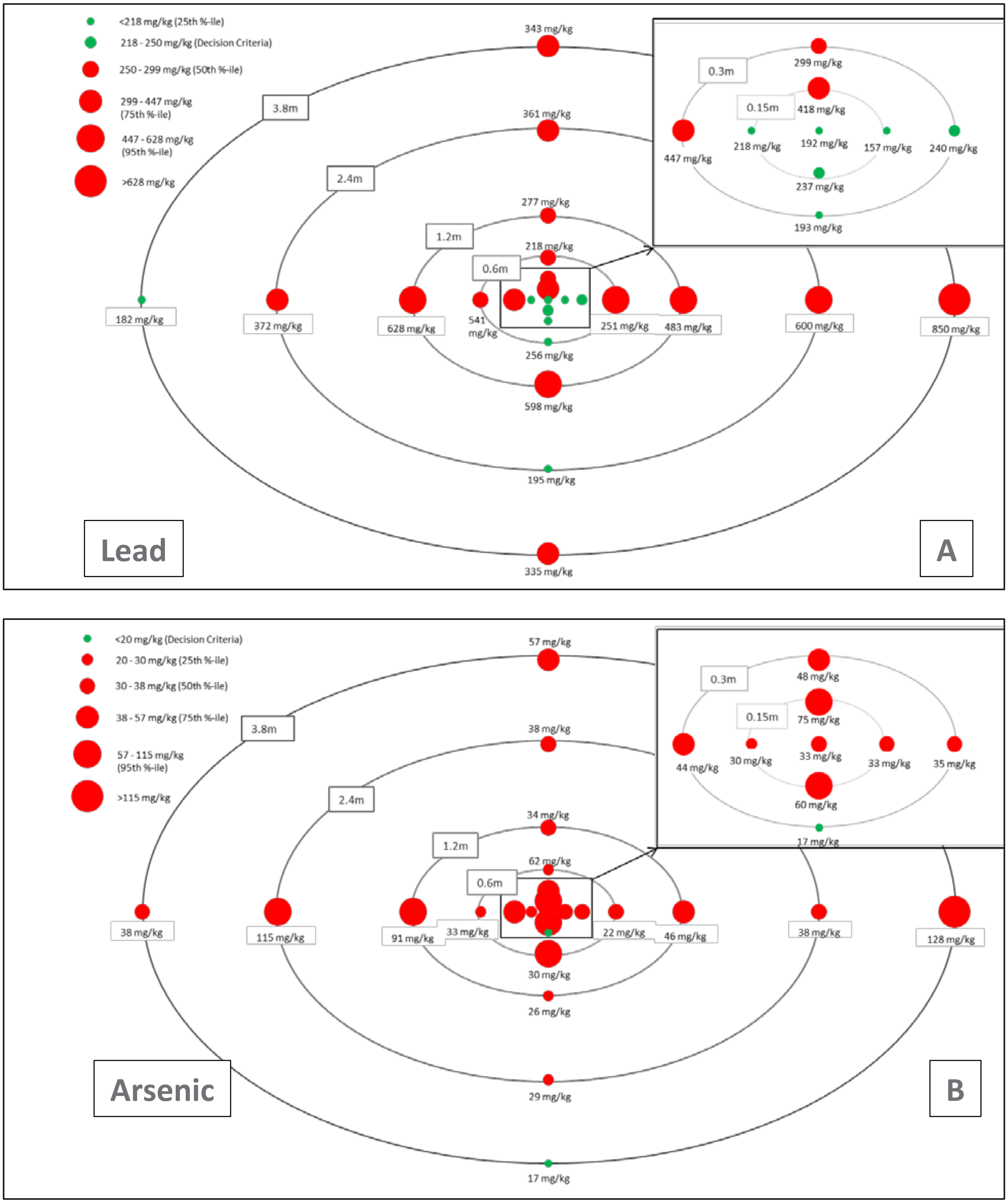


Figure 4.21. Spatial representation of lead (A) and arsenic (B) concentrations in surface soils for a transect at IU6-4. Inset on the right upper corner shows values measured at the center of the transect and at 0.15 and 0.3 m. Note: Data in figure is for information only.

Table 4.2. Summary statistics for transect sampling conducted with the XRF analyzer. Note: Data in figure is for information only.

	OL-14 Transect Site 1[a]		OL-14 Transect Site 2[b]		IU6-4 Transect Site 3[c]	
	Lead	Arsenic	Lead	Arsenic	Lead	Arsenic
Number of Samples	29	29	29	26[d]	25	25
Average (mg/kg)	513	61	122	18	356	47
Maximum (mg/kg)	1442	154	453	67	850	128
Minimum (mg/kg)	50	10	20	5[d]	157	17
Standard Deviation	372	46	95	15	176	28
RSD	73%	76%	78%	81%	50%	60%

(a) Near location 16 in OL-14.
(b) South of location 16 in OL-14.
(c) Near location 6 in IU6-4.
(d) Three arsenic samples for transect 2 were measured at concentrations less than the detection limit. Those three results are not included in summary statistics.

The significance of the contamination in each decision unit was evaluated considering three criteria: (1) the true mean concentration is less than the screening criteria; (2) no more than 10% of the samples exceed the screening criteria; and (3) no single sample exceeds two times the screening criteria. These criteria are consistent with determining if the monitoring results are in compliance with Washington State's Model Toxics Control Act (MTCA) soil cleanup levels (WAC 173-340-740(7)(e)). The criteria are useful in screening the results and interpreting the data collected during the pilot study. Table 4.3 summarizes the comparison of the results for each decision unit to these three criteria.

None of the decision units sampled for the pilot study showed compliance with the soil screening levels and would not have passed MTCA's "three-part rule" (WAC 173-340-740(7)(e)). Since the average of the sample set is not necessarily equal to the true mean, the VSP software package was used to analyze the results to determine if, with 95% confidence, the true mean was less than the screening criteria. While the average concentration of lead and arsenic measured in the decision units was generally below, or close to, the screening criteria (Table 4.3), the maximum measured concentration in every decision unit exceeded two-times the screening criteria concentration for both lead and arsenic. In most of the decision units, more than 10% of the individual measured concentrations exceeded the screening criteria.

Table 4.3. Comparison of each decision unit and analyte for compliance with soil screening levels

		Criteria for Compliance with Soil Screening Levels			
Decision Unit	Spatial Density (sample locations per acre)	Average Concentration (mg/kg)[(a),(b)]	Number of Locations Greater than Screening Criteria	Number of Locations Greater than Two Times Screening Criteria	Maximum Measured Concentration (mg/kg)
		Lead			
OL-14	0.86	214	13 (33%)	4	1111
OL-32	1.4	260	8 (20%)	4	4187
FR2-1	0.83	81	2 (5%)	1	1303
IU6-4	0.16	101	7 (18%)	1	758
		Arsenic			
OL-14	0.86	21	14 (35%)	7	113
OL-32	1.4	27	13 (33%)	4	415
FR2-1	0.83	9.8	2 (5%)	1	117
IU6-4	0.16	14	9 (23%)	3	112

(a) Averages were calculated by replacing non-detected results with the MDL for calculation purposes.

(b) Screening criteria: 250 mg/kg lead, and 20 mg/kg arsenic.

(c) Red shading indicates results that exceed the criteria for evaluating compliance with the screening level.

4.2.2 Evaluating the Size of Decision Units

Dividing the 100-OL-1 OU into decision units provides defined areas to be evaluated for lead arsenate residues and provides information for the feasibility study. The selection of decision units for the pilot study is discussed in section 2.1. The XRF results for the pilot study are evaluated in this section to support recommendations for operation (count time) of the XRF analyzer, the size of the decision unit, and the number of locations to evaluate in a decision unit.

During sample collection at OL-IU6-4, data were collected to assess results using a 30-second count duration. To accomplish this, the arsenic and lead concentrations after 30 seconds were read from the XRF analyzer display screen and recorded on the field data sheet. These data were then compared to the final result recorded by the XRF analyzer after a 60-second count duration. Thus, the result after 30 seconds could be directly compared to the results of the soil at exactly the same location after 60 seconds, with no variability associated with a different XRF scan or change in the soil location. Seventeen sampling locations were compared in this manner for the three replication measurements at a location, providing 51 samples with paired results. The results indicate that a 30-second count duration provides a result that does not differ significantly from the result provided by a 60-second count duration (Figure 4.22). Additionally, the RSD of the three replicates at a location was compared for both 30- and 60-second count durations. The range of RSD for detectable concentrations of both lead and arsenic measured with a 30-second count duration was similar to the range observed after a 60-second count duration (Figure 4.23). The RSD was less than 20% for nearly all the samples, which is consistent with the count duration assessment performed with site-specific reference material (see section 3.1.2). The only apparent disadvantage of using a 30-second count duration is the practical quantification limit for measuring arsenic. When using a 30-second count duration, the XRF instrument did not report detectable concentrations of arsenic below 6 mg/kg. When a 60-second count duration was used, the instrument reported detectable concentrations down to 4 mg/kg. This resulted in 35 of the 51 samples being reported as non-detectable when a 30-second count duration was used, while only 17 of the 51 samples were reported as non-detectable when a 60-second count duration was used. Since the screening criteria for arsenic is 20 mg/kg, the slightly higher quantification limit of 6 mg/kg arsenic would not affect the assessment of a decision unit. That is, the quantification limit would still be less than half of the 20 mg/kg screening criteria for arsenic, and a 30-second count duration would be appropriate. If the screening criteria were lower than 20 mg/kg for arsenic, then a 30-second count duration might not be appropriate.

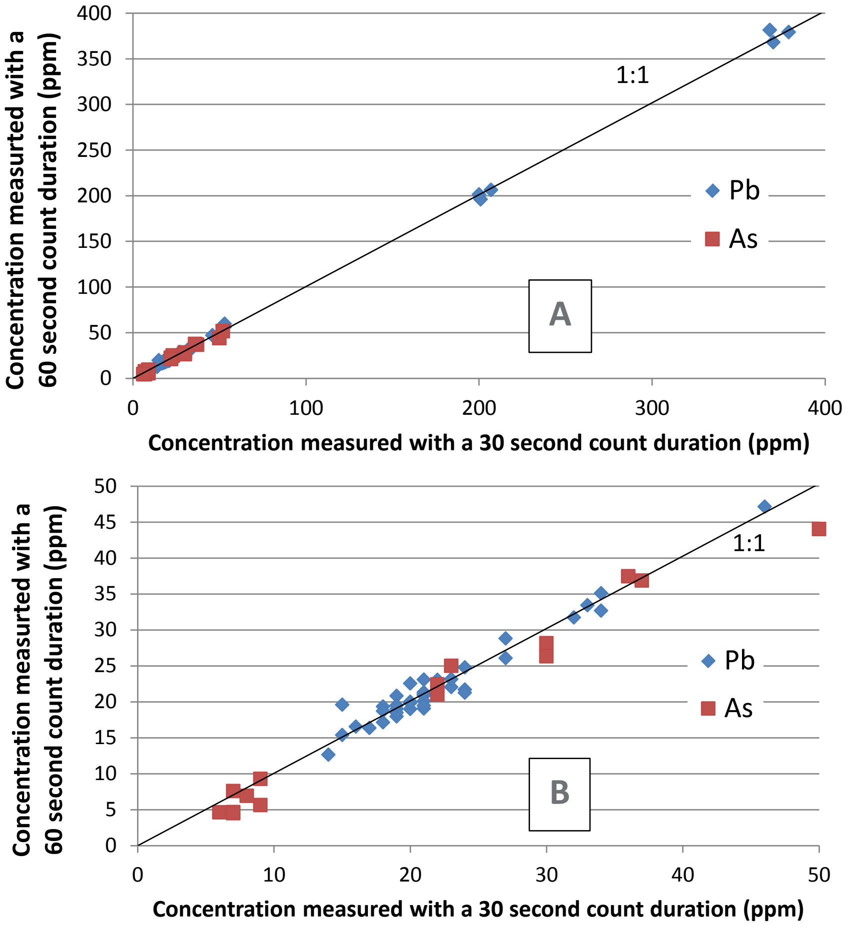


Figure 4.22. (A) Comparison of results obtained using 30- and 60-second count durations, and (B) same data focusing on the samples with lower concentration

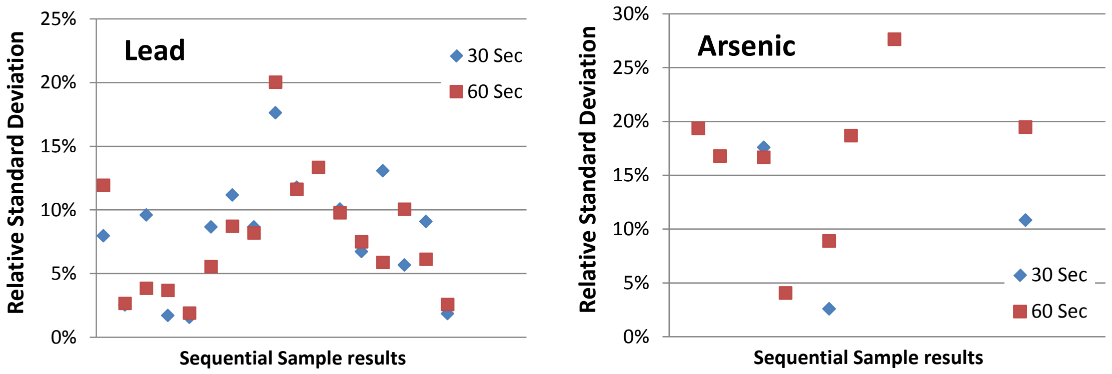


Figure 4.23. RSDs of three replicates analysis for detectable lead and arsenic concentrations measured with 30- and 60-second count durations

The pilot study measured the soil concentration at 40 locations in decision units ranging from 28 to 250 acres (Table 2.1), which were more than enough locations to evaluate the results for determining if the average concentration across a decision unit exceeded the screening criteria with a 95% upper confidence limit (DOE-RL 2014). The distribution of lead and arsenic concentrations in the decision units was different from what was predicted by the initial conceptual site model for understanding the areas exceeding the soil screening criteria. Most of the decision units considered across the 100-OL-1 OU would probably not pass the comparison for screening criteria (Table 4.3). Considering the summary statistics for the results of the four decision units (Table 4.1), the current methodology used to define the size (acreage) of the decision units and the number of locations evaluated in a decision unit could be improved.

One approach to address the size (acreage) of the decision unit would be to define the area of the decision units to be less than a predetermined number of acres. With several of the decision units being considered, more than 40 locations would be necessary for the analysis to state with 95% confidence that the average concentration did not exceed the screening criteria. The number of locations measured in a decision unit is related to the range of concentrations across the area. If there are elevated concentrations in the decision unit, the RSD increases significantly. As demonstrated in the pilot study, the RSD measured at the decision units varied between 125% and 266%. To demonstrate the relationship of the locations measured to the RSD, the results in the pilot study decision units were separated into two groups: “low” concentration and “high” concentration. For this example, the decision units were separated into two distinct portions along straight lines using professional judgment. Table 4.4 summarizes the results of the “low” concentration group. The results of the “low” concentration group would pass the criteria for compliance with the soil screening levels (as evaluated in Table 4.3). The “high” concentration group results are not summarized, and would not pass the criteria for compliance with the soil screening levels.

Table 4.4. Summary statistics for "low" concentration group within each decision unit

Decision Unit	OL-14		OL-32		FR2-1		IU6-4	
Analyte	Lead	Arsenic	Lead	Arsenic	Lead	Arsenic	Lead	Arsenic
Average	40	6.8	59	8.5	30	6.3	48	8.7
RSD	91%	49%	102%	69%	103%	60%	169%	115%
Number of samples	23		22		35		23	
Compliance with soil screening levels?	Yes		Yes		Yes		Yes	

The results of the pilot study can be analyzed to evaluate the size of the defined area to be measured considering the spatial density of sampling locations within a decision unit. From a statistical perspective, the spatial density of sampling results does not affect the assessment of whether a decision unit meets the tests for compliance with soil screening levels. However, from a characterization perspective, the spatial density of data is important and contributes to the evaluation of options in the feasibility study. The spatial density of the four decision units in the pilot study varied (Table 4.3). OL-32 had the highest spatial density (1.4 sample locations per acre) because it was the smallest decision unit analyzed (28.7 acres); IU6-4 had the lowest spatial density (0.16 sample locations per acre) because it was the largest decision unit (250.6 acres).

To evaluate the appropriate spatial density for the remedial investigation during the pilot study, one decision unit was sampled twice. That is, 40 locations were measured with the XRF analyzer at OL-14 on two different days. For the second analysis, a new set of coordinates was calculated using the same methodology that was used for the first set (section 2.2), but with a different random starting location. However, the second data set was not validated according to project procedures, and is available for information only. These two data sets for OL-14 are compared to determine if different conclusions would have resulted from a more spatially rich data set.

Figure 4.24 shows a side-by-side comparison of the lead results in the surface soil at different locations evaluated in OL-14, and it is easy to see the same general area in the decision unit exceeds the screening criteria. In both cases, the area that exceeds the screening criteria (and can generally be considered affected by residual lead arsenate contamination) constitutes half of the area, and is the northeast portion of the decision unit.

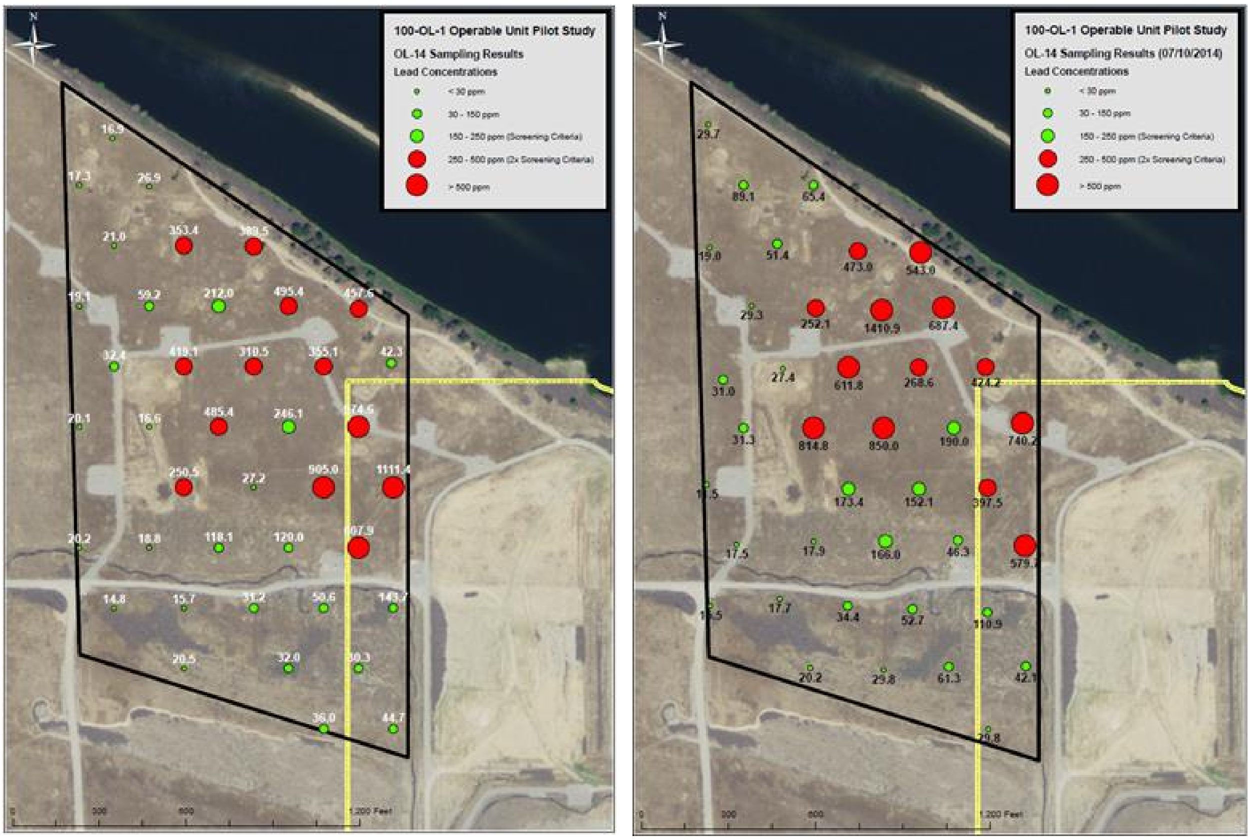


Figure 4.24. Comparison of results for lead obtained from OL-14 during two different sampling efforts. Note: Data from the figure on the right is for information only.

A quantitative comparison of the summary results obtained for the two sampling efforts on OL-14 indicates that there is very little difference in the results (Table 4.5). The average concentration measured during the primary data set was slightly lower for both lead and arsenic compared to the secondary data set. Similarly, the number of results that exceeded two times the screening criteria was lower during the primary sampling. However, both data sets would have resulted in the decision unit failing the test for compliance with soil screening levels for both lead and arsenic. And, in both instances, lead would have failed for two of the three tests, and arsenic would have failed for all three tests for compliance with soil screening levels.

Table 4.5. Summary statistics for two data sets collected at OL-14 and comparison for compliance with soil screening levels. Second data set is for information only.

	Average Concentration (mg/kg)[(a)]	Standard Deviation (and RSD)	Number of Locations Greater than Screening Criteria	Number of Locations Greater than Two Times Screening Criteria	Maximum Measured Concentration (mg/kg)
			Lead		
OL-14 - Primary	214	284 (132%)	13 (33%)	4	1111
OL-14[(b)] - Secondary	240	318 (132%)	13 (33%)	8	1411
			Arsenic		
OL-14 - Primary	21	26 (125%)	14 (35%)	7	113
OL-14[(b)] - Secondary	27	34 (126%)	12 (30%)	10	135

(a) Averages were calculated by replacing non-detected results with the MDL.
(b) These data are for information only.
(c) Red shading indicates results that exceed the criteria for evaluating compliance with the screening level.

The OL-14 decision unit is 46.4 acres, and was sampled each time with a spatial density of sampling locations of 0.86 sample locations per acre. The distribution of the lead and arsenic concentrations across the decision unit does not change when both sets of data (80 locations; 1.7 sample locations per acre) are shown together (Figure 4.25). Based on the results obtained at OL-14, this spatial density of 0.86 sample locations per acre appears to be sufficient to adequately characterize the lead arsenate residues across a decision unit.

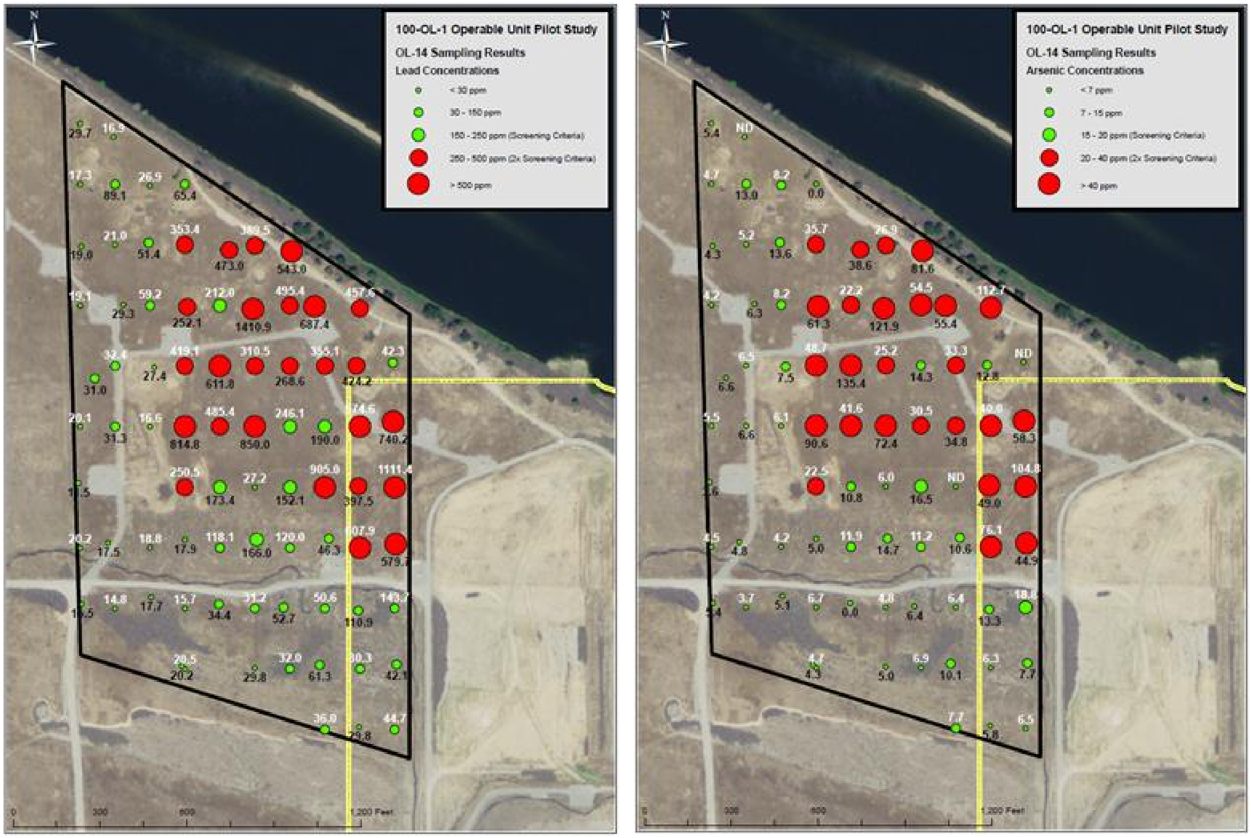


Figure 4.25. Combination of results for lead (right) and arsenic (left) from the primary (white results) and secondary (black results) data sets in OL-14. Note: Secondary data is for information only.

While 40 locations within a decision unit of 46.4 acres appears adequate, lower spatial densities (fewer sample locations per acre) was considered using the secondary data set collected from OL-14 (collected for information only). For this assessment, the results for the 40 locations were summarized in two batches of 20 samples (even and odd location points within the decision unit) and one batch of seven locations (randomly chosen within the decision unit using a random number generator). This provided a comparison of the decision unit size relative to the screening criteria for different spatial densities, and was representative of the spatial densities for FR2-1 and IU6-4 (Table 4.3). Table 4.6 demonstrates that the summary statistics of the sampling results were very similar for the different spatial density scenarios evaluated. For OL-14, the same conclusion would have been reached even if only seven samples had been collected across the decision unit. All three additional scenarios evaluated failed two of the three tests for compliance with soil screening levels. The results of this assessment indicate that a sample collection frequency of one sample for every 6.7 acres (0.15 sample locations per acre) would be an adequate spatial density for evaluating the lead and arsenic concentrations to the tests for compliance with soil screening levels. Note that the collection frequency and spatial density of 0.15 sample locations per acre is similar to the spatial density for IU6-4 decision unit (Table 4.3)

Table 4.6. Summary statistics for the secondary set of locations measured in OL-14 and comparison for compliance with soil screening levels. Data is for information only.

OL-14 Secondary Data Set	# of Samples	Spatial Density (locations per acre)	Average Concentration (mg/kg)(a)	Standard Deviation (and RSD)	Number of Locations Greater than Screening Criteria	Number of Locations Greater than Two Times Screening Criteria	Maximum Measured Concentration (mg/kg)
Lead							
All Locations	40	0.86	240	318 (132%)	13 (33%)	8	1411
Odd locations	20	0.43	259	263 (101%)	8 (40%)	5	815
Even locations	20	0.43	222	372 (168%)	5 (13%)	3	1411
Random locations	7	0.15	177	240 (136%)	2 (29%)	1	612
Arsenic							
All Locations	40	0.86	27	34 (126%)	12 (30%)	10	135
Odd locations	20	0.43	33	37 (113%)	8 (40%)	7	135
Even locations	20	0.43	21	30 (144%)	4 (10%)	3	122
Random locations	7	0.15	25	49 (199%)	1 (14%)	1	135

(a) Averages were calculated by replacing non-detected results with the MDL.
(b) Red shading indicates results that exceed the criteria for evaluating compliance with the screening level.

Another way to illustrate the number of locations needed to determine with 95% confidence that a site is “clean” is demonstrated with varying the average concentration and the RSD for a decision unit. This evaluation is based on VSP’s true average verses fixed threshold analysis option, assuming non-normally distributed data, and the lower bound of the gray region set to 1/10th of the screening criteria concentration. The Shapiro-Wilk test demonstrated that, with 95% confidence, the results across all locations in each decision unit are not normally distributed (Matzke et al. 2010; EPA 2002). The gray region is related to the Type II error rate (Beta) or the false acceptance rate, which is the probability of assuming the area is “dirty” when it is “clean” (EPA 2002). For this analysis, we chose 25 mg/kg lead as an acceptable lower bound to the gray region. If the true mean is above 25 mg/kg lead, but below 250 mg/kg lead (screening criteria), there would be a 5% chance of classifying the decision unit, or a portion of the decision unit, as “dirty” when it was actually “clean.” Using a similar approach with lead, we chose 2 mg/kg arsenic as an acceptable lower bound to the gray region, that is, a 10/1 ratio between the screening criteria and the lower bound of the gray region for both lead and arsenic. The RSDs used in this analysis are based on the range for the measured locations across the decision units in the pilot study.

Table 4.7 shows the results of the analysis with VSP and the number of locations for evaluation in a decision unit based on different average concentrations of an analyte and different RSDs for the distribution of contamination in the area. As few as 11 sampling locations could be analyzed with XRF within a decision unit that has an average lead concentration of 30 mg/kg. With a concentration this low, the number of locations necessary was independent of the RSD. Additional locations need to be analyzed in a decision unit if the average concentration or the RSD increases. That is, since the average concentration of a "low" concentration group within a decision unit is less than the average of the entire decision unit, fewer samples are necessary to determine, with 95% confidence, that the true mean does not exceed the screening criteria (Table 4.7).

Table 4.7. Number of locations required to determine, with 95% confidence, that a site is clean for various average concentrations and RSDs

Average Concentration of Analyte (mg/kg)		Number of Locations within a Decision Unit)			
Lead	Arsenic	100% RSD	125% RSD	185% RSD	250% RSD
30	2.4	11	11	11	11
50	4	11	11	12	13
100	8	12	13	18	28
150	12	15	19	32	54
250	20	28	39	78	137

The results of this study also highlighted the need to refine the operable unit boundaries. At some of the decision units evaluated, it appeared that the boundary of the decision unit was not inclusive of the area that had been farmed and/or in orchards. In particular, at OL-32 there were tree stumps and branches visible outside of the decision unit boundary.

4.3 Information for Consideration to Improve the Remedial Investigation

The pilot study provided information that could be used to improve the planning of the remedial investigation for the revised work plan. The process for ecological and cultural resources clearance to work in the field with the XRF analyzer provided a basis for future work. The approach for analysis of a decision unit provided a basis for conducting further evaluations of the decision units in the field.

The ecological and cultural resources clearance for working in the pilot study decision units opened a dialogue with DOE, site contractors, and cultural resources monitors that provides a basis for planning the remedial investigation. The process, as documented in Appendix B, includes performing the work at times of the year when ecological resources will likely not be disturbed by activities. The predetermined sampling locations were compared to buffer areas established to minimize the disturbance of wildlife. If necessary, sampling locations could be moved away from sensitive species, or the area could be evaluated during a different season when the disturbance would be minimal. The ecological review process can contribute to the order for evaluating the decision units during the remedial investigation and minimize any disturbances to the wildlife.

Evaluating the contamination of surface soils with the XRF analyzer minimized soil disturbances. However, the collection of soil for the site-specific reference material and the confirmatory samples for ICP-MS analyses required removal of soil below the surface, deeper than required for the XRF analysis. The clearance process included a previously reviewed project analysis conducted in accordance with the

National Historic Preservation Act (NHPA), as amended, and implemented regulation 36 CFR Part 800. Regions within 100-OL-1 OU that had previously been evaluated under Section 106 of NHPA were identified in OL-14 and IU6-4. The soil samples collected in these locations were useful for understanding the variability of the soil contamination and QA of the XRF analyzer (section 3.1). The cultural resource monitors during the soil collection helped to establish some of the protocols for the field sampling. The same cultural resources clearance process could be conducted for the remedial investigation and contribute to the order for evaluating the decision units.

Field evaluations were completed with three to four staff and one XRF analyzer. One or two people found the sample location using predetermined coordinates from VSP, started a field data sheet, cleared the area for the XRF analyzer, placed a flag and the data sheet at the position, and moved to the next sample location. Two people trailed with the XRF analyzer, conducted the three replicate analyses of the cleared surface soil, and completed the field data sheet. Each location was analyzed within 5 to 7 minutes, including 3 minutes to conduct the three replicate soil analyses with the XRF analyzer. A typical field day included approximately 2 hours of travel time and 1 hour for precision checks with the XRF analyzer. The field teams easily finished analyzing the 40 sample locations within 5 hours for all the decision units, including the 250 acres of IU6-4.

More than one field team could be deployed if additional XRF analyzers were available. One concern would be establishing QC and QA criteria for comparison of multiple XRF analyzers. Prioritizing decision units for analyses based on ecological and cultural resources concerns would be a consideration in the deployment of multiple teams. For example, if disturbances of ecological resources are minimized by sampling in the summer months, more field teams could keep the remedial investigation on schedule and offset the additional cost of multiple XRF analyzers.

The schedule for the remedial investigation needs to be flexible to address weather conditions. Light rain occurred on July 22 and 25, 2014, while field sampling at FR2-1, and on one of the two days for sampling IU6-4. The rain was so light that the Hanford meteorological reports for stations 5 and 16, closest to IU6-4 and FR2-1, did not record any precipitation during the field sampling. Fortunately, the process to clear away the vegetation cover and prepare the soil surface for the XRF analysis exposed dry soil during those days. The average temperature for the field work in June and July was 80°F, but the maximum temperature was over 98°F. The field teams scheduled their work to avoid the hottest times of the day. The schedule needs to allow for postponement of field activities when the XRF analyses could be compromised by soil moisture and to consider the health and welfare of the people in the field.

As discussed in section 4.2, the pilot study provided information about the count time for the XRF, the number of sample locations, and the size of the decision unit. This information can be used for the data quality objectives in the revised work plan to optimize the field sampling effort. Efficiencies by reducing the count times, replicate in situ analyses, or the number of sample location in a decision unit without compromising the quality of the results will allow the field teams to cover more ground in a day.

5.0 Recommendations

This pilot study addresses questions about the 100-OL-1 OU and provides information to improve the work plan for the remedial investigation and feasibility study. This section provides specific recommendations to address EPA and Ecology concerns regarding the work plan.

XRF analysis was performed within the QC and QA guidelines for evaluating lead as well as arsenic in surface soils as established by EPA for the field portable instrument (EPA 2007). The Niton XLt3 950 demonstrated that the analyses were precise, accurate, and repeatable. The sensitivity of the instrument was low enough to distinguish between concentrations below and at the soil screening criteria for lead (250 mg/kg) and arsenic (20 mg/kg). Confirmatory soil samples analyzed by ICP-MS and XRF (Figure 3.2) demonstrated that the XRF measurements meet QC guidelines to consider the results for screening level data and potentially meet definitive level data criteria (EPA 2007).

Recommendation: The work plan should design the characterization efforts in the remedial investigation using XRF measurements with confirmatory ICP-MS analyses.

The evaluation of the range of size of decision units in the pilot study demonstrated that the defined areas less than 50 acres (OL-14, OL-32, and FR2-1) revealed a pattern of elevated lead and arsenic concentrations. All four decision units evaluated in the pilot study failed the tests for compliance with screening levels (Table 4.3), and would require evaluation in the feasibility study. The spatial density of the evaluation of soil concentrations in IU6-4 (the largest decision unit at 250 acres) demonstrated that lead and arsenic concentrations in some of the agricultural areas exceeded the screening criteria (Figure 4.15 and Figure 4.16), but the spatial density of the results does not indicate whether there are additional areas of concern. The pattern of contamination is important information to evaluate remedial alternatives in the feasibility study. Several areas of 100-OL-1 OU exceed 50 acres in size, and these areas could be divided along roads and other land use changes based on 1943 aerial imagery. The decision units can be defined to manageable areas for conducting a field evaluation that will provide information for consideration in the feasibility study.

Recommendation: The work plan should establish decision units of similar defined areas.

Concentrations of lead and arsenic exceeding the screening criteria were found in soil samples at locations along the edges of all four decision units. In some cases, the edge of the decision unit was the border to other decision units that would be evaluated at a later date. However, in other cases, the edge of the decision unit was also the edge of the 100-OL-1 OU. To assist with questions about the area to be evaluated in the feasibility study, the remedial investigation should include a process for the field investigators to evaluate whether the contamination significantly extends away from the decision unit. The process for additional sampling along the edge of the OU should be included in the data quality objectives of the work plan.

Recommendation: The work plan should define the process for field investigation of soil concentrations exceeding the screening criteria at the edge of the 100-OL-1 OU.

The pilot study evaluated aspects of the sampling approach with the XRF analyzer to provide confidence in data for assessing areas above and below the lead and arsenic screening criteria. These include the number of locations to evaluate in a decision unit, the number of replicate soil analyses at each location, and the length of count time for the XRF analyzer to meet quality criteria for lead and arsenic data. The cost and schedule for the field activities of the remedial investigation vary based on these parameters associated with the sampling approach. Data quality objectives should define the sampling approach for the remedial investigation.

Recommendation: The pilot study results should be used in defining the data quality objectives for the work plan and to refine the sampling approach for the remedial investigation.

6.0 References

40 CFR Part 136. Code of Federal Regulations, Title 40, *Protection of the Environment*, Part 136, Appendix B, “Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11.”

Delistraty D and J Yokel. 2011. “Ecotoxicological Study of Arsenic and Lead Contaminated Soils in Former Orchards at the Hanford Site, USA.” *Environmental Toxicology*. doi:10.1002/tox.20768

DOE-RL (U.S. Department of Energy-Richland Operations Office). 1993. *Hanford Site Background: Part 1, Soil Background for Nonradioactive Analytes*. DOE-RL-92-24, Rev. 1, Richland, Washington.

DOE-RL (U.S. Department of Energy-Richland Operations Office). 2007. *Hanford Analytical Services Quality Assurance Requirements Documents.* DOE-RL-96-68, 2007, Rev. 3, Volumes 1, 2, 3, and 4. Richland, Washington.

DOE-RL (U.S. Department of Energy, Richland Operations Office). 2014. *100-OL-1 Operable Unit Field Portable X-Ray Fluorescence (XRF) Analyzer Pilot Study Plan*. DOE-RL-2014-38, Rev. 0, Richland Operations Office, Richland, Washington.

EPA (U.S. Environmental Protection Agency). 2002. *Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites*. EPA 540-R-01-003, OSWER 9285.7-41, Office of Emergency and Remedial Response, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2007. *Method 6200: Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*. Office of Solid Waste and Emergency Response, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2011. *Field X-ray Fluorescence Measurement*. Science and Ecosystem Support Division, Athens, Georgia.

Matzke BD, JE Wilson, LL Nuffer, ST Dowson, JE Hathaway, NL Hassig, LH Sego, CJ Murray, BA Pulsipher, B Roberts, and S McKenna. 2010. *Visual Sample Plan Version 6.0 User's Guide*. PNNL 19915, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://vsp.pnnl.gov/docs/pnnl16939.pdf.

MacLean KS and WM Langille. 1981. “Arsenic in Orchard and Potato Soils and Plant Tissue.” *Plant and Soil* 61:413–418.

Newton K, D Amarasiriwardena, and B Xing. 2006. “Distribution of Soil Arsenic Species, Lead and Arsenic Bound to Humic Acid Molar Mass Fractions in a Contaminated Apple Orchard.” *Environmental Pollution* 143:197–205.

Peryea FJ and TL Creger. 1994. “Vertical Distribution of Lead and Arsenic in Soils Contaminated with Lead Arsenate Pesticide Residues.” *Water, Air and Soil Pollution* 78:297–306.

Poston, TM, JP Duncan, and RL Dirkes. 2010. *Hanford Site Environmental Report for Calendar Year 2009*. PNNL-19455, Pacific Northwest National Laboratory.

Renshaw CE, BC Bostick, X Feng, CK Wong, ES Winston, R Karimi, CL Folt, and CY Chen. 2006. "Impact of Land Disturbance on the Fate of Arsenical Pesticides." *Journal of Environmental Quality* 35:61–67.

Sharpe JJ. 1999. *Pre-Hanford Agricultural History: 1900-1943*. BHI-01326, Rev. 0, Bechtel Hanford, Inc., Richland, Washington.

Staed JB, DM Miller, KR Brye, TC Daniel, C Rom, and EE Gbur. 2009. "Land Use Effects on Near-Surface Soil Arsenic in the Ozark Highlands." *Soil Science* 174:121–129.

TPA (Tri-Party Agreement). 2012. *Change Control Form: Creation of New Operable Unit for Pre-Hanford Orchard Lands Along the River Corridor of the Hanford Site*. TPA-C-12-01, May 7, 2012, U.S. Department of Energy, Richland Operations Office, U.S. Environmental Protection Agency, and Washington State Department of Ecology, Richland, Washington.

Veneman PLM, JR Murray, and JH Baker. 1983. "Spatial Distribution of Pesticide Residues in a Former Apple Orchard." *Journal of Environmental Quality* 12:101–104.

WAC 173-340-740(7)(e). "Model Toxics Control Act – Unrestricted Land Use Soil Cleanup Standards." *Washington Administrative Code*, Olympia, Washington.

Yokel J and DA Delistraty. 2003. "Arsenic, lead, and other trace elements in soils contaminated with pesticide residues at the Hanford Site (USA)." *Environmental Toxicology* 18:104–114.

Appendix A

Sampling and Analysis Plan and Quality Assurance Project Plan

Appendix A

Sampling and Analysis Plan and Quality Assurance Project Plan

A.1 Sampling and Analysis Plan Introduction

The sampling and analysis plan (SAP) for the pilot study addresses the characterization efforts necessary to evaluate the use of a field portable X-ray fluorescence (XRF) analyzer to analyze the extent of lead and arsenic soil contamination in selected decision units within the 100-OL-1 Operable Unit (OU). The sampling approach for this document was reported in the *100-OL-1 Operable Unit Field Portable X-Ray Fluorescence (XRF) Analyzer Pilot Study Plan* (DOE-RL 2014). The quality assurance project plan (QAPP), field sampling plan, and health and safety plan are discussed in sections A.2, A.3, and A.4, respectively.

A.1.1 Pilot Study Background

The pilot study was conducted to support the approval of the remedial investigation/feasibility study (RI/FS) work plan to evaluate the 100-OL-1 OU pre-Hanford orchard lands (DOE-RL 2013). Based on comments received from the U.S. Environmental Protection Agency (EPA) and Washington State Department of Ecology (Ecology), the pilot study was to evaluate the use of a field-portable XRF analyzer for evaluating lead and arsenic concentrations on the surface of the soil, as an indicator of past use of lead arsenate pesticide residue in the OU. In addition, the pilot study was to make recommendations about the size of decision units for evaluation within the OU and the associated sampling approach. The work was performed during the summer of 2014.

A.1.2 Decision Units for the Pilot Study

Table A.1 identifies the four locations within 100-OL-1 OU selected for the pilot study evaluation (see Figure A.1 for an aerial photograph of the locations). The sites are decision units, or portions of decision units, identified in the draft work plan (DOE-RL 2013). The following discusses the differences in the pilot study decision units and how these decision units represent the breadth of environmental conditions representing the 100-OL-1 OU.

Table A.1. Summary of characteristics of pilot study decision units

Decision Unit ID	Acreage	Presence of Trees in 1943 Aerial Imagery?	Evidence of Soil Disturbance Since 1943?	WIDS[(a)] Site within Decision Unit Boundaries?	Previously Sampled?
OL-14	46.4	Yes	Yes	Yes	Yes
OL-32[(b)]	28.7	Yes	No	No	Yes[(c)]
FR2-1[(b)]	48.0	No	Yes	Yes	Yes
IU6-4	250.6	Yes	Yes	Yes	Yes

(a) Waste Information Data System

(b) These decision units are a portion of the areas defined with the same name in the draft work plan (DOE-RL 2013).

(c) Yokel and Delistraty 2003; Delistraty and Yokel 2011

OL-14 is located to the northwest of 100 H Area, near the Columbia River (Figure A.1). Historical records indicate that this area was a commercial orchard operation prior to March 1943, and later was a military site. Cleanup actions in this area focused on soil contamination from military activities. Currently, there are several locations with wells for pump and treat activities. Past sampling activities indicate the presence of lead concentrations ranging from background (10 mg/kg) to greater than 500 mg/kg. The U.S. Department of Energy (DOE) Richland Operations Office (RL) Cultural Resources Program approved a small region of OL-14 for soil sampling (Appendix B). In the designated area for soil sampling, soil was collected for the site-specific reference material and confirmatory samples.

OL-32 is located south of 100 H Area (Figure A.1). The area remains relatively undisturbed; tree stumps and branches from past orchards are still evident at this location. There are no signs of soil disturbances since orchard operations ceased, and there are no known waste sites in this decision unit. Yokel and Delistraty (2003) and Delistraty and Yokel (2011) discuss previous sampling efforts in this location. No soil samples were collected in OL-32.

FR2-1 is located in the southeast corner of 100 F Area (Figure A.1). In 1943 aerial imagery, there are no trees similar to those in other known orchard locations, but there does appear to be agricultural activities in the decision unit. The decision unit has been disturbed by activities associated with the operation of the 100 F reactor (e.g., burial grounds and process sewer), and the decision unit overlaps with the 100-FR-2 OU. No soil samples were collected in FR2-1.

IU6-4 is located north of the Hanford townsite (Figure A.1). This is the largest of the decision units for the pilot study. The 1941-1943 aerial imagery shows that most of this decision unit was used for orchards and other agricultural activities. Several areas of the decision unit were disturbed by past agricultural activities and remediated as part of the River Corridor activities (less than 5 acres), e.g., the removal of the Buckholdt Ranch toilet pits and several barrels of lime sulfur. The Critical Mass Laboratory Complex from the Cold War era was also located in this decision unit and is currently in the interim closeout process. The DOE-RL Cultural Resources Program approved a small region of IU6-4 for soil sampling. In the designated area for soil sampling, soil was collected to prepare the site-specific reference material and confirmatory samples.

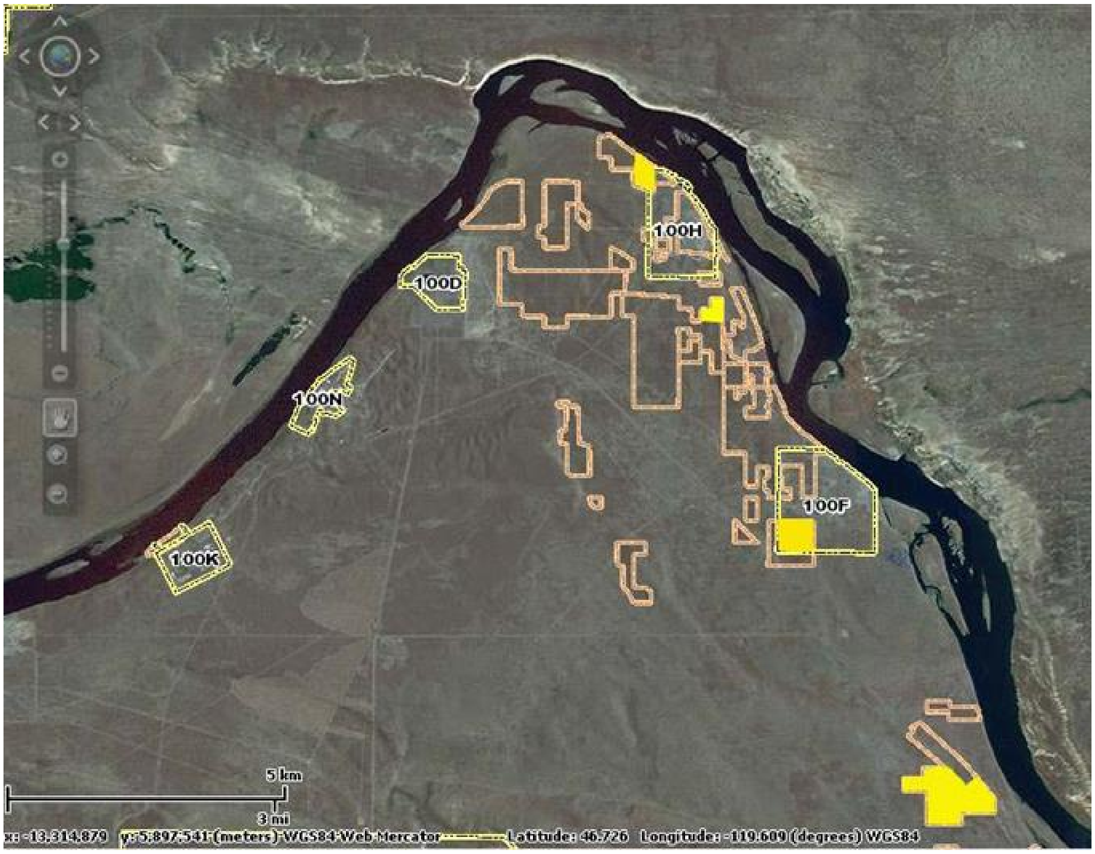


Figure A.1. Pilot study decision units (yellow fill) within the 100-OL-1 OU

A.1.3 Analytes of Concern

The data quality objectives (DQOs) for the draft RI/FS work plan for the 100-OL-1 OU identified lead and total inorganic arsenic in soil as the only contaminants of concern for the characterization efforts. DQOs were identified during meetings with program managers and technical leads from DOE-RL, Ecology, and EPA. The decision was to limit the contaminants of concern to lead and total inorganic arsenic based on the conceptual site model for evaluating lead arsenate residues, research on historical orchard practices in the region, and the limits of the Tri-Party Agreement (TPA) description of the 100-OL-1 OU (TPA 2012a, b). Delistraty and Yokel (2011) demonstrated that more than 99% of the total inorganic arsenic existed as arsenic (V) in the surficial soils of the orchards sites evaluated. This supports the decision to characterize only for total inorganic arsenic. The description and justification for the 100-OL-1 OU (TPA 2012a) identified contamination from lead arsenate in the non-contiguous historical orchard lands on the south side of the Columbia River.

A.1.4 Screening Criteria for Evaluating Lead and Arsenic in Surface Soil

DOE-RL, Ecology, and EPA identified the following screening criteria for the lead and arsenic in the pilot study (DOE-RL 2014):

- 250 mg/kg lead (total)
- 20 mg/kg arsenic (total)

A.1.5 Data Needs

The data needs for the pilot study included ecological and cultural resources compliance reviews, soil samples for site-specific reference material, and compliance sampling for inductively coupled plasma mass spectroscopy (ICP-MS) analyses.

A.1.5.1 Ecological and Cultural Resources Compliance Review

Ecological and cultural resource specialists reviewed the plans for the pilot study to determine if there were any sensitive resources that could be disturbed at the time of the field activities and in the specific locations selected for analyses (Appendix B). Plants were not of concern because the field samplers were not to drive off road and the XRF and soil sampling did not require removal of plants. During the field sampling season, there were very few bird species in the area that could be disturbed from nests or burrows. No locations were relocated to avoid ecological resources.

Prior to starting the pilot study, the DOE-RL Cultural Resources Program considered the sampling approach for the pilot study, and determined that the XRF measurements would not cause a soil disturbance. The XRF analyzer needed an area of 60 cm^2 of soil cleared of debris for a measurement. Removal of soil for the site-specific reference material and confirmatory analysis required more consideration. The clearance process included a previously reviewed project analysis conducted in accordance with the *National Historic Preservation Act* (NHPA), as amended, and implemented regulation 36 CFR Part 800. Those regions within 100-OL-1 OU previously evaluated under section 106 of NHPA were in OL-14 and IU6-4. Soil was collected only from the small portions of these decision units, and cultural resource specialists monitored the collection process.

A.1.5.2 Soil Samples for Site-Specific Reference Material

Empirical calibrations of the XRF analyzer (EPA 2007a) used soil collected from OL-14 and IU6-4. The XRF analyzer was used in a screening capacity (30-second count times) to select locations for soil collection. In total, seven soil samples were collected on June 13, 2014: four from decision unit OL-14 and three from decision unit IU6-4 (Table A.2). The targeted concentrations were soils with lead and arsenic concentrations close to the screening criteria (250 mg/kg and 20 mg/kg, respectively), and then soil with concentrations both above and below the screening criteria.

To collect the soil samples, the soil surface was cleared of any non-representative debris (rocks, vegetation, roots) with an acid washed polypropylene spatula (24 cm long; McMaster-Carr, Sante Fe Springs, CA). An acid-washed, 1.9 L polyethylene scoop (15.5 cm wide, 21 cm long; McMaster-Carr, Sante Fe Springs, CA) was used to remove several kilograms of surface soil (top 15 cm) and the soil was put into pre-cleaned, 2 L, high-density polyethylene bottles (VWR Scientific, Radnor, PA). To acid wash equipment that was not pre-cleaned and sealed to Level 1 quality assurance (QA) standards by the manufacturer, the equipment was soaked for 24 hr in 10% double-distilled nitric acid and rinsed four times in deionized water. Each bottle was labeled with the sample ID and the approximate soil concentrations, as measured by the XRF analyzer. Additionally, latitude and longitude of each sample collection location was measured (Montana GPS, Garmin, Olathe, KS) and recorded on each sample jar.

In a laboratory at Pacific Northwest National Laboratory (PNNL), the soil samples were homogenized and stored for optimization studies and as daily instrument checks for the XRF analyzer. Sample preparation first involved the removal of large non-soil particles (e.g., rocks and vegetation). The sample was spread out on a clean sheet of paper (Whatman Benchkote 2300-594) and the non-soil particles were removed manually. The sample was then homogenized by placing 150 to 200 g of soil on parchment paper (45 × 45 cm), alternately lifting corners, and rolling the soil onto itself towards the opposite corner 20 times (EPA Method 6200). The site-specific reference material was stored in the original container once homogenization was complete.

Subsamples of site-specific sample material were analyzed with the XRF analyzer as well as with ICP-MS. Empirical calibration involved three of the site-specific reference material soil samples. The soil samples ranged below, above, and around the screening criteria for lead and arsenic. Each field sampling day, the XRF analyzer was checked using these samples.

Table A.2. Site-specific reference material collected from OL-14 and IU6-4 on June 13, 2014

Decision Unit	Sample ID	Sample Coordinates	Use of Sample
OL-14	OL-14-L	N: 46.71070 W: 119.49406	
	OL-14-M1[(a)]	NA	
	OL-14-M2[(a)]	NA	Daily Instrument Check
	OL-14-H	N: 46.71065 W: 119.49327	
IU6-4	IU6-4-L	N: 46.60656 W: 119.42300	
	IU6-4-M	N: 46.60696 W: 119.42300	Daily Instrument Check
	IU6-4-H	N: 46.60663 W: 119.42283	Daily Instrument Check

(a) Soil from OL-14-M filled two containers, labeled M-1 and M-2.

A.1.5.3 Confirmatory Soil Samples

The XRF analyzer is a screening tool for field use, and the results are to be compared to another analytical technique for confirmation (EPA 2007a). Confirmatory soil samples were collected on July 17, 2014, in the same manner as the site-specific reference material. The eight soil samples were analyzed by both XRF and ICP-MS. The number of confirmatory samples satisfied the guidance in EPA Method 6200 for a minimum of 1 sample submitted for confirmatory analysis for each 20 XRF analyzed samples.

A.1.6 Sampling Design

The *100-OL-1 Operable Unit Field Portable X-Ray Fluorescence (XRF) Analyzer Pilot Study Plan* (DOE-RL 2014) describes the sampling design for evaluating with XRF the decision units for the pilot study. The probability-based sampling design provides the best approach for evaluating the nature and extent of lead and arsenic soil concentrations within the pilot study decision units (EPA 2002; DOE-RL 2013). A probabilistic sampling design, compared to a judgmental sampling design, allows for statistical inferences about the sampled population and the data obtained from the sampled units. This design meets the approach for evaluating the average concentration of lead and arsenic in a decision unit and for comparing the average to the 95th percentile upper confidence limit for the lead and arsenic screening criteria. The layout of the sampling locations within a decision unit was selected using a random-start, systematic-grid-sampling design. The Visual Sampling Plan tool (Matzke et al. 2010) identified the sample locations prior to field activities. Some sample locations within the decision units were relocated at the discretion of the field team when the location was disturbed or had substantial vegetation (e.g., piles of tumbleweeds). Examples of disturbances requiring relocation of the field measurement point were layback areas from remediation activities (that were not included in the GIS information for WIDS), groundwater well pads, and abandoned materials from past settler activities. Field samplers relocated the measurements to the closest area that has not been disturbed and recorded the GPS location.

The XRF analyzer measured the lead and arsenic concentrations in 40 surface soil samples. This number of samples is based on (1) a review of the lead measurements in soil across the 100-OL-1 OU, the background of lead in soil, and the screening criteria for evaluating lead contamination; and (2) a review of past results of soil analyses in the 100-OL-1 OU and a best estimate for providing sufficient information to allow statistical evaluation of the field results and meet the screening criteria for the pilot study. Based on the variability of arsenic, 26 surface soil samples (DOE-RL 2013) are needed. Additional measurements will allow further statistical analyses for the remedial investigation sampling design.

A.1.7 Project Schedule

The field sampling activities for the pilot study were completed by July 2014, and the ICP-MS results were available by September 2014. Dates of critical field activities in the pilot study are in Table A.3. This information will assist with future planning purposes.

Table A.3. Schedule of field activities for the pilot study

Date	Activity
June 5, 2014	Received ecological and cultural clearance
June 11, 2014	Received Niton XL3t 950 XRF from Thermo Scientific
June 16, 2014	Collected site-specific reference material soil samples from OL-14 and IU6-4
July 10, 2014	Completed initial set of 40 field sampling locations at OL-24, called “secondary sample set” (results for information only)
July 15, 2014	Completed field sampling at OL-32
July 17, 2014	Collected confirmatory soil samples from OL-14 and IU6-4. Started field sampling at IU6-4.
July 22, 2014	Completed field sampling at IU6-4. Started field sampling at FR2-1.
July 25, 2014	Completed field sampling at FR2-1
July 31, 2014	Completed sampling at OL-14, called “primary sample set” (data for decision purposes)

A.2 Standard Operating Procedure for XRF Analyzer

The standard operating procedure is based on EPA Method 6200, *Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentration in Soil and Sediment* (EPA 2007a), and the Niton XL3 guide for soil analysis (Thermo Scientific). It is applicable for the analysis of lead and total inorganic arsenic in soil, as well as other metals of environmental concern. This procedure is for the soil analysis mode of the Niton XL3, and is optimum for any sample whose elements of interest are present at less than 1%. The Niton XL3 XRF can analyze for the following elements in standard soil mode: Ba, Cs, Te, Sb, Sn, Cd, Ag, Pd, Zr, Mo, Sr, U, Rb, Th, Pb, Se, As, Hg, Zn, Au, W, Cu, Ni, Co, Fe, Mn, Cr, V, Ti, Sc, Ca, K, and S.

The method detection limit (MDL) for the Niton XL3t 950 XRF analyzer was determined using site-specific reference material in accordance with 40 CFR 136, Appendix B. The MDL is 2.6 mg/kg for lead and 3.9 mg/kg for arsenic. Thermo Scientific provided a certificate of analysis with the instrument, and the site-specific MDL is within the limits of quantification for the instrument. The XRF analyzer will not provide a measured sample concentration for a metal if the concentration is less than three times the standard deviation of the measurement. In that case, the instrument will record “<LOD” (less than level of detection).

A.2.1 Summary of Method

XRF spectrometry is an analytical technique that can provide rapid, multi-element analysis of metals. Samples are exposed to X-ray energy, which liberates electrons in the inner shell of metal atoms. As the outer electrons cascade toward the inner shells to fill the vacancies, energy is released (fluorescence). The fluorescing energy spectrum identifies the metals and the intensity is proportional to concentration.

Under this method, inorganic analytes of interest will be identified and quantitated using a Niton® XL3t™, 950 Series™ GOLDD+ Technology Mining and Environmental field portable XRF analyzer (Thermo Scientific, Tewksbury, MA) equipped with a Ag anode (6-50 kC, 0-200 µA max) tube and a Geometrically Optimized Large Area Drift Detector (GOLDD) with 180,000 throughput cps (resolution of <185 eV at 60,000 cps at 4 µ sec shaping time).

The Niton XL3t 950 XRF analyzer operates in two sampling modes: intrusive and in situ analyses. Intrusive analyses are performed in a laboratory and in the field with the XRF instrument analyzing previously collected soil packed into 33 mm sample cups (PN 187-466, Thermo Scientific, Tewksbury, MA) covered with polypropylene film (PN 187-461, Thermo Scientific, Tewksbury, MA). In situ analyses are performed in the field with direct contact between the XRF measurement window and the soil surface. The instrument is operated by hand or with a computer interface for either sampling mode.

The count time for the instrument was optimized with site-specific reference material in the sample cups with the intrusive XRF analyses. A 60-second count duration was chosen for the in situ analyses; for arsenic concentrations near the screening criteria, the variability attributable to the counting duration is expected to be less than 10% with a 60-second count.

XRF instruments can be calibrated using the following methods: empirically based on site-specific calibrations standards, semi-standardless calibration using fundamental parameters or Compton Peak ratio (EPA 2007a). For this method, the Niton XL3t 950 XRF analyzer automatically runs a Compton normalization calibration when set to the “soil mode.”   For the pilot study, the instrument was calibrated using an empirically based site-specific calibration standards technique.

A.2.2 Interferences

The total method error for XRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in XRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are briefly discussed below. For a more detailed discussion of these interferences, see EPA Method 6200 (EPA 2007a).

Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface conditions. Field studies have shown that the heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples (EPA 2007a).

Moisture content affects the accuracy of analysis of soil sample analyses. Generally, the overall error from moisture may be minimal when the moisture content is between 5% and 20% (EPA 2007a). However, for arsenic analyses with XRF, Parsons et al. (2012) found that soil moisture was significant in altering the precision of arsenic analyses: 20% soil moisture resulted in a decrease in recorded arsenic concentration of 37.0% compared to the same dry sample.

Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur either as either spectral interferences (peak overlaps) or as X-ray absorption and enhancement phenomena. For example, iron tends to absorb copper X-rays, reducing the intensity of copper measured by the detector, while chromium will be enhanced at the expense of iron. These effects can be corrected mathematically using FP coefficients or compensated for using site-specific calibration standards (EPA 2007a).

Spectrum overlaps occur when certain X-ray lines from different elements are close in energy and therefore cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. The most common spectrum overlaps are the K_α/K_β line overlaps (e.g., Fe:Co) and in some cases the K/L, K/M, and L/M line overlaps (e.g., As K_α /Pb L_α). No instrument can fully compensate for this interference. Various options exist for minimizing this and the other interferences previously discussed.

XRF analyses of site-specific reference material were recorded to evaluate the physical and chemical effects. The lead and arsenic concentration of the site-specific reference material was confirmed with ICP-MS analyses. Because XRF measures the total concentration of an element, a total digestion procedure (e.g., EPA Method 3052 [EPA 1996a]) allows for better comparability between XRF measurements and ICP results (EPA 2007a).

A.2.3 Standards

The standards needed for calibration and instrument quality control (QC) procedures include blank samples, standard reference material (SRM), and site-specific reference material. The blank sample was a “clean” quartz or silicon dioxide matrix that was free of any analytes at concentration above the MDLs. Thermo Scientific supplied one blank sample, used in the instrument calibration and documented in the certificate of calibration. Other blanks were prepared during the pilot study with Accusand (Unimin silica sand, A20/30, Target Products, Ltd., Burnaby, British Columbia, Canada). These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

Standard reference materials are standards containing certified amounts of metals in soil or sediments. These standards are used for accuracy and performance checks of XRF analyses. Several suppliers of certified reference material were evaluated for the pilot study. The National Research Council Canada (Ottawa, Ontario) had certified reference material with the values for lead and arsenic closest to the screening criteria for the pilot study. PACS-3 marine sediment certified reference material for trace metals (Lot G 4169010, Serial CC 569102) and other constituents had certified quantity values for lead (188 ± 7 mg/kg) and arsenic (30.3 ± 2.3 mg/kg).

Site-specific calibration standards were prepared from soil collected at OL-14 and IU6-4, homogenized, and then analyzed by ICP-MS. The site-specific reference material was packed in sample cups for intrinsic analyses. The material confirmed the performance of the XRF analyzer in the field and in the laboratory.

A.2.4 Field Sampling Protocol

This section includes the operating procedures for sampling with the XRF in the field. The method was used for the field activities, including collecting the soil for the site-specific reference material and confirmatory samples, evaluating transects to understand spatial variability, and analyzing the sampling locations in the decision units. They apply for in situ and intrusive XRF analyses.

A.2.4.1 Field Sampling Protocol for XRF Analysis

This section describes the steps for analysis in the field with the XRF analyzer, and the steps in the laboratory after field analyses are completed. Note: Once on, the XRF analyzer should remain on until all analyses are complete. If travelling to a different location, rerun a QC check before commencement of analysis. If the XRF analyzer is shut off at any point, restart following these steps.

1. Insert battery, and log on to the XRF using given password (1234).

2. Isolate the XRF analyzer from other electronic devices (minimum of 2 ft).

3. Wait 5 minutes to allow instrument to stabilize (energy calibration check by the XRF analyzer).

4. Verify date/time by selecting the “Specs” icon from the system menu in the main menu.

5. Optional: Connect the analyzer to a computer via USB cable.

6. Run the “System Check” by selecting it from the main menu; select “yes” and wait for the system check to be completed. If the system check fails twice, contact Thermo Scientific for further assistance.

7. Verify that the filter is set to analyze “soils” by selecting the “Advanced” menu and then the “Element Range” icon. In the drop down menu, select “Soil mode.” Ensure that the “Main” range is the only range selected and that “Low” and “High” ranges are not checked. The main range time should be set to 180.0 seconds. Select “save.”

8. Before starting the first sample analysis, select the maximum time. This is done through the “Advanced” menu by selecting the “Start/Stop” icon and entering the appropriate time. If screening the soil for presence or absence of lead and arsenic, a 30-second count time is adequate. All other analyses require a 60-second count time.

9. Ensure the Garmin Montana 650t GPS is functioning. In the “System” menu select the “Bluetooth” icon and turn on the GPS device. In the main window select “Q-STAR” and select “connect.” Once it is connected, select GPS to ensure that it is transmitting data. If it is not transmitting data, wait until it begins and then proceed.

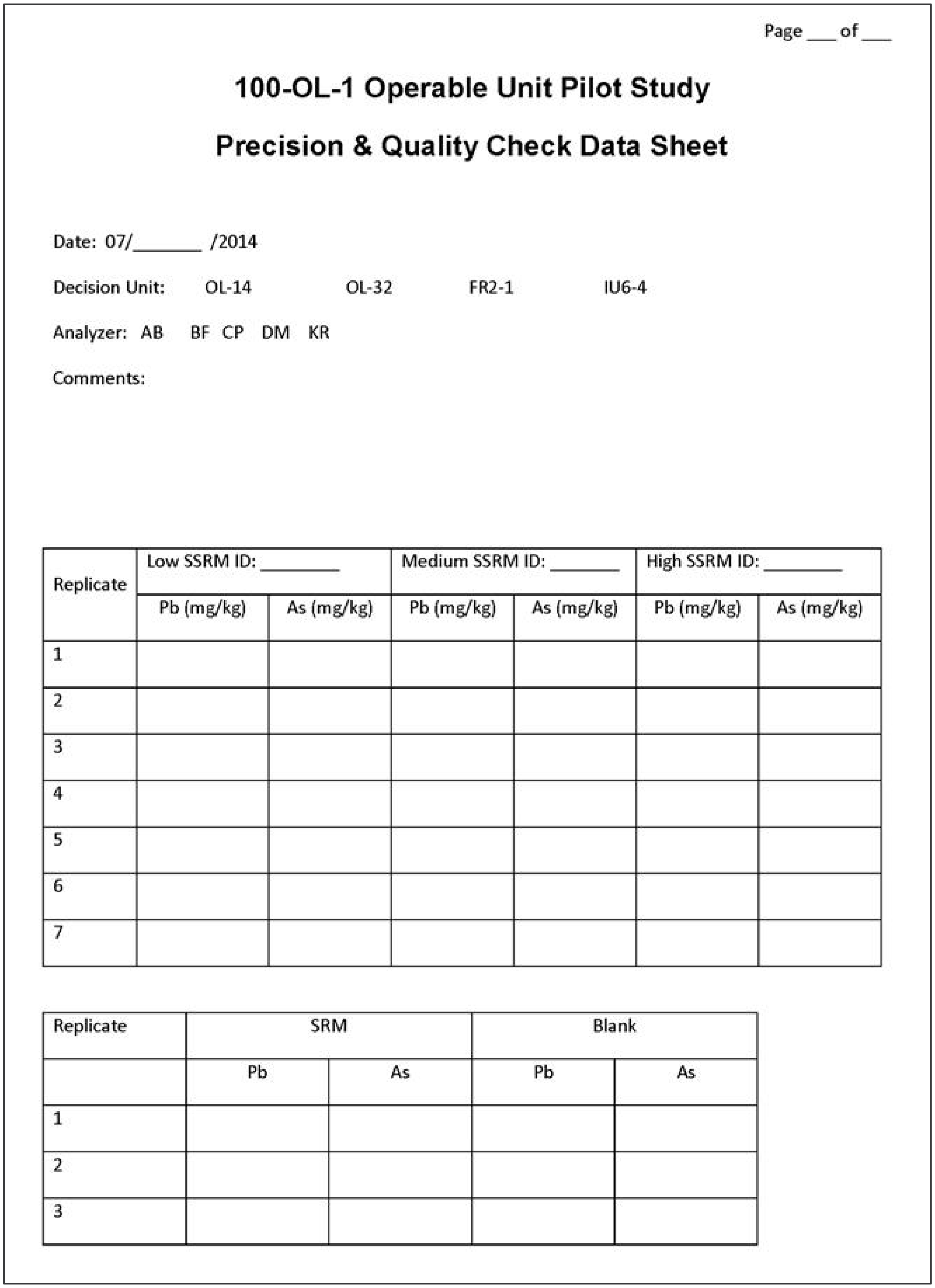
10. Perform the daily instrument check of the XRF analyzer:

10a. Precision test:

- Select three of the site-specific reference material sample cups with low, medium, and high concentrations of lead and arsenic (Table A.4). The medium sample should have concentrations near the screening criteria for lead and arsenic.
- Record the sample ID on the field datasheet (Figure A.2).
- Analyze each sample for 60.0 seconds with seven repetitions each.
- Ensure that the values for the repetitions are compared to each other (within the standard deviation of the data in Table A.4). If not, repeat the analyses.

Table A.4. Standards for use in daily instrument check of XRF analyzer

Sample Cup ID for Site-Specific Reference Material, Standard Reference Material or Blank	Lead		Arsenic	
	Average (mg/kg)	Standard Deviation (mg/kg)	Average (mg/kg)	Standard Deviation (mg/kg)
OL-14-L-1	19.34	1.39	6.24	1.09
OL-14-L-2	18.76	0.98	6.39	1.25
OL-14-L-3	19.96	2.08	6.10	1.53
OL-14-M1-1	43.06	1.75	14.63	0.90
OL-14-M1-2	42.26	1.74	13.13	1.23
OL-14-M1-3	41.54	2.31	13.12	2.21
OL-14-M1-4	42.22	2.31	13.12	2.20
Ol-14-M2-1	42.25	1.42	14.71	1.06
OL-14-M2-2	43.93	1.27	13.08	1.55
OL-14-M2-3	44.64	2.64	13.50	1.36
OL-14-H-1	1072	6.30	160.8	5.54
OL-14-H-2	1044	18.17	156.5	7.38
OL-14-H-3	1048	9.05	149.9	3.17
OL-IU6-4-L-1	175.9	3.93	37.32	2.92
OL-IU6-4-L-2	158.0	3.72	36.68	2.54
OL-IU6-4-L-3	166.5	5.85	36.64	2.83
OL-IU6-4-M-1	207.2	2.56	42.69	2.72
OL-IU6-4-M-2	183.3	2.47	32.12	2.37
OL-IU6-4-M-3	192.0	3.39	35.35	3.06
OL-IU6-4-M-4	197.5	3.95	26.74	3.12
OL-IU6-4-M-5	212.4	3.51	36.34	2.38
OL-IU6-H-1	929.6	7.13	234.4	7.23
OL-IU6-H-2	1061	4.91	288.4	2.91
OL-IU6-4-H-3	959.5	8.40	218.8	5.20
OL-IU6-4-H-4	894.9	8.41	245.1	5.29
SRM-1	166.6	3.32	28.03	2.64
SRM-2	170.6	2.35	27.34	1.79
SRM-3	173.4	3.26	29.11	1.30
BLANK-1	<LOD	N/A	<LOD	N/A
BLANK-2	<LOD	N/A	<LOD	N/A
BLANK-3	<LOD	N/A	<LOD	N/A



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100-OL-1 Operable Unit Pilot Study

Precision & Quality Check Data Sheet

Date: 07/_______ /2014

Decision Unit: OL-14 OL-32 FR2-1 IU6-4

Analyzer: AB BF CP DM KR

Comments:

Replicate	Low SSRM ID: ________		Medium SSRM ID: _______		High SSRM ID: ________	
	Pb (mg/kg)	As (mg/kg)	Pb (mg/kg)	As (mg/kg)	Pb (mg/kg)	As (mg/kg)
1						
2						
3						
4						
5						
6						
7						

Replicate	SRM		Blank	
	Pb	As	Pb	As
1				
2				
3				

Figure A.2. Field datasheet for precision and quality checks

10b. Accuracy Check: Analyze the SRM and blank sample for 60.0 seconds and ensure that the measurements are within the accepted values for each, respectively, as listed in Table A.6.

11. Begin in-situ analyses with the XRF analyzer.
    - Walk to VSP GPS coordinates using the Garmin.
        - Power on Garmin Montana 650t.
        - Select “Map” icon.
        - Locate desired “waypoint” marked with a flag on the screen of the GPS.
        - Proceed to destination.
    - Start new datasheet for location (Figure A.3).
    - Determine if site needs to be relocated or cleared of vegetation. Relocate the site if there is an obstruction (large bush, tree stump, road, etc.). Note the new location and comment on datasheet why the site needed to be moved. Remove any large, non-representative debris from the soil with pre-cleaned spatula before beginning analysis.
    - Put flag at new location.
    - Take pictures of location: ground to be analyzed, then looking north, and finally looking east. Use compass to determine direction of pictures.
    - Surveyor can leave datasheet at location and proceed to next location, or wait for the analyzer team to arrive at location.
    - On the XRF analyzer, set the range and appropriate time using steps listed above.
    - Enter sample name, or any other pertinent data into the XRF analyzer by selecting the “Data Entry” button from the “Ready to Test” screen.
    - Position the XRF analyzer over soil location cleared by the field surveyor, make contact between the XRF window and soil, and begin count time.
    - Repeat for a total of three analyses at a location.
    - Complete field datasheet, and proceed to the next sampling area.

12. After every 20 analyses, repeat the accuracy check with the SRM and blank.

13. After the last location is analyzed, repeat the accuracy check with the SRM and blank.

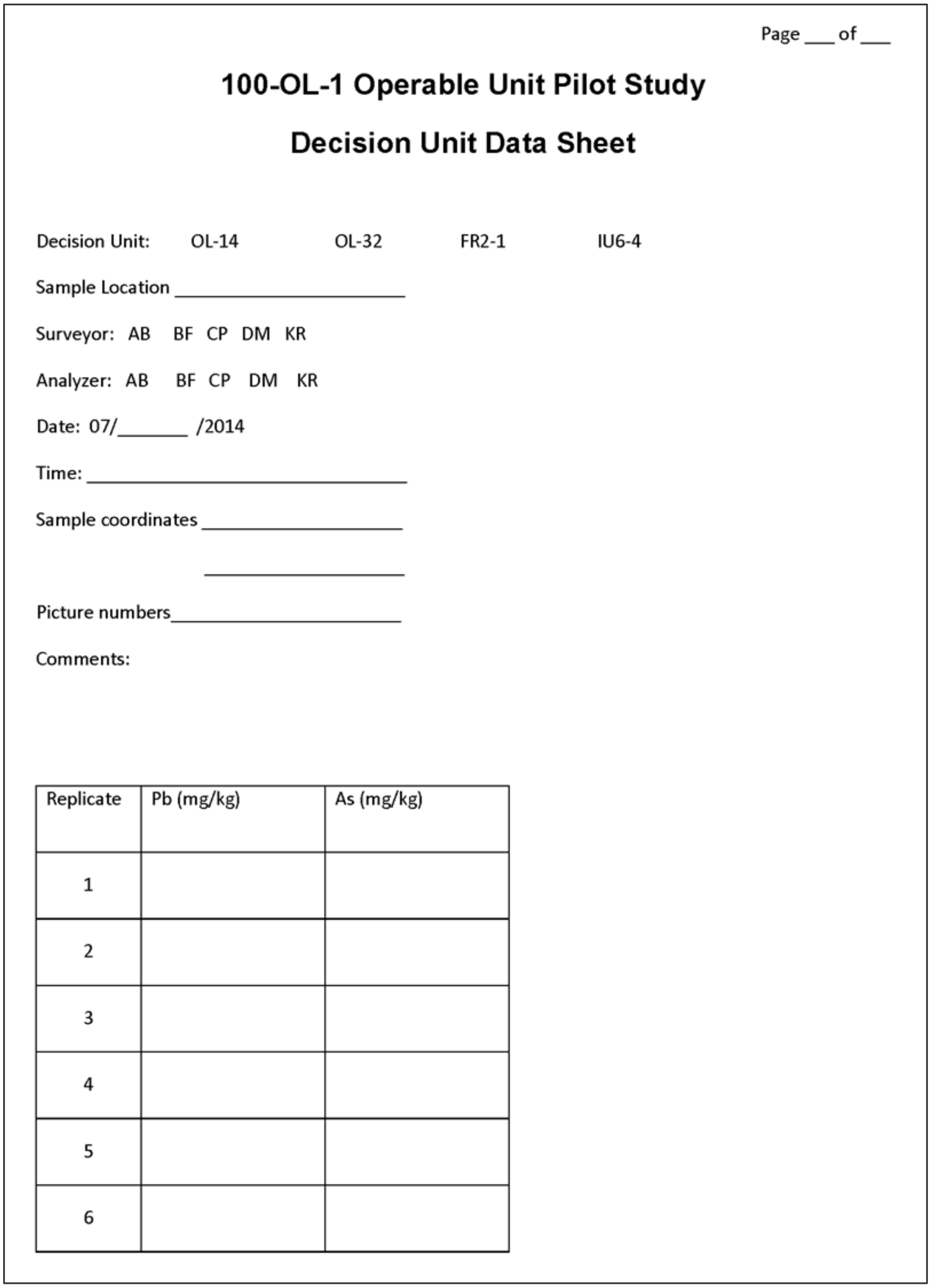
14. Download and save to the project folders the appropriate pictures from that day. Label with decision unit, date, and orientation of picture (ground, north, or east).

15. Download all results from the XRF analyzer to the project computer server.
    - Connect the analyzer to a computer via USB cable.
    - Open NDT software.
    - Select the “Download” icon located at the top of the screen.

- Select “Settings” at the bottom of the pop-up and in the drop down menu select “USB port.”
- Select “Connect” and when device is connected select “Query Readings.”
- In the right window, the display will show all data currently on the analyzer. To select data to export, click the box next to each sample desired.
- Select “Download” and when complete, select “Done.”
- A new screen will appear with all the desired data.
- Important: Before exporting the data, find the columns labeled “Pb” and “As” and drag them to the front of the list of elements. This will help with data analyses later. When this is complete, select “Export.”
- A .csv file will open automatically on the laptop. Save file to project folders. File can be saved as a .xlsx file, if needed.

16. Add the “Decision Unit” and “Sample Location” to the XRF data results file. Verify the information in the datasheet matches the entered data.

17. Add the coordinates for each location to the file using either the pre-determined locations or the field recorded locations (if the site was relocated by the field team).



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100-OL-1 Operable Unit Pilot Study

Decision Unit Data Sheet

Decision Unit: OL-14 OL-32 FR2-1 IU6-4

Sample Location ______________________

Surveyor: AB BF CP DM KR

Analyzer: AB BF CP DM KR

Date: 07/_______ /2014

Time: ______________________________

Sample coordinates ___________________

____

Picture numbers______________________

Comments:

Replicate	Pb (mg/kg)	As (mg/kg)
1		
2		
3		
4		
5		
6		

Figure A.3. Field datasheet for collection of information at a location in a decision unit

Table A.5 lists the equipment to support the field activities. The field activities were remote and equipment was split between materials needed during in situ analyses and the field vehicle.

Table A.5. List of equipment for field activities

Surveyor's Backpack Garmin Montana 650t GPS Clipboard Acid-washed, bagged spatulas Surveyor flags Sharpies and extra pens 40 datasheets Tape measure Nitrile gloves Sunglasses Extra binder clips Tissues Scissors Tape Sunscreen Camera Compass	Analyzer's Backpack Bibulous paper Kimwipes Screwdriver (from XRF toolkit) SSRM precision samples SRM samples Blank samples 2 clamps XRF screen brushes Spare Niton XL3t windows Clipboard Sharpies and extra pens Q-Starz GPS (Bug) Cellphone
XRF Carrycase Niton XL3t 950 analyzer XL3t holster XL3t battery charger (base and power) XL3t battery holster Extra XLt3 6 cell battery pack XL3t Quick Start Guide 2mm USB 2.0 type A to mini B cable X-ray tube regulatory form XL3-NDT disk	For Field Vehicle Dell Latitude laptop Extra laptop batteries Water jug (for drinking water) Water jug (for hand washing) Water bottles Paper towels Trash bag Health & safety plan

A.2.5 Quality Control for the XRF Analyzer

This section provides an overview of the QC for the XRF analyses. This is performed in accordance with the QAPP. Data quality criteria for XRF analysis of the soil samples are summarized in Table A.6.

Table A.6. Data quality criteria for XRF analysis of soil samples

QC Parameter	Measure of Acceptance Criteria	Corrective Action
Accuracy • Instrument Blank (quartz)	Sample Values >10X Method Blank	• Review data and analysis for possible sources of contamination. Reanalyze and document corrective action.
• Sample Reference Material (PACS-3)	± 20 % Recovery	• Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action.
Precision • Duplicate	+ 20% Relative Standard Deviation	• Review data to assess impact of matrix. • Document any corrective action.

A.2.5.1 System Check and Internal Calibration

The Niton XL3t 950 XRF analyzer performs a system check every time the instrument is turned on. The system check allows the instrument's electronics to stabilize and perform an internal calibration check. The four LED lights on the analyzer will blink during calibration. The system check and internal calibration requires about 5 minutes. During that time, the XRF analyzer should be isolated from any electronic devices (devices generating electronic fields) by 2 ft, and vibrations minimized.

A.2.5.2 Instrument Blank

The instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window. The instrument blank is quartz sand (Accusand, Unimin silica sand, A20/30, Target Products, Ltd., Burnaby, British Columbia, Canada) packed into a polypropylene sample cup (Thermo Niton part number 187-466) covered with 1/4 mil polypropylene film (Thermo Niton part number 187-461). The instrument blank is analyzed on each working day before and after analyses are conducted and once per every 20 samples. No element concentrations above the MDLs should be found in the instrument blank.

A.2.5.3 Calibration Verification Checks

A calibration verification check sample is used to check for the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. National Research Council Canada "PACS-3" certified reference material was used to verify the accuracy of the instrument. PACS-3 is a marine sediment certified reference material for trace metals and other constituents. The certified quantity values are 188 ± 7 mg/kg lead and 30.3 ± 2.3 mg/kg arsenic. The measured value should be within 20% of the certified value for the calibration verification check to be acceptable.

A.2.5.4 Precision Measurements

The Niton XL3t XRF analyzer reports the results in parts per million, which is equivalent to mg/kg, and reports the precision of the measurement, which is two times the standard deviation (2σ). The instrument will report a measurement as "<LOD" (less than the level of detection) if the measurement of that element is less than 1.5 times the precision of that measurement.

The precision of the method is monitored by analyzing a sample with low, moderate, or high concentration of lead and arsenic. A minimum of one precision sample should be run per day. Each precision sample should be analyzed three times in replicate. The relative standard deviation (RSD) of the sample mean is used to assess method precision. The RSD should not be greater than 20% for each target analyte. The equation for calculating RSD is as follows:

$$\mathrm{RSD} = (\mathrm{SD}/\text{Mean Concentration}) \times 100$$

Where:

RSD = relative standard deviation for the precision measurement for the analyte
SD = standard deviation of the concentration for the analyte
Mean Concentration = mean concentration for the analyte.

The precision check for the field analyses of the decision units consists of measuring the low, medium, and high site-specific reference material soil samples. At the beginning of sampling at a decision unit, the precision check for the XRF analyzer included seven replicate measurements of each of the low, medium, and high site-specific reference material soil samples, triplicate measurements of the PACS-3 SRM, and triplicate measurements of the blank.

A.2.5.5 Detection Limits

The MDL for the XRF analyzer was determined using site-specific reference material soil collected at OL-14. The MDL for the Niton XL3t was determined using EPA's procedure for determination of the MDL as described in 40 CFR 136, Appendix B. The site-specific reference material sample OL-14-L (Table A.2) was measured seven times. Following the procedure, the average concentration of the replicate analyses, the standard deviation of the replicates, and the Student's T-value for seven samples were determined. The MDL is the product of the Student's T-value and the standard deviation. The results of the study indicate that under ideal conditions, the lead and arsenic MDLs for the XRF analyzer are 2.6 and 3.9 mg/kg, respectively. The MDL was used to replace "<LOD" recorded by the XRF and calculate the average of the three replicate samples at a location in a decision unit.

A.2.5.6 Calibration and Standardization

Instrument calibration procedures vary among XRF instruments. Generally, three types of calibration procedures exist for XRF instruments: FP calibration, empirical calibration, and the Compton Peak ratio or normalization method. For more details regarding these procedures, see Method 6200 (EPA 2007a). The NITON XL3t 950 analyzer in the standard soil mode is calibrated using a semi-standardless FP routine.

The backscatter FP calibration is for soil analyses where the percentage of analytes of interest is less than 1.0%, light matrix material, and composition of elements with atomic number greater than iron does not exceed several percent. Based on the Niton XL3t 900 Series User's Guide:

> Standard Soil Mode utilizes the Compton Scatter (Inelastic Collisions) of a particular sample. Compton scatter occurs when primary X-rays do not cause fluorescence but instead collide with the atoms of the sample. The Compton Scatter that occurs is directly proportional to the density (average atomic number (Z)) of the sample. A light matrix material, such as an oil or sand, will have a much greater scatter than that of a heavy matrix, such as ore. The analyzer measures this scatter peak and automatically adjusts the concentration based on the matrix of the specific calibration standards.

Empirical calibration of the XRF analyzer is the daily precision instrument check described in section A.2.5.4. The Niton XL3t 900 Series User's Guide states that the frequency for measuring the SRM is after turning on the XRF analyzer and before analysis of soil samples, as well as every 1 to 2 hours thereafter. The frequency of sampling in the decision units (one location every 5 to 7 minutes) is equivalent to reading the SRM after every 20 locations.

A.2.5.7 Sample Preparation and Analysis Procedure

For the pilot study, the analyses were performed in situ or intrusive samples were prepared and analyzed. For in situ analysis, the analysis involved placing the XRF analyzer measurement window on the surface of the soil and holding the trigger on the analyzer for the predetermined period (60-second count). The soil surface was cleared of debris before placement of the analyzer on the soil. For intrusive analysis, the analyzer was set up with the measurement window on the sample cup packed with the soil sample. A computer interface option allowed the XRF analyzer to be operated without a user holding the analyzer. Intrusive analyses were performed in a laboratory and in the field using previously collected samples.

A.2.5.8 Data Analysis and Calculations

The Niton XL3t has a computer interface and all data and spectra are transferred from the instrument to a computer for data analysis. Field personnel downloaded the data file from the XRF and saved the file as a .csv file. The file was modified and resaved as an .xlsx file. The modifications included the sample location information and the predetermined location coordinates or new coordinates collected from the field if the site was relocated. All modifications were verified against the field data sheets.

A.2.6 Quality Control for the ICP-MS

Subsamples from soil collection for the site-specific reference material and confirmatory samples were analyzed by ICP-MS. Aliquots of the homogenized soil (15 to 20 g) were placed in pre-cleaned, pre-tarred, 50 mL polypropylene sample bottles and sent to the PNNL Marine Sciences Laboratory (Sequim, Washington) for ICP-MS analyses.

The soil samples were digested using a procedure based on a modification of EPA Method 3050B (EPA 1996a). An approximately 400 mg (dry weight) aliquot of each sample was combined with a 3:1 ratio of nitric and hydrochloric acids (aqua regia) in a Teflon digestion vessel and heated in an oven at 130°C (±10°C) for a minimum of 8 hours. After heating and cooling, deionized water was added to the sediment digestate to achieve analysis volume. Digested samples were analyzed for arsenic and lead using ICP-MS. This procedure is based on two methods modified and adapted for analysis of low-level sediment and tissue samples: EPA Methods 1638 and 200.8 (EPA 1996b and 1994, respectively).

The samples were analyzed within 10 days of receipt. Analytical results were reported with respect to the annual sediment MDL study derived using seven replicates of quartz sand (0.006 mg/kg dry weight lead; 0.3 mg/kg dry weight arsenic). Two method blanks were analyzed with this batch of samples. Metal concentrations above the reporting limits (0.02 mg/kg dry weight lead; 1.0 mg/kg dry weight arsenic) were not detected in the method blank. Two laboratory control samples (LCS) were analyzed with the batches of samples. The LCS recoveries were within the quality control (QC) acceptance criterion of ±25% recovery for all metals. Two soil samples were selected for matrix spikes (MS). The MS recoveries were within the QC acceptance criterion of ±25% recovery for all metals. Precision for this set of samples was evaluated by the analysis of laboratory duplicates and expressed as the relative percent difference (RPD) of replicate results. The RPD values for the duplicate samples were within the QC criterion of ≤25% RSD for all metals. The standard reference material (SRM) accuracy was expressed as the percent difference (PD) between the measured and certified or reference value for the

SRM. Recovery of a particular analyte exceeded the QC criterion if the PD exceeded 20%. The SRM PACS-3 *Marine Sediment Certified Reference Material for Trace Metals and Other Constituents* was analyzed with these samples (National Research Council Canada, Ottawa, Ontario, Canada). The percent differences were within the QC acceptance criterion of PD ± 20%.

A.3 Quality Assurance Project Plan

The PNNL QA Program is based on the requirements as defined in DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A, Quality Assurance Requirements (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.
- ASME NQA-1-2000, Part II, Subpart 2.7, Quality Assurance Requirements for Computer Software for Nuclear Facility Applications, including problem reporting and corrective action.
- ASME NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The procedures necessary to implement the requirements are documented through PNNL's "How Do I…? (HDI), a system for managing the delivery of laboratory-level policies, requirements, and procedures.

The *DVZ-AFRI Quality Assurance Plan* is the minimum applicable QA document for all Deep Vadose Zone Applied Field Research Initiative (DVZ-AFRI) projects. This QA plan also conforms to the QA requirements of DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, Subpart A, Quality Assurance Requirements. The DVZ-AFRI is subject to the *Price Anderson Amendments Act*.

The implementation of the DVZ-AFRI QA program is graded in accordance with NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The work for this report was performed under the technology level of Applied Research. Basic Research consists of research tasks that are conducted to acquire and disseminate new scientific knowledge. During basic research, maximum flexibility is desired in order to allow the researcher the necessary latitude to conduct the research.

Applied Research consists of research tasks that acquire data and documentation necessary to ensure satisfactory reproducibility of results. The emphasis during this stage of a research task is on achieving adequate documentation and controls necessary to be able to reproduce results.

Development Work consists of research tasks moving toward technology commercialization. These tasks still require a degree of flexibility and a degree of uncertainty still exists in many cases. The role of quality on development work is to make sure that adequate controls to support movement into commercialization exist.

Research and Development Support Activities are conventional and secondary in nature to the advancement of knowledge or development of technology, but allow the primary purpose of the work to be accomplished in a credible manner. An example of a support activity is controlling and maintaining documents and records. The level of quality for these activities is the same as for developmental work.

Within each technology level, the application process for QA controls is graded such that the level of analysis, extent of documentation, and degree of rigor of process control are applied commensurate with their significance, importance to safety, life-cycle state of a facility or work, or programmatic mission.

A.3.1 Project Management and Task Organization

PNNL is responsible for planning, coordinating, collecting, and analyzing field samples, and preparing, packaging, and shipping samples to the laboratory, as defined in its contract. The following sections describe the project organization, relative to sampling and characterization, which is also shown graphically in Figure A.4. The project lead maintains a list of individuals or organizations as points of contact for each functional element shown in the figure. For each functional primary contractor role, a corresponding oversight role exists within DOE.

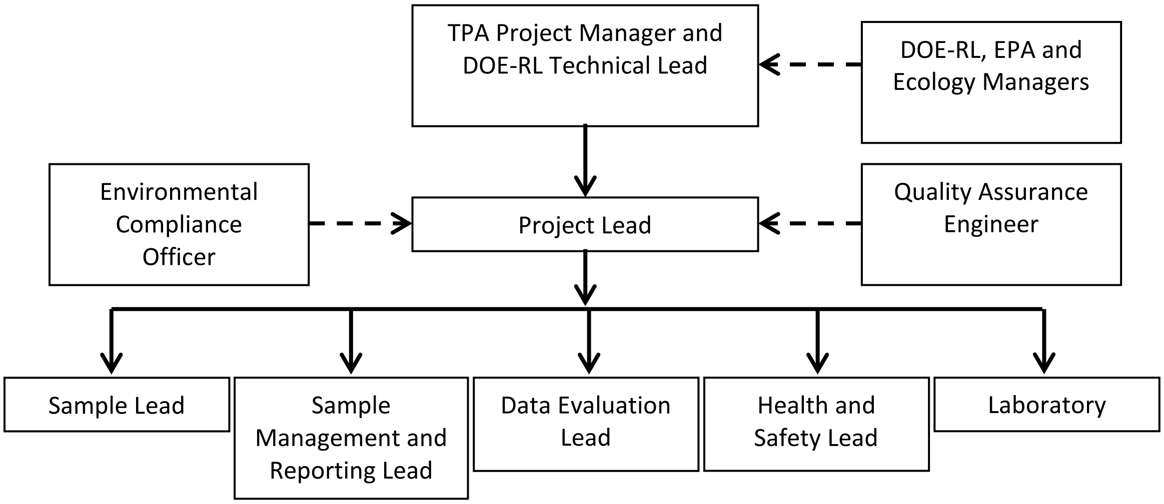


Figure A.4. Project organization

DOE-RL, EPA, and Ecology Project Managers. EPA and Ecology will be the lead organizations for the 100-OL-1 OU (TPA 2012b), working with DOE-RL. Each organization has assigned project managers responsible for overseeing the activities identified in the plan to accomplish the scope of this plan. EPA and Ecology will work with DOE-RL to resolve concerns about the work as described in this SAP, in accordance with the TPA (Ecology et al. 1989). The managers will be responsible for the risk management evaluation of the remedial investigation characterization results and will determine if additional characterization efforts are needed before proceeding with the feasibility study.

Tri-Party Agreement Project Manager and DOE-RL Technical Lead. The TPA project manager is responsible for

- authorizing RI/FS activities for the 100-OL-1 OU
- obtaining regulatory approval of the work plan and SAP that authorize the RI/FS activities under the TPA (Ecology et al. 1989).

The DOE-RL technical lead is responsible for

- overseeing the contractor in performing the work scope
- working with the contractor and the regulatory agencies to identify and work through issues
- providing technical input to the TPA project manager.

Project Lead. The project lead is responsible for

- planning and implementing work scope
- managing sampling documents and requirements, field activities, and subcontracted tasks, and ensuring that personnel are working in accordance with the most current job requirements
- requesting and obtaining permission from the DOE-RL Cultural Resources Program before initiating any field activities, and ensuring that the mitigation actions are incorporated and implemented into the field activities
- Maintaining version control for the SAP.

The project lead will work closely with the QA engineer, the health and safety lead, and the sample lead to integrate these and the other lead disciplines in planning and implementing the work scope. The project lead will maintain a list of individuals or organizations that fill each of the functional elements of the project organization (Figure A.4). The project lead will work with the data evaluation lead and the sample lead after field characterization begins to propose any changes to the SAP to optimize the sampling design. The project lead also will coordinate with DOE-RL and the primary contractor management on sampling activities. The project lead will support DOE-RL in coordinating sampling activities with the regulators.

Environmental Compliance Officer. The environmental compliance officer will be responsible to the project lead and will be responsible for

- providing technical oversight, direction, and acceptance of project and subcontracted environmental work
- developing appropriate mitigation measures with a goal of minimizing adverse environmental impacts
- reviewing plans, procedures, and technical documents to ensure that environmental requirements have been addressed
- identifying environmental issues affecting operations and developing cost-effective solutions
- responding to environmental/regulatory issues or concerns raised by DOE-RL and/or regulatory agencies.

The environmental compliance officer also may oversee project implementation to ensure compliance with applicable internal and external environmental requirements.

Quality Assurance Engineer. The QA engineer will be responsible to the project lead and will be responsible for QA issues on the project. Responsibilities will include

- overseeing implementation of the project QA requirements
- reviewing project documents, including data needs summary reports, the field sampling plan, and the QAPP
- participating in QA assessments on sample collection and analysis activities, as appropriate.

The QA engineer must be independent of the unit generating the data.

Waste Management Lead. The waste management lead will be responsible for

- communicating policies and procedures
- ensuring project compliance with requirements for providing storage, transportation, disposal, and waste tracking in a safe and cost-effective manner
- identifying waste management sampling and characterization requirements to ensure regulatory compliance
- interpreting the characterization data to generate waste designations and profiles
- maintaining other documents that confirm compliance with waste acceptance criteria.

Sample Lead. The sample lead will have overall responsibility for planning, coordinating, and executing sampling activities. Specific responsibilities will include

- converting the sampling design requirements into field task instructions that provide specific direction for field activities
- implementing any cultural resources mitigation activities
- directing training, mock-ups, and practice sessions with field personnel to ensure that the sampling design is understood and can be performed as specified
- communicating with the project lead to identify field constraints or emergent conditions that will affect sampling design and/or execution
- managing field collection efforts
- procuring and installing material and equipment needed to support field work
- preparing data packages based on instructions from the project lead and information contained in this SAP.

The shipping lead will report to the sample lead for shipment authorization.

Sample Management and Reporting Lead. The sample management and reporting lead will be responsible for

- managing and reporting of soil analyses
- coordinating with laboratory analytical work
- ensuring that the laboratories conform with Hanford Site internal laboratory QA requirements, or their equivalent, as approved by DOE-RL, EPA, and Ecology
- entering data into the Hanford Environmental Information System (HEIS)
- arranging for and overseeing data validation of all analyses
- informing the project lead of any issues reported by the analytical laboratory.

The sample management and reporting organization also will be responsible for conducting the data needs process, or equivalent. Additional related responsibilities will include developing the SAP, including documenting the data needs and the sampling design; preparing associated presentations; resolving technical issues; and preparing revisions to the SAP. Samples collected in the field for shipping and analysis, as well as the resulting data, will be managed in accordance with applicable procedures and work plans.

Data Evaluation Lead. The data evaluation lead will be responsible for evaluating the results of the field characterization, performing the statistical analyses, and evaluating the data to meet DQOs. The data evaluation lead will work with the project lead and sample lead on the recommendations and any proposed revisions to the SAP.

Health and Safety Lead. The health and safety lead will be responsible for coordinating industrial safety and health support for the project through health and safety plans, job hazard analyses, and other pertinent safety documents required by federal regulations or by internal primary contractor work requirements. The health and safety lead will work with the project lead. In addition, the health and safety lead will assist project personnel in complying with applicable health and safety standards and requirements, particularly for decision units located in other operable units.

Laboratory. PNNL’s Marine Science Laboratory will analyze soil samples in accordance with established procedures, provide necessary sample reports, and explain results in support of data validation. The Marine Science Laboratory meets site-specific QA requirements and has an approved QA plan in place.

A.3.1.1 Problem Definition/Background

The pilot study plan (DOE-RL 2014) describes the sampling and analysis approach for the characterization of soil in selected decision units of the 100-OL-1 OU. Figure 2.2 through Figure 2.5 show the areas for sampling within the scope of this pilot study. The purpose and objectives of the pilot study are described in section 1.0 of this report.

A.3.1.2 Quality Objectives and Criteria

The QA objective of this plan is to develop implementation guidance for providing data of known and appropriate quality. The applicable QC guidelines, quantitative target limits, and levels of effort for assessing data quality are dictated by the intended use of the data and the nature of the analytical method. The principal data quality indicators are precision, bias or accuracy, representativeness, comparability, completeness, and sensitivity. These data quality indicators are defined for the purposes of this document in Table A.7, and include precision, accuracy, representativeness, comparability, completeness, and sensitivity.

Table A.7. Data quality indicators

Data Quality Indicator	Definition	Example Determination Methodologies	Project-Specific Information	Corrective-Action Examples
Precision	The measure of agreement among repeated measurements of the same property under identical or substantially similar conditions; calculated either as the range or as the standard deviation. May also be expressed as a percentage of the mean of the measurements, such as relative range, relative percent difference, or relative standard deviation (coefficient of variation).	Use same analytical instrument to make repeated analyses on same sample. Use same method to make repeated measurements of same sample by laboratory Split a sample in field and submit for sample handling, preservation and storage, and analytical measurements. Collect, process, and analyze co-located samples for information on sample acquisition, handling, shipping, storage, preparation, and analytical processes and measurements.	Field XRF precision: Analyze intrusive samples of low, medium, high site-specific reference material seven times at beginning of each day in field. 60-second count time. Laboratory precision for ICP-MS: analysis of laboratory duplicate or matrix spike duplicate samples.	If XRF precision check does not meet objective: • Evaluate apparent cause (e.g., sample heterogeneity). • Request reanalysis or re-measurement. • Qualify the data before use.
Accuracy	A measure of the overall agreement of a measurement to a known value; includes a combination of random error (precision) and systematic error (bias) components of sampling and analytical operations.	Analyze a reference material or reanalyze a sample to which a material of known concentration or amount of pollutant has been added (a spiked sample).	Field accuracy for XRF based on intrusive sample of SRM at beginning of day, every 20 samples and end of day. Laboratory accuracy for ICP-MS determination based on matrix spike and matrix spike duplicate results.	If recovery does not meet objective: • Qualify the data before use. • Request reanalysis or re-measurement.

Data Quality Indicator	Definition	Example Determination Methodologies	Project-Specific Information	Corrective-Action Examples
Representativeness	A qualitative term expressing "the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition" (ANSI/ASQ 1995).	Evaluate whether measurements are made and physical samples are collected in such a manner that the resulting data appropriately reflect the environment or condition being measured or studied.	Samples will be collected as described in the sampling design. Judgment sampling ensures areas most likely to be contaminated, based on current information, will be evaluated.	If results are not representative of the system sampled: • Identify the reason the result is not representative. • Reject the data, or, qualify the data for limited use, and define the portion of the system the data represent. • Redefine sampling and measurement requirements and protocols. • Resample and reanalyze.
Comparability	A qualitative term expressing the measure of confidence that one data set can be compared to another and can be combined for the decision(s) to be made.	Compare count times, soil surface preparation, sample collection and handling methods, sample preparation and analytical procedures, holding times, stability issues, and QA protocols. Compare XRF and ICP-MS results on same soil samples.	Sampling personnel will use the same sampling protocols. Analyses with XRF will be completed with same analyzer. ICP-MS results will be completed on digested samples as stated in EPA Method 6200.	If data are not comparable to other data sets: • Identify appropriate changes to data collection and/or analysis methods. • Identify quantifiable bias, if applicable. • Qualify the data as appropriate. • Resample and/or reanalyze if needed. • Revise sampling/analysis protocols to ensure future comparability.
Completeness	A measure of the amount of valid data needed to be obtained from a measurement system.	Compare the number of valid measurements completed (samples collected or samples analyzed) with those established by the project's data needs.	The percent complete will be determined during data validation. Measure 40 locations per decision unit.	If data set does not meet completeness objective: • Identify appropriate changes to data collection and/or analysis methods. • Identify quantifiable bias, if applicable. • Qualify the data as appropriate. • Resample and/or reanalyze, if needed. • Revise sampling/analysis protocols to ensure future comparability.

Data Quality Indicator	Definition	Example Determination Methodologies	Project-Specific Information	Corrective-Action Examples
Sensitivity	The capability of a method or instrument to discriminate among measurement responses representing different levels of the variable of interest.	Determine the minimum concentration or attribute to be measured by a method (MDL), by an instrument (instrument detection limit), or by a laboratory (quantitation limit). The practical quantitation limit is the lowest level that can be routinely quantified and reported by a laboratory.	Ensure that sensitivity, as measured by detection limits, is appropriate for the action levels.	If sensitivity does not meet objective: • Request reanalysis or re-measurement. • Qualify/reject the data before use.

Table A.8 presents the DQOs and laboratory analytical performance requirements for an ICP-MS analysis of soil samples based on site-specific lists for arsenic and lead. Laboratory operations and analytical services will be performed in compliance with Volume 4 of the *Hanford Analytical Services Quality Assurance Requirements Documents* (HASQARD; DOE-RL 2007) and specific criteria identified in Table A.8. The criteria listed in Table A.8 take precedence over similar criteria in the HASQARD. In consultation with the laboratory, the project lead and/or sample management and reporting lead can approve changes to analytical methods as long as the method is based on a nationally recognized (e.g., EPA, American Society for Testing and Materials [ASTM]) method, the new method achieves project DQOs as well as or better than the replaced method, and the new method is required due to the nature of the sample (e.g., high radioactivity).

Table A.8. Laboratory analytical performance requirements for ICP-MS soil analyses

Analyte	Benchmarks for the Pilot Study[a]	Range of Recovery (Accuracy)	SRM Accuracy	Relative Precision	Achieved Detection Limits[b] (µg/g dry wt.)	Reporting Limit[c] (µg/g dry wt.)
Arsenic	Soil Background: 6.47 mg/kg Screening Criteria: 20 mg/kg	75–125%	±20%	≤25%	0.3	1
Lead	Soil Background: 10.2 mg/kg Screening Criteria: 250 mg/kg	75–125%	±20%	≤25%	0.006	0.02

(a) Soil background is the 90th percentile for the Hanford Site (DOE-RL 1993), and the unrestricted land-use soil cleanup standard is the *Model Toxics Control Act* Method A (WAC 173-340-740).
(b) Annually verified sediment/soil MDL.
(c) Reporting limit defined as 3.18*MDL.

A.3.1.3 Special Training and Certification

A graded approach is used to ensure workers receive a level of training commensurate with responsibilities, and it complies with applicable DOE orders and government regulations. The sample lead, in coordination with line management, will ensure that sample personnel meet special training requirements.

Because the pilot study is covering areas that were not disturbed by the Manhattan Project or later soil-disturbing activities, training requirements for personnel will reflect what is needed to enter and perform sampling activities at these locations. These requirements may change for further work in the 100-OL-1 OU. Typical training requirements or qualifications include those imposed by the contract, regulations, DOE orders, DOE contractor requirements documents, the American National Standards Institute and the American Society of Mechanical Engineers, and the Washington Administrative Code. For example, the environmental, safety, and health training program provides workers with the knowledge and skills necessary to execute assigned duties safely. Sample personnel typically will have completed the following training before starting work:

- Hanford general employee radiation training
- Hanford general employee training

Project-specific safety training, geared specifically to the project and the day’s activity, will be provided. Project-specific training requirements include the following:

- Training requirements or qualifications needed by sampling personnel will be in accordance with DVZ-AFRI QA program requirements.
- Samplers are required to have training and/or experience with soil sampling being performed in the field.
- Samplers are required to have read the user’s guide for the Niton XL3t 950 analyzer and be familiar with operation of the system.

In addition, pre-job briefings will be performed to evaluate an activity and its hazards by considering many factors, including

- objective of the activities
- individual tasks to be performed
- hazards associated with the planned tasks
- controls applied to mitigate the hazards
- environment in which the job will be performed
- facility where the job will be performed
- equipment and material required
- safety procedures applicable to the job
- training requirements for individuals assigned to perform the work
- level of management control
- proximity of emergency contacts.

Line management will confirm an individual employee’s training is appropriate and up-to-date before performing any field work.

A.3.1.4 Documents and Records

The project lead is responsible for ensuring the current version of the SAP is being used and for providing updates to sample personnel. Version control is maintained through the administrative document control process. Before implementation of field activities, the project lead will obtain permission to proceed from the DOE-RL Cultural Resources Program, any recommendations from the biological review of the area will be considered, and the project lead will update any part of the SAP necessary to incorporate mitigation actions. DOE-RL and the regulatory agencies will review and approve changes to the sampling plan that affect the data needs. Information pertinent to sampling and analysis will be recorded in field datasheets in accordance with existing sample collection protocols in the HASQARD (DOE-RL 2007) and the DVZ-AFRI QA plan (QA-DVZ-AFRI-001, Rev. 1).

The sample lead is responsible for ensuring the field sampling protocol (section A.2.4) is maintained up-to-date and aligned with revisions or other approved changes to the SAP. The sample lead will ensure that deviations from the SAP or problems encountered in the field are documented appropriately (e.g., in the field datasheet, on nonconformance report forms) in accordance with internal corrective action procedures.

The project lead, sample lead, or designee, will be responsible for communicating field corrective action requirements and for ensuring immediate corrective actions are applied to field activities. Table A.9 presents the change control for this project.

Table A.9. Change control for the 100-OL-1 OU remedial investigation

Type of Change	Action	Documentation
By sample lead: • Relocation of a pre-determined soil sampling location due to cultural resources or presence of soil disturbances (e.g., waste site lay down material) • Location of focused sampling effort around orchard tree stumps	No SAP revision necessary	Field datasheets
By project lead: • Changes to field sampling plan	Revise SAP; obtain regulatory approval; distribute SAP	Revised SAP or approved TPA change notice

Datasheets (Figure A.2 and Figure A.3) are required for field activities. Only authorized persons may make entries in datasheets. Datasheets will be maintained as part of the test data package in accordance with DVZ-AFRI QA program. Datasheet entries will be made in indelible ink. Corrections will be made by striking through the erroneous data with a single line of ink, entering the correct data, and initialing and dating the changes.

XRF analyzer results are electronic material, downloaded from the XRF instrument to project share drive. The verification of the data will follow DVZ-AFRI QA plan (QA-DVZ-AFRI-001, Rev. 1).

The project lead is responsible for ensuring the project file is properly maintained. The project file will contain the records or references to their storage locations. The project file will include the following, as appropriate:

- field datasheets or operational records
- Global Positioning System (GPS) data
- chain-of-custody forms for soil samples to laboratory
- sample receipt records
- inspection or assessment reports and corrective action reports
- interim progress reports
- final reports
- laboratory data packages
- verification and validation reports.

The laboratory is responsible for maintaining and having available upon request, the following:

- analytical logbooks
- raw data and QC sample records
- standard reference material and/or proficiency test sample data
- instrument calibration information.

Records may be stored in either electronic or hard copy format. Documentation and records, regardless of medium or format, are controlled in accordance with internal work requirements and processes to ensure accuracy and availability of stored records. Records required by the TPA will be managed in accordance with the requirements of the Agreement.

A.3.2 Data Generation and Acquisition

The following sections address data generation and acquisition to ensure the project methods for sampling, measurement and analysis, data collection or generation, data handling, and QC activities are appropriate and documented.

A.3.2.1 Sampling Process Design (Experimental Design)

As discussed previously, the sampling approach for XRF analysis of surface soils in select decision units uses a probability-based design. Probability-based sampling designs apply sampling theory and involve random selection of the location of the sampling. An important feature of a probability-based sample is that each member of the population from which the sample was selected has a known probability of being selected. Thus, when a probability-based design is used, statistical inferences are made about the sampled population from the data obtained; e.g., comparing the 95th percentile upper confidence limit for lead or arsenic in a decision unit to a benchmark. A random-start, systematic-grid-sampling design will be used to determine the locations within a decision unit. The sample lead, or designee, may modify the exact location for soil collection to avoid cultural resources or other features not readily observable prior to field activities. Section 2.0 provides the types, number, and location of samples.

A.3.2.2 Sample Handling and Custody

Soil samples from the culturally cleared areas in OL-14 and IU6-4 are returned to PNNL for homogenizing before further analysis. A sampling and data tracking database is used to track the samples from the point of collection through the laboratory analysis process. The field sample lead assigns a sample number to each soil sample, using the name of the decision unit. Laboratory analytical results are entered into project-specific files.

Sample custody during laboratory analysis is addressed in the applicable laboratory standard operating procedures. Laboratory custody procedures will ensure that sample integrity and identification are maintained throughout the analytical process. Storage of samples at the laboratory will be consistent with laboratory instructions prepared by sample management and reporting lead.

A.3.2.3 Analytical Methods

The analytical methods are controlled in accordance with the laboratory's QA plan and the requirements of this QAPP. EPA Method 6200 (EPA 2007a) is the basis for the XRF analyses. The procedure for the digestion of soil is based on EPA Method 3050B (EPA 1996a), and the procedures for ICP-MS analyses are based on EPA Methods 1638 and 200.8 (EPA 1994 and 1996b).

If the laboratory uses a nonstandard or unapproved method, the laboratory must provide method validation data to confirm the method is adequate for the intended use of the data. This includes information such as determination of detection limits, quantitation limits, typical recoveries, and analytical precision and bias. In consultation with the laboratory, the project lead and/or sample management and reporting lead can approve changes to analytical methods as long as the method is based on a nationally recognized (e.g., EPA, ASTM) method, the new method achieves project DQOs as well as or better than the replaced method, and the new method is required due to the nature of the sample.

Laboratories providing analytical services in support of this SAP will have in place a corrective action program addressing analytical system failures and documenting the effectiveness of corrective actions. Issues affecting analytical results are to be resolved by the sample management and reporting lead in coordination with the project lead.

A.3.2.4 Quality Control

Quality control procedures must be followed in the field and laboratory to ensure reliable data are obtained (DOE-RL 2007, Volume 2). Table A.10 provides information about the requirements and frequency for field and laboratory quality control samples. Field personnel will collect QC samples to evaluate the potential for cross-contamination and to provide information pertinent to field variability. Field QC for sampling will require a daily instrument check for precision, and the collection of triplicate measurements for each location per decision unit. For the collected soil, the soil will be homogenized and split for intrinsic XRF samples and ICP-MS analyses, each in triplicate. The QC samples and frequency are listed in Table A.11 for XRF measurements and in Table A.12 for ICP-MS.

Table A.10. Definitions, requirements, and frequency for field and laboratory quality control samples

QC Sample	Definition/Purpose	Frequency
Field Precision Checks	Estimate precision, including sampling and analytical variability	Precision instrument check once per field day Three measurements per location per decision unit
Method or Procedural Blank (MB) for ICP-MS	A combination of solvents, surrogates, and all reagents used during sample processing, processed concurrently with the field samples. Monitors purity of reagents and laboratory contamination.	1 per 20 samples batch All analytes
Standard Reference Material (SRM)	An external reference sample that contains a certified level of target analytes; serves as a monitor of accuracy. For ICP-MS analyses, SRM is extracted and analyzed with samples of a like matrix.	XRF measurement of SRM at beginning and end of each field day, and after every 20 samples 1 per sample batch for ICP-MS
Matrix Spike (MS)	A field sample spiked with the analytes of interest is processed concurrently with the field samples; monitors effectiveness of method on sample matrix; performed in duplicate for sediments. An MS must be processed for each distinct matrix.	1 per sample batch for ICP-MS
Duplicate Sample for ICP-MS	Second aliquot of a field sample processed and analyzed by ICP-MS to monitor precision	1 per sample batch for ICP-MS

Field assessment sampling as outlined in this plan is designed to assess sampling reproducibility. If sampling requirements cannot be met due to sampling or measurement system failure, field conditions, or other factors that cannot be controlled, corrective actions will be discussed with the sample lead, project lead, QA engineer, and DOE-RL technical lead. A corrective action will be agreed upon based on the critical/non-critical nature of the parameter, documented in the field datasheet, and communicated to the sampling team. In general, if critical measurements or samples cannot be collected, sampling will be rescheduled. If a non-critical measurement or sample cannot be collected, the deviation will be documented. The QA engineer will review corrective actions to assess their effectiveness. Any deviations from the SAP will be documented.

The study design and QC samples are intended to help assess the major components of total study error, which facilitates the final evaluation of whether environmental data are of sufficient quality to support the related decisions. The QC sample requirements are designed to provide measurement error information that can be used to initiate corrective actions with the goal of limiting the total measurement error. Measurement quality objectives for the analyses can be expressed in terms of accuracy, precision, completeness, and sensitivity goals. Accuracy and precision are monitored through the analysis of QC samples. Table A.11 and Table A.12 define the required accuracy and precision for QC samples, along with corrective actions that must be implemented when QC criteria are not met.

Table A.11. Measurement quality criteria for XRF

QC Parameter	Acceptance Criteria	Corrective Action
Accuracy: - *Standard Reference Material (SRM)*	Metals: ≤20% PD (percent difference) Determined vs. certified range	Review data to assess impact of matrix. Reanalyze sample and/or document corrective action. If other QC data are acceptable then flag associated data if sample is not reanalyzed.
Precision: - *Field precision check*	Metals: ≥20% RPD (relative standard deviation)	Review data to assess impact of matrix. If other QC data are acceptable, then flag associated data. If QC data are not affected by matrix failure, then re-process duplicate. If not possible, then notify client and flag associated data.

Table A.12. Measurement quality criteria for ICP-MS

QC Parameter	Acceptance Criteria	Corrective Action
Accuracy: - Method Blank (MB) for ICP-MS	MB undetected or MB < MDL If MB > MDL and < RL, then perform corrective action	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action.
	If MB > MDL and > RL; sample values >10X MB, then perform corrective action	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action. Data must be flagged.
	If MB > MDL and > RL; sample values ≤10X MB, then perform corrective action	Perform corrective action as above and re-process (extract, digest) sample batch. If batch cannot be re-processed, notify client and flag data.
- Standard Reference Material (SRM)	Metals: ≤20% PD (percent difference). Determined vs. certified range.	Review data to assess impact of matrix. Reanalyze sample and/or document corrective action. If other QC data are acceptable then flag associated data if sample is not reanalyzed.
- Matrix Spike (MS)/ MS Duplicate (MSD)	Metals: 75% to 125% recovery	Review data to assess impact of matrix. If other QC data are acceptable and no spiking error occurred, then flag associated data. If QC data are not affected by matrix failure or spiking errors occurred, then re-process MS. If not possible, then notify client and flag associated data.
- Laboratory Control Sample (LCS)	Metals: 75% to 125% recovery	Perform corrective action. Reanalyze and/or re-process sample batch. Batch data associated with failed LCS (LCS data outside control limits) cannot be reported. If batch cannot be re-processed, notify client, flag data, discuss impact in report narrative.
Precision: - Laboratory Duplicates	Metals: ≥25% RPD (relative percent difference)	Review data to assess impact of matrix. If other QC data are acceptable, then flag associated data. If QC data are not affected by matrix failure, then re-process duplicate. If not possible, then notify client and flag associated data.

Table A.13 provides formulas for the calculation of QC sample assessment statistics. All QC sample failures and associated corrective actions will be documented. If data must be reported with failing QC results, then data qualifiers will be assigned to the QC sample data. Table A.14 defines project data qualifiers.

Table A.13. Calculation of quality control assessment statistics

Percent Recovery

The percent recovery is a measurement of accuracy, where one value is compared with a known/certified value. The formula for calculating this value is:

$$Percent\ Recovery = \frac{amount\ detected}{amount\ expected} \times 100$$

Percent Difference

The percent difference (PD) is a measurement of precision as an indication of how a measured value is different from a "real" value. It is used when one value is known or certified, and the other is measured. The formula for calculating PD is:

$$Percent\ Difference = \frac{X_2 - X_1}{X_1} \times 100$$

where X_1 is the known value (e.g., SRM-certified value) and X_2 is the determined value (e.g., SRM concentration determined by analyst).

Relative Percent Difference

The RPD is a measurement of ***precision***; it is a comparison of two similar samples (matrix spike/matrix spike duplicate pair, field sample duplicates). The formula for calculating RPD is:

$$RPD = \left| \frac{2 \times (X_1 - X_2)}{(X_1 + X_2)} \right| \times 100$$

where X_1 is the concentration or percent recovery in sample 1 and X_2 is the concentration or percent recovery in sample 2.

Note: Report the absolute value of the result – the RPD is always positive.

Relative Standard Deviation

The RSD is a measurement of ***precision***; it is a comparison of three or more similar samples (e.g., field sample triplicates, initial calibration, MDLs). The formula for calculating RSD is:

$$\%RSD = \frac{Standard\ Deviation\ of\ all\ Samples}{Average\ of\ all\ Samples} \times 100$$

Table A.14. Project data qualifiers

Method Qualifiers	
NR	Method qualifier − Analyte was not required
P	Method qualifier – ICP
Data Qualifiers	
B	Analyte found in both sample and associated blank. The “B” will be reported on the result associated with the field samples, not the blank.
J	Estimated concentration between the MDL and RL
U	The concentration is less than the MDL, or the analyte was not detected; the MDL value with a U flag is reported.
W	Post-digestion matrix or blank spike out of control limits
Quality Control Qualifiers	
N	Spiked sample recovery not within control limits
&	Accuracy result not within control limits (outside recovery of SRM)
*	Precision result not within control limits

A.3.2.5 Instrument and Equipment Testing, Inspection, and Maintenance

Equipment used for collection, measurement, and testing should meet the applicable standards (e.g., ASTM standards) or have been evaluated as acceptable and valid in accordance with the procedures, requirements, and specifications. The sample lead or equivalent will ensure that the data generated with computer software systems are backed up and/or downloaded on a regular basis. Software configuration will be acceptance tested before use in the field.

Measurement and testing equipment used in the field or in the laboratory that directly affects the quality of analytical data will be subject to preventive maintenance measures to minimize measurement system downtime. Laboratories and onsite measurement organizations must maintain and calibrate their equipment. Maintenance requirements (such as documentation of routine maintenance) will be included in the individual laboratory and the onsite organization QA plan or operating procedures, as appropriate. Maintenance of laboratory instruments will be performed in a manner consistent with three- and four-digit EPA methods (EPA 1983, 1994, 2007), or consistent with auditable Hanford Site and contractual requirements. Consumables, supplies, and reagents will be reviewed in accordance with SW-846 (EPA 2007b) requirements and will be appropriate for their use.

A.3.2.6 Instrument and Equipment Calibration and Frequency

Section A.3.4 provides specific field equipment calibration information. Analytical laboratory instruments and equipment are calibrated in accordance with the laboratory’s QA plan.

A.3.2.7 Inspection and Acceptance of Supplies and Consumables

Supplies and consumables used in support of sampling and analysis activities will be procured in accordance with internal work requirements and processes described in the contractor acquisition system. Responsibilities and interfaces necessary to ensure items are procured and/or acquired for the contractor must be in place and meet specific technical and quality requirements. The procurement system ensures purchased items comply with applicable procurement specifications. Supplies and consumables will be checked and accepted by users before use. Supplies and consumables procured by the analytical laboratories will be purchased, checked, and used in accordance with the laboratories' QA plans.

A.3.2.8 Non-direct Measurements

Non-direct measurements include data obtained from sources such as computer databases, programs, literature files, and historical databases. Non-direct measurements will not be evaluated as part of the work within the scope of this SAP.

A.3.2.9 Data Management

The sample management and reporting lead, in coordination with the project lead, is responsible for ensuring analytical data are appropriately reviewed, managed, and stored in accordance with the applicable programmatic requirements governing data management procedures. Electronic data access, when appropriate, will be via a database (e.g., HEIS, a project-specific database). Where electronic data are not available, hard copies will be provided in accordance with section 9.6 of the TPA (Ecology et al. 1989).

Laboratory errors will be reported to sample management and reporting routinely. For reported laboratory errors, a sample issue resolution form will be initiated in accordance with contractor procedures. This process is used to document analytical errors and to establish resolution with the project lead. The sample issue resolution forms become a permanent part of the analytical data package for future reference and for records management.

Planning for sample collection and analysis will be in accordance with the programmatic requirements governing fixed-laboratory sample collection activities, as discussed in sampling procedures. If specific procedures do not exist for a particular work evolution, or it is determined additional guidance is needed to complete certain tasks, a work package will be developed to adequately control the activities, as appropriate. Examples of the sampling procedure requirements include activities associated with

- chain-of-custody/sample analysis requests
- project and sample identification for sampling services
- control of certificates of analysis
- logbooks
- checklists
- sample packaging and shipping.

When this SAP is implemented, approved work control packages and procedures will be used to document field activities, including radiological and nonradiological measurements. Field activities will be recorded in the field logbook.

A.3.3 Assessment and Oversight

Assessment and oversight address the activities for assessing the effectiveness of project implementation and associated QA/QC activities. The purpose of assessment is to ensure that the QAPP is implemented as prescribed.

A.3.3.1 Assessments and Response Actions

Project management, quality, and/or health and safety organizations may conduct random surveillance and assessments to verify compliance with the requirements outlined in this SAP, procedures, and regulatory requirements. Additional assessment activities will be performed if circumstances in the field dictate the need. Deficiencies identified by these assessments will be reported in accordance with existing programmatic requirements. The project’s line management chain will coordinate the corrective actions and/or deficiencies in accordance with the contractor QA program, the corrective action management program, and associated procedures that implement these programs. Oversight activities in the analytical laboratories, including corrective action management, will be conducted in accordance with the laboratories’ QA plans.

A.3.3.2 Reports to Management

Data quality issues will be reported to the project lead. Issues reported by the XRF samplers or by the laboratory will be communicated to the sample management and reporting lead, who will initiate a sample issue resolution in accordance with contractor procedures. This process is used to document analytical or sample issues and to establish resolution with the project lead.

At the end of the project, a data quality assurance (DQA) report will be prepared to determine whether the type, quality, and quantity of collected data met the quality objectives described in this SAP.

A.3.4 Data Validation and Usability

The elements under data validation and usability address the QA activities occurring after the data collection phase of the project is completed. Implementation of these elements determines whether the data conform to the specified criteria, thereby satisfying the project objectives.

A.3.4.1 Data Review, Verification, and Validation

The criteria for verification include, but are not limited to, review for completeness (samples were analyzed as requested), use of the correct analytical method or procedure, transcription errors, correct application of dilution factors, appropriate reporting of units (e.g., dry weight versus wet weight), and correct application of conversion factors. Laboratory personnel may perform data verification.

Validation activities will be based on EPA functional guidelines and the HASQARD (DOE-RL 2007). Data validation may be performed by the sample management and reporting organization and/or by a party independent of both the data collector and the data user. Data validation qualifiers must be compatible with the HEIS database.

Data validation will be performed to ensure that the data quality goals established during the planning phase have been achieved. Data validation will be performed in accordance with internal procedures. The criteria for data validation are based on a graded approach. Five levels of validation have been defined, Level A through Level E. Level A is the lowest level and is the same as verification. Level E is a 100% review of data (e.g., calibration data; calculations of representative samples from the data set). Validation will be performed to Level C, which is a review of the QC data. Level C validation specifically requires verification of deliverables; requested versus reported analyses; and qualification of the results based on analytical holding times, method blank results, matrix spike/matrix spike duplicate results, surrogate spike recoveries, and duplicate sample results. Level C validation will be performed on at least 5% of the data by matrix and analyte group. For this QAPP, analyte group refers to categories such as lead or arsenic. The goal is to cover the various analyte groups and matrices during the validation.

When outliers or questionable results are identified, the data associated with these outliers and questionable data will be validated and additional data validation will be performed. This data validation will consist of selecting up to an additional 5% of the data for the analytical method for which statistical outliers and/or questionable data were found during the initial round of data validation. The additional validation will begin with Level C and may increase to Levels D and E, as needed, to ensure that data are usable. Level C validation is a review of the QC data, while Levels D and E include review of calibration data and calculations of representative samples from the data set. Data validation will be documented in data validation reports. An example of questionable data is when the positive detections are greater than the practical quantitation limit or reporting limit in soil/aquifer sediment from a site that should not have exhibited contamination. Similarly, results below background would not be expected and could trigger a validation inquiry. Data validation will be documented in data validation reports, which will be included in the project file.

Relative to analytical data in sample media, physical data and/or field screening results are of less importance in making inferences of risk. Field QA/QC data will be reviewed to ensure that physical property data and/or field screening results are usable.

A.3.4.2 Reconciliation with User Requirements

The DQA process compares completed field sampling activities to those proposed in corresponding sampling documents and provides an evaluation of the resulting data. The purpose of the data evaluation is to determine whether quantitative data are of the correct type and are of adequate quality and quantity to meet the project data needs. The results of the DQA will be used in interpreting the data and determining whether the objectives of this activity have been met. The DQA will be in accordance with EPA's *Data Quality Assessment: A Reviewer's Guide*, and *Data Quality Assessment: Statistical Methods for Practitioners* (EPA 2006a, b).

A.3.4.3 Corrective Actions

The responses to data quality defects identified through the DQA process will vary and may be data- or measurement-specific. Some pre-identified corrective actions are identified in Table A.7 and Table A.11 and Table A.12.

A.4 Health and Safety Plan

Date: June 1, 2014 through September 30, 2014	**Author: Brad Fritz (field team lead)**
Project #: 65905	**Project Title**: Soil Sampling former Hanford Orchards Properties

Describe Activities: Collect surface soil samples and analyze soil concentrations of metals in-situ with XRF

Between 150 and 200 locations in 4 different areas will be analyzed for trace metals concentrations. This in-situ analysis will be done with a portable XRF instrument (Niton XL3T950). This instrument does not contain a sealed source; it generates x-rays using an x-ray tube. Additionally, 10 to 20 surface soil samples will be collected. These will be 10 to 50 g samples scraped from the surface and stored in plastic bags or jars. All sampling locations will be accessed on foot; vehicles will not drive off-road. The summer conditions that will exist during the collection effort will be the largest risk associated with this sampling effort.

Work Location: Hanford Site

ES&H Hazards:
- ☐ Chemical
- ☐ Biological
- ☐ Radiological
- ☐ NIR: Lasers/RF/ magnetic field
- ☐ U/W diving
- ☐ Electrical hazards
- ☐ Powered equipment
- ☐ Manual lifting
- ☐ Working alone
- ☐ Work at heights
- ☐ Industrial site
- ☐ Use of Firearms
- ☐ Traffic
- ☐ Off-road vehicles
- ☐ Boats/water hazards
- ☐ Aviation
- ▪ Environmental/ temp. extremes
- ☐ Other ES&H risks:
- ▪ Fatigue/physical stress
- ▪ Hazardous flora/fauna
- ☐ Hazardous activities nearby
- ☐ Other dangerous environment
- ☐ Waste generation/ treatment/disposal

Risk Analysis: *(describe level of risk associated with the work activities and why it is acceptable)*

Minimal risk. The primary risk associated with this project is from conducting work in hot conditions at a remote field site. Adequate water will be taken to the field by the field team. Sun block, appropriate clothing, etc, will minimize sun exposure. The work will not be physically strenuous (slow pace, no heavy lifting), which will minimize work load.

Hazard Mitigation: *(for each activity list specific hazards of concern and mitigation methods)*

Activity	Hazard(s)	Hazard Control/Mitigation
Sample Collection	WALKING/WORKING SURFACES	Wear boots or sturdy, close toed, above the ankle shoes.
	ADVERSE WEATHER CONDITIONS thunderstorms/lightning.	Avoid doing field work when thunder showers are expected. If storm is approaching, drive to nearest large enclosed building. If caught out in open when a thunder shower occurs, take shelter in vehicles with windows rolled up
	REMOTE WORK AREA	Know your location- carry hard copy maps and gps Communication available – cell service is available at all locations Have first aid kit and trained personnel available. Know emergency numbers. Use buddy system- a minimum of two people required for sample collection
	TEMPERATURE EXTREMES	Drink cool liquids as appropriate. Wear appropriate clothing for hot-sunny conditions (loose clothes, hats, etc). Use sunscreen. Discuss signs/symptoms of cold/heat stress in pre-job meeting-Hyperthermia or heats stroke is the result of significant overexposure to the factors of heat stress. Symptoms are chills, irritability, hot and dry skin, convulsions leading to unconsciousness. Potable water should be carried into the field in appropriate containers when working in remote areas. Coffee, tea and caffeine-containing soft drinks should be avoided.
		Staff will make noise, walk with heavy steps, and remain alert for the

	HAZARDOUS FLORA/FAUNA Rattlesnakes, bees/wasps	presence of snakes. Avoid stepping over rocks with holes or gaps underneath. Try to walk in open spaces between brush and other potential cover used by snakes. Staff will not approach snakes. If a rattle is heard, staff members will stop, look around for the presence of the snake, and back away from the snake (or sound) slowly. Be alert for bees and wasp. Avoid bushes or locations with bee/wasp activity
	CONTAMINATED SOIL	The concentrations of lead and arsenic expected in soil samples are not too high. However, staff may elect to wear nitrile or latex gloves during sample collection. Additionally, wash water will be available in the field for staff to rinse hands if desired. Staff will be expected to wash hands after handling soil and prior to eating or drinking.
Sample Analysis	NON-IONIZING RADIATION XRF instrument	Follow all manufactures instructions for use Do not activate instrument when pointed at body parts

Emergency Response:

FOR ALL EMERGENCIES, CALL Hanford Site Emergency Number 373 - 0911

WHEN THE CONDITION HAS STABILIZED, report the emergency or incident (injuries, potential exposures, motor vehicle accident, fire, etc.) to the PNNL single point contact 375-2400

Nearest Hospital: Kadlec Medical Center

NOTE: If you need to make pen and ink changes to this plan or need clarification, contact your S&H Rep. (Mike Fullmer 372-6370) .

Approval

Role	Print Name	Signature	Date
Project Manager	Dawn Wellman		5/14/14
S&H Rep	Mike Fullmer	Mike Fullmer	5/1/14
Line Manager	Brian Opitz	Brian Opitz	5/2/14
Product Line Manager	Michelle Johnson	mjohnson	6.4.2014

Authorized Workers

I have read the ES&H Plan, understand the hazards and controls associated with this work, and will implement the controls as indicated. I will inform the activity lead if there are changes to the hazards or if the controls appear to be inadequate.

Print Name	Signature	Date

A.5 References

10 CFR 830. Code of Federal Regulations, *Energy/Nuclear Safety Management*, Subpart A, “Quality Assurance Requirements.”

36 CFR Part 800. Code of Federal Regulations, Title 36, *Parks, Forests, and Public Property*.

40 CFR Part 136. Code of Federal Regulations, Title 40, *Protection of the Environment*, Part 136, Appendix B, “Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11.”

ASME NQA-1-2000. *Quality Assurance Requirements for Nuclear Facility Applications.* American Society of Mechanical Engineers, New York, New York.

ANSI/ASQ (American National Standards Institute/American Society for Quality). 1995. *Introduction to Attribute Sampling*. ANSI/ASQ S2-1995, New York.

Delistraty D and J Yokel. 2011. “Ecotoxicological Study of Arsenic and Lead Contaminated Soils in Former Orchards at the Hanford Site, USA.” *Environmental Toxicology.* doi:10.1002/tox.20768.

DOE Order 414.1D. *Quality Assurance*. U.S. Department of Energy, Washington, D.C.

DOE-RL (U.S. Department of Energy-Richland Operations Office). 1993. *Hanford Site Background: Part 1, Soil Background for Nonradioactive Analytes*. DOE-RL-92-24, Rev. 1, Richland, Washington.

DOE-RL (U.S. Department of Energy-Richland Operations Office). 2007. *Hanford Analytical Services Quality Assurance Requirements Documents.* DOE-RL-96-68, 2007, Rev. 3, Volumes 1, 2, 3, and 4, Richland, Washington.

DOE-RL (U.S. Department of Energy-Richland Operations Office). 2013. *Remedial Investigation/Feasibility Study Work Plan to Evaluate the 100 OL-1 Operable Unit Pre Hanford Orchard Lands*. DOE-RL-2012-64, Draft A. Richland, Washington.

DOE-RL (U.S. Department of Energy, Richland Operations Office). 2014. *100-OL-1 Operable Unit Field Portable X-Ray Fluorescence (XRF) Analyzer Pilot Study Plan*. DOE-RL-2014-38, Rev. 0, Richland Operations Office, Richland, Washington.

Ecology (Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy). 1989. *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement). Document No. 89-10, as amended, Olympia, Washington.

EPA (U.S. Environmental Protection Agency). 1983. *Methods for Chemical Analysis of Water and Wastes*. EPA-600/4-79-020, Office of Research and Development, Cincinnati, Ohio.

EPA (U.S. Environmental Protection Agency). 1994. *Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry*. Rev. 5.4, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, Ohio.

EPA (U.S. Environmental Protection Agency). 1996a. *Method 3050B: Acid Digestion of Sediments, Sludges, and Soils*. Office of Solid Waste and Emergency Response, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 1996b. *Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma – Mass Spectrometry*. Office of Water, Engineering and Analysis Division, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2002. *Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites*. EPA 540-R-01-003, OSWER 9285.7-41, Office of Emergency and Remedial Response, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2006a. *Data Quality Assessment: A Reviewer's Guide*. EPA QA/G-9R, EPA/240/B-06/002, Office of Environmental Information, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2006b. *Data Quality Assessment: Statistical Methods for Practitioners*. EPA QA/G-9S, EPA/240/B-06/003, Office of Environmental Information, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2007. *Method 6200: Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*. Office of Solid Waste and Emergency Response, Washington, D.C.

EPA (U.S. Environmental Protection Agency). 2007b. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW-846, Third Edition, Final Update IV-B, as amended, Office of Solid Waste and Emergency Response, Washington, D.C.

Matzke BD, JE Wilson, LL Nuffer, ST Dowson, JE Hathaway, NL Hassig, LH Sego, CJ Murray, BA Pulsipher, B Roberts, and S McKenna. 2010. *Visual Sample Plan Version 6.0 User's Guide*. PNNL 19915, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://vsp.pnnl.gov/docs/pnnl16939.pdf.

TPA (Tri-Party Agreement). 2012a. *Change Control Form: Creation of New Operable Unit for Pre-Hanford Orchard Lands Along the River Corridor of the Hanford Site*. TPA-C-12-01, May 7, 2012, U.S. Department of Energy, Richland Operations Office, U.S. Environmental Protection Agency, and Washington State Department of Ecology, Richland, Washington.

TPA (Tri-Party Agreement). 2012b. *Change Control Form: Establish a New Milestone to Develop a Remedial Investigation/Feasibility Study Work Plan to Evaluate the 100-OL-1 Operable Unit*. TPA-M-15-12-02, May 7, 2012, U.S. Department of Energy, Richland Operations Office, U.S. Environmental Protection Agency, and Washington State Department of Ecology, Richland, Washington.

WAC 173-340-740(7)(e). "Model Toxics Control Act – Unrestricted Land Use Soil Cleanup Standards." *Washington Administrative Code*, Olympia, Washington.

Yokel J and DA Delistraty. 2003. "Arsenic, Lead, and Other Trace Elements in Soils Contaminated with Pesticide Residues at the Hanford Site (USA)." *Environmental Toxicology* 18:104–114.

Appendix B

Ecological and Cultural Clearance for the 100-OL-1 Operable Unit Pilot Study

Appendix B

Ecological and Cultural Clearance for the 100-OL-1 Operable Unit Pilot Study

This appendix contains a copy of the letter Pacific Northwest National Laboratory (PNNL) received from Mission Support Alliance documenting the ecological and cultural clearance to conduct work associated with the pilot study. This letter describes the requirements for PNNL staff had to meet to conduct work on the Hanford Site in a manner that did not result in unacceptable disturbance of ecological or cultural resources. This letter also documents that PNNL adhered to applicable Hanford Site procedures and processes, as they relate to cultural and ecological resources.

Mission Support Alliance
Post Office Box 650
Richland, Washington 99352

June 5, 2014

MSA-1402281

Amoret Bunn
Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352

Dear Ms. Bunn:

ECOLOGICAL AND CULTURAL CLEARANCE FOR 100-OL-1 ORCHARDS OPERABLE UNIT PILOT STUDY, IN THE 600 AREA OF THE HANFORD SITE (HCRC# 2011-600-025, HCRC# 2013-100-019, ECR-2014-618)

Reference: MSA Service Catalog Request#KSR000000128227, A. L. Johnson, MSA, April 28, 2014.

PROJECT DESCRIPTION

The project as planned will include the sampling and characterization activities supporting the pilot study for the 100-OL-1 Orchards Operable Unit project. The project will include the use of portable X-ray Florescence (XRF) equipment to analyze surface soils at 40 locations within 4 selected Decision Units. The Decision Units that have been selected for this pilot study are: OL-14, OL-32, OL-FR2-1, and OL-IU6-4 (Figure 1). The use of XRF includes scanning the ground surface with a hand-held device to gather information about the surface sediments. The use of XRF is a non-intrusive activity that will not cause any ground disturbance. To support the use of XRF, sediment samples will be collected within two of the decision units and be used as reference standards to help calibrate the XRF equipment. The collection of these sediment samples will be performed by scraping the ground surface with hand tools to collect approximately 10 grams of sediment. The OL-14 and OL-IU6-4 Decision Units have been identified as the locations from which sediment samples will be collected. Access to the Decision Units will be by existing asphalt, gravel or two-track roadways. Sampling staff will reach individual sample locations within a decision unit by foot. No off-road driving will occur during the completion of this project.

ECOLOGICAL RESOURCES (ECR-2014-618)

Mission Support Alliance (MSA) Environmental Compliance staff performed a pedestrian survey of project areas on May 28, 2014. The project will be performing sampling events throughout selected pre-Hanford historic orchard locations. The orchard vegetation communities are dominated by cheat grass (*Bromus tectorum*). Wildlife use evident during field survey included Western Meadowlark (*Sturnella neglecta*), Horned Lark (*Eremophila alpestris*), Burrowing Owl (*Athene cunicularia*), Common Raven (*Corvus corax*), Swainson's Hawk (Buteo swainsoni), coyote (*Canis latrans*), mule deer (*Odocoileus hemionus*), Elk (*Cervus canadensis*) and Nuttal's cottontail (*Sylvilagus nuttallii*).

OL-14- This decision unit is located within the boundaries of a Bald Eagle (*Haliaeetus leucocephalus*) night roost buffer. These 400 meter buffers are active from November 15 through March 15 of each year. Any work that may take place when these buffers are active shall occur between 10:00 am and 2:00 pm. Staff shall notify 376-BIRD (376-2473) prior to entering buffer areas.

OL-32- This decision unit boundary encroach on the Columbia River shoreline which falls within the boundaries of a Bald Eagle (*Haliaeetus leucocephalus*) night roost buffer. These 400 meter buffers are active from November 15 through March 15 of each year. Any work that may take place when these buffers are active shall occur between 10:00 am and 2:00 pm. Staff shall notify 376-BIRD (376-2473) prior to entering buffer areas.

OL-FR2-1- This decision unit has no outstanding ecological restraints.

OL-IU6-4- This decision unit contains active migratory bird nests within its boundaries. A Common Raven has a nest in a tree and a Swainson's Hawk in a tree directly adjacent to the unit (Figure 2). The scope of work as described is not anticipated to adversely impact either nest. However, **all project personnel must be directed to limit the flushing of parents from the nest to less than 30 minutes every 4 hours.** Additionally four active Burrowing Owl burrows are located within the OL-IU6-4 decision unit. The burrow located the furthest southwest in the attached Figure 2 (Northing 141946.64, Easting 582469.38) has the highest activity and should be buffered from all activities to a distance of by 100m. Limiting the time around the active burrows shown in the attached Figure 2 will reduce the possibility of disturbance.

The active burrows within this decision unit are located at state plane GPS coordinates are as follows

Northing	Easting
141946	582469
142390	582783
142157	582838
142154	582895

No plant or animal species protected under the Endangered Species Act, candidates for such protection, or species listed by the Washington State government as threatened or endangered were observed in the vicinity of the proposed project site.

There is always the potential for birds to nest within the project area on the ground, on buildings, or equipment. The nesting season in our area is typically from mid-March to mid-July. The active nests (containing eggs or young) of migratory birds, including Burrowing Owls, Common Raven and Swainson's Hawk are protected by the Migratory Bird Treaty Act (MBTA) of 1918. The MBTA makes it illegal for people to "take" migratory birds, their eggs, feathers, or nests. Take is defined in the MBTA to include by any means or in any manner, any attempt at hunting, pursuing, wounding, killing, possessing, or transporting any migratory bird, nest, egg, or part thereof. **Personnel working on this project must be instructed to watch for nesting birds.** If any nesting birds (if not a nest, a pair of birds of the same species or a single bird that will not leave the area when disturbed) are encountered or suspected, or bird defensive behaviors (flying at workers, refusal to leave area, strident vocalizations) are observed within the project area, contact the author of this section to evaluate the situation.

No adverse impacts are anticipated from the proposed project activities if these recommendations are followed. If there are any changes in the scope of these activities that could result in disturbances outside of the description of this review please complete a Service Catalog Request http://msc.rl.gov/ServiceCatalog/index.cfm for an additional ecological review and reference the ecological review number above to determine if a follow-up Ecological Resources clearance should be conducted.

This review is valid for one year from the letter date listed above.

Technical questions should be directed to J.W. Wilde at 376-2473.

CULTURAL RESOURCES (HCRC-2011-600-025/2013-100-019)

A Cultural Resources assessment of the proposed project was conducted by Keith Mendez of the MSA Cultural and Historic Resources Program on May 28, 2014. This assessment determined that all Section 106 requirements for this undertaking have been previously met as documented by Purtzer (2013) in the *Cultural Resources Review for Remedial Actions at the 100-H-56 Waste Site North of the 100-H Area Hanford Site, Benton County, Washington (HCRC#2013-100-019)* and Purtzer (2011) in the *No Historic Properties Affected (NHPA) Cultural Resources Review for the Remediation of the 600-331 and 600-315 Waste Sites in the 600 Area (HCRC#2011-600-025).* This assessment was approved by DOE-RL on May 28, 2014.

The OL-14 sediment samples will be collected from within the Area of Potential Effect (APE) as defined in HCRC#2013-100-019 (Figure 2). Potential impacts to historic properties from sediment sampling within this area have been previously considered; therefore, the findings and conclusions identified in HCRC#2013-100-019 are relevant and applicable to the actions being considered in support of the 100-OL-1 Orchards Operable Unit Pilot Study at OL-14. **In order to maintain adherence to the conclusions reached in HCRC#2013-100-019, cultural resources monitoring of sediment collection at OL-14 will be conducted.** Because section 106 requirements have been previously met, no additional review of the project is required.

The OL-IU6-4 sediment samples will be collected from within the APE as defined in HCRC#2011-600-025 (Figure 3). Potential impacts to historic properties from sediment sampling within this area have been previously considered; therefore, the findings and conclusions identified in HCRC#2011-600-025 are relevant and applicable to the actions being considered in support of the 100-OL-1 Orchards Operable Unit Pilot Study at OL-IU6-4. **In order to maintain adherence to the conclusions reached in HCRC#2011-600-025, intermittent cultural resources monitoring of sediment collection at OL-IU6-4 will be conducted.** Because section 106 requirements have been previously met, no additional review of the project is required.

Although no cultural resources are expected, there is the potential to discover subsurface archaeological deposits. **Monitoring by a Cultural Resources professional is required for ground disturbing activities associated with this project. Please notify T. E. Marceau (376-0605) at least 7 days prior to the beginning of soil sample collections to schedule a time for an archaeological monitor to observe the collection activities.** If there are changes in the scope of activities that could result in disturbances outside of the description of this project or outside the project boundaries identified on the attached map, contact T. E. Marceau at 376-0605 and submit a new Request for Cultural Resources Review through the MSA Service Catalog for a follow-up Cultural Resources Review and referencing the HCRC number listed above to determine if a follow-up Cultural Resources review should be conducted.

This Cultural Resources Review was written by Keith Mendez, who meets the Secretary of the Interior's Standards for Professional Archaeologists.

Technical questions should be directed to T. E. Marceau at 376-0605.

Sincerely,

April Johnson

April L. Johnson, Manager
Ecological Monitoring and Compliance

jww:kmm

Attachment(s) 1

Cc: ^MSA Correspondence Distribution
^MSA Cultural Resources Program Admin Record
A. L. Johnson, MSA
T. E. Marceau, MSA
J. J. Sharpe, MSA
J. W. Wilde, MSA

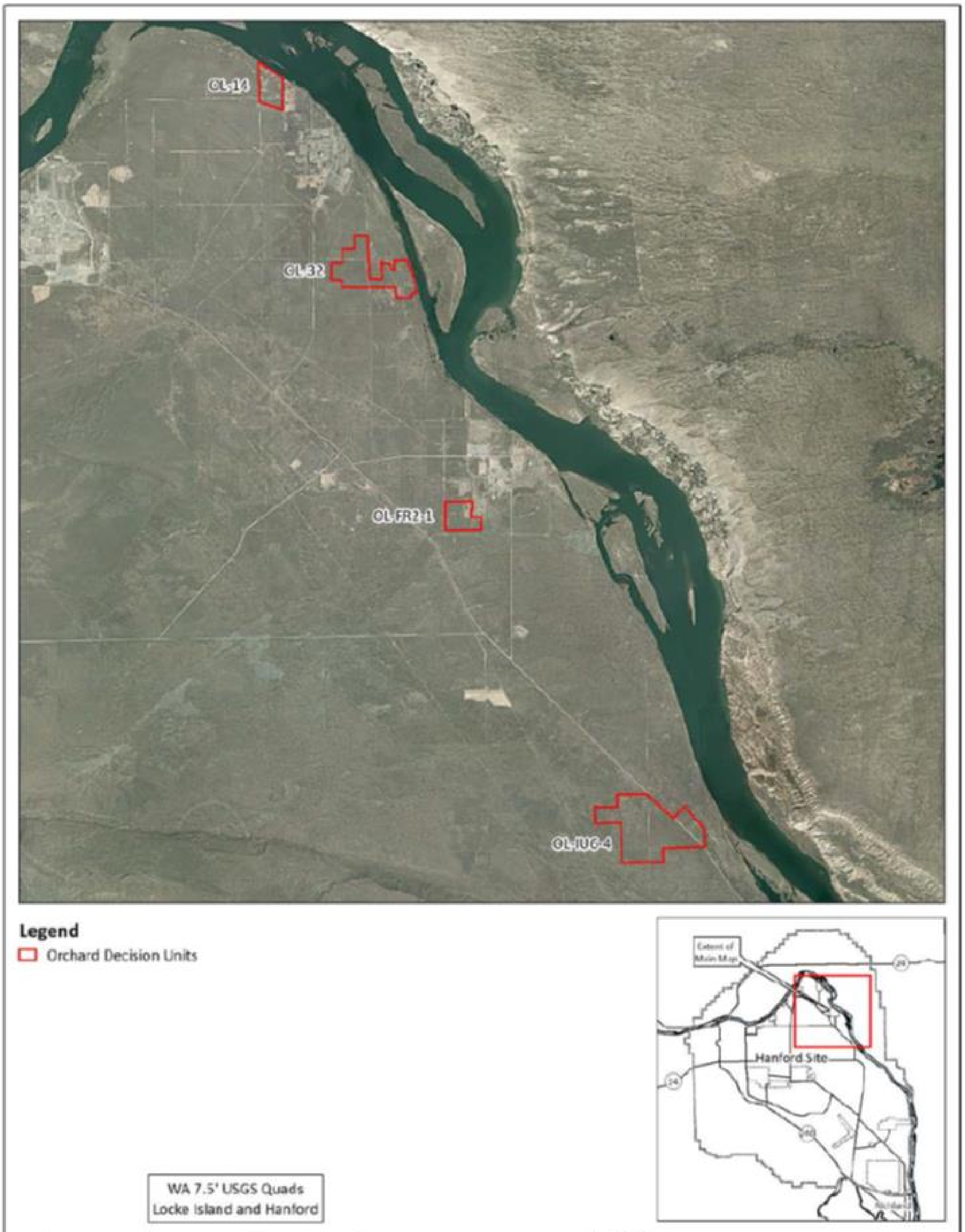
MSA-1402281

ATTACHMENT

June 5, 2014

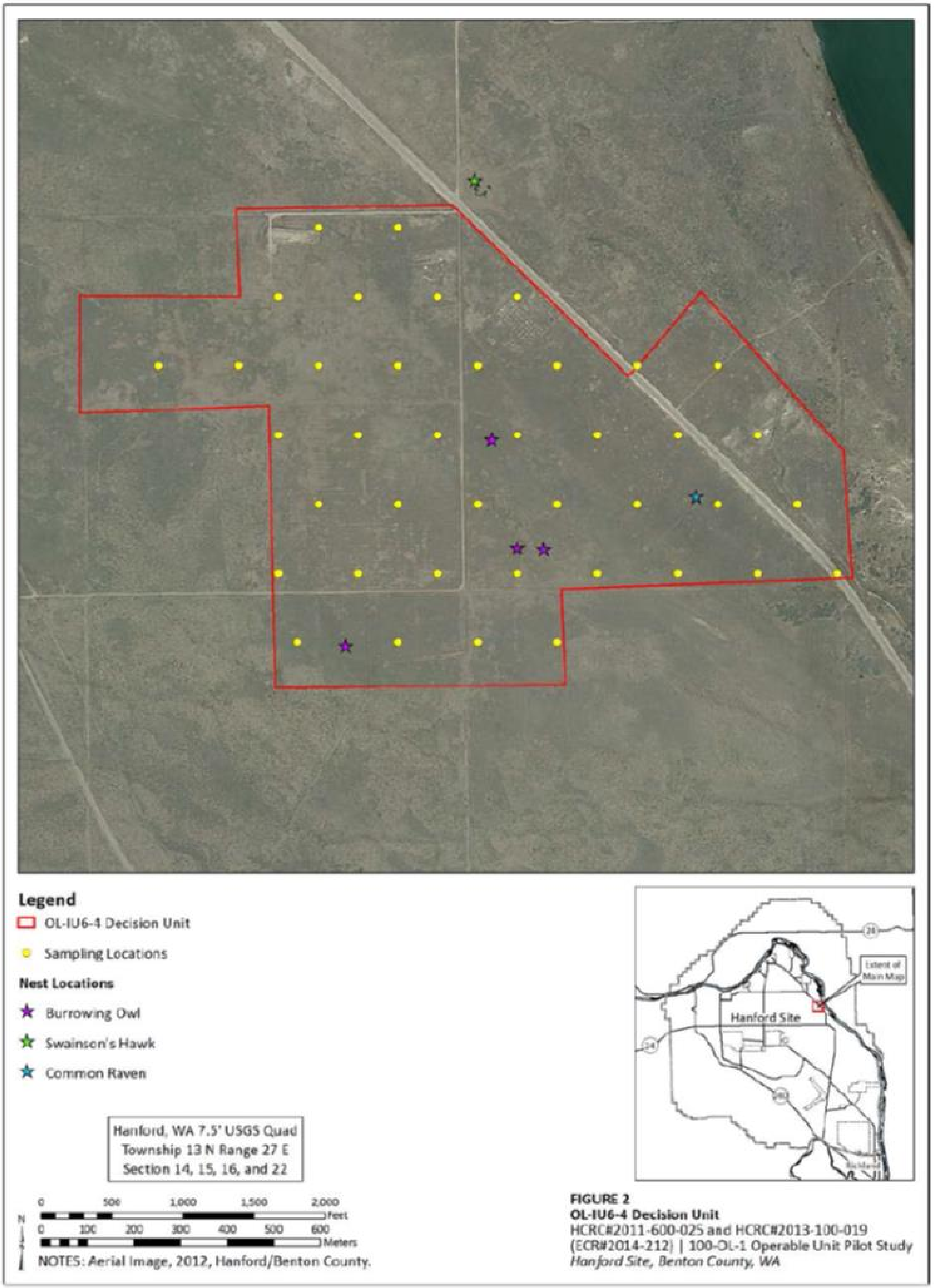
PROJECT LOCATION FOR THE 100-OL-1 ORCHARDS OPERABLE UNIT PILOT STUDY, IN THE 600 AREA OF THE HANFORD SITE
(HCRC# 2011-600-025, HCRC# 2013-100-019, ECR-2014-618)

Consisting of 3 pages,
Including this cover page



NOTES: Aerial Image, 2012, Hanford/Benton County.

FIGURE 1
Project Location
HCRC#2011-600-025 and HCRC#2013-100-019
(ECR#2014-212) | 100-OL-1 Operable Unit Pilot Study
Hanford Site, Benton County, WA



NOTES: Aerial Image, 2012, Hanford/Benton County.

FIGURE 2
OL-IU6-4 Decision Unit
HCRC#2011-600-025 and HCRC#2013-100-019
(ECR#2014-212) | 100-OL-1 Operable Unit Pilot Study
Hanford Site, Benton County, WA

Appendix C

Verified and Validated Data for 100-OL-1 Operable Unit Pilot Study

Appendix C

Verified and Validated Data for 100-OL-1 Operable Unit Pilot Study

This appendix includes all quality assurance (QA) verified and validated data presented in this report. These data were subject to QA review according to Pacific Northwest National Laboratory (PNNL) Nuclear Quality Assurance Level 1 (NQA-1) project procedures (QA-DVZ-AFRI-304). The calculation package number for each table is included in the table caption for referencing back to project records. The data in this appendix include the raw sample results collected at each decision unit, summarized results for each decision unit, a summary of the daily QA check results conducted in the field, the X-ray fluorescence (XRF) method detection limit (MDL) calculation data and the inductively coupled plasma mass spectroscopy (ICP-MS) analytical results. Not included in this appendix are the field data sheets. Those data were subject to QA verification according to PNNL procedures, and are stored in project records as Test Data Package TDP-DVZ-AFRI-004.pdf, but are not included here.

Table C.1. Sample locations for pilot study decision units (CALC-DVZ-AFRI-104)

Sample #	Sample ID	Easting	Northing	Latitude	Longitude
1	OL-14-1R	576855	153414	46.70917	-119.49483
2	OL-14-2R	576855	153541	46.71031	-119.49480
3	OL-14-3R	576855	153669	46.71146	-119.49478
4	OL-14-4R	576855	153797	46.71261	-119.49476
5	OL-14-5R	576890	153846	46.71305	-119.49429
6	OL-14-6R	576892	153350	46.70859	-119.49435
7	OL-14-7R	576892	153605	46.71088	-119.49431
8	OL-14-8R	576892	153733	46.71203	-119.49429
9	OL-14-9R	576929	153414	46.70916	-119.49386
10	OL-14-10R	576929	153541	46.71031	-119.49384
11	OL-14-11R	576929	153669	46.71145	-119.49382
12	OL-14-12R	576929	153795	46.71259	-119.49380
13	OL-14-13R	576965	153286	46.70801	-119.49340
14	OL-14-14R	576965	153350	46.70858	-119.49339
15	OL-14-15R	576965	153478	46.70973	-119.49337
16	OL-14-16R	576965	153605	46.71087	-119.49335
17	OL-14-17R	576965	153733	46.71202	-119.49333
18	OL-14-18R	577002	153414	46.70915	-119.49290
19	OL-14-19R	577002	153541	46.71030	-119.49288
20	OL-14-20R	577002	153669	46.71144	-119.49286
21	OL-14-21R	577039	153350	46.70857	-119.49243
22	OL-14-22R	577039	153478	46.70972	-119.49241
23	OL-14-23R	577039	153605	46.71087	-119.49239
24	OL-14-24R	577039	153732	46.71201	-119.49236
25	OL-14-25R	577076	153286	46.70799	-119.49196
26	OL-14-26R	577076	153414	46.70914	-119.49194
27	OL-14-27R	577076	153541	46.71029	-119.49191

Sample #	Sample ID	Easting	Northing	Latitude	Longitude
28	OL-14-28R	577076	153669	46.71144	-119.49189
29	OL-14-29R	577113	153223	46.70742	-119.49149
30	OL-14-30R	577113	153350	46.70856	-119.49146
31	OL-14-31R	577113	153478	46.70971	-119.49144
32	OL-14-32R	577113	153605	46.71086	-119.49142
33	OL-14-33R	577150	153286	46.70798	-119.49099
34	OL-14-34R	577150	153414	46.70913	-119.49097
35	OL-14-35R	577150	153541	46.71028	-119.49095
36	OL-14-36R	577150	153666	46.71140	-119.49093
37	OL-14-37R	577184	153609	46.71088	-119.49049
38	OL-14-38R	577186	153223	46.70741	-119.49052
39	OL-14-39R	577186	153350	46.70855	-119.49050
40	OL-14-40R	577186	153478	46.70970	-119.49048
1	OL32-1	578149	150952	46.68687	-119.47833
2	OL32-2	578203	150952	46.68686	-119.47762
3	OL32-3	578257	150952	46.68685	-119.47691
4	OL32-4	578311	150952	46.68685	-119.47620
5	OL32-5	578365	150952	46.68684	-119.47549
6	OL32-6	578419	150952	46.68684	-119.47479
7	OL32-7	578473	150952	46.68683	-119.47408
8	OL32-8	578121	150998	46.68729	-119.47867
9	OL32-9	578176	150998	46.68729	-119.47796
10	OL32-10	578230	150998	46.68728	-119.47726
11	OL32-11	578284	150998	46.68727	-119.47655
12	OL32-12	578338	150998	46.68727	-119.47584
13	OL32-13	578392	150998	46.68726	-119.47513
14	OL32-14	578446	150998	46.68725	-119.47442
15	OL32-15	578149	151045	46.68771	-119.47831
16	OL32-16	578203	151045	46.68770	-119.47760
17	OL32-17	578257	151045	46.68770	-119.47689
18	OL32-18	578311	151045	46.68769	-119.47619
19	OL32-19	578365	151045	46.68769	-119.47548
20	OL32-20	578419	151045	46.68768	-119.47477
21	OL32-21	578473	151045	46.68767	-119.47406
22	OL32-22	578338	151092	46.68811	-119.47582
23	OL32-23	578392	151092	46.68810	-119.47512
24	OL32-24	578446	151092	46.68810	-119.47441
25	OL32-25	578311	151139	46.68854	-119.47617
26	OL32-26	578365	151139	46.68853	-119.47546
27	OL32-27	578419	151139	46.68852	-119.47475
28	OL32-28	578473	151139	46.68852	-119.47405
29	OL32-29	578284	151186	46.68896	-119.47652
30	OL32-30	578338	151186	46.68895	-119.47581
31	OL32-31	578392	151186	46.68895	-119.47510
32	OL32-32	578446	151186	46.68894	-119.47439
33	OL32-33	578311	151233	46.68938	-119.47615
34	OL32-34	578365	151233	46.68937	-119.47545
35	OL32-35	578419	151233	46.68937	-119.47474
36	OL32-36	578473	151233	46.68936	-119.47403

Sample #	Sample ID	Easting	Northing	Latitude	Longitude
37	OL32-37	578284	151280	46.68980	-119.47650
38	OL32-38	578338	151280	46.68980	-119.47579
39	OL32-39	578392	151280	46.68979	-119.47508
40	OL32-40	578446	151280	46.68979	-119.47438
1	FR2-1-1	579656	146873	46.65000	-119.45933
2	FR2-1-2	579736	146873	46.64999	-119.45828
3	FR2-1-3	579816	146873	46.64998	-119.45723
4	FR2-1-4	579896	146873	46.64997	-119.45618
5	FR2-1-5	579977	146873	46.64996	-119.45513
6	FR2-1-6	580057	146873	46.64995	-119.45409
7	FR2-1-7	579696	146942	46.65062	-119.45879
8	FR2-1-8	579776	146942	46.65061	-119.45774
9	FR2-1-9	579856	146942	46.65060	-119.45669
10	FR2-1-10	579937	146942	46.65059	-119.45565
11	FR2-1-11	580017	146942	46.65058	-119.45460
12	FR2-1-12	580097	146942	46.65057	-119.45355
13	FR2-1-13	580177	146942	46.65056	-119.45250
14	FR2-1-14	579656	147012	46.65125	-119.45930
15	FR2-1-15	579736	147012	46.65124	-119.45826
16	FR2-1-16	579816	147012	46.65123	-119.45721
17	FR2-1-17	579896	147012	46.65122	-119.45616
18	FR2-1-18	579977	147012	46.65121	-119.45511
19	FR2-1-19	580057	147012	46.65120	-119.45406
20	FR2-1-20	580137	147012	46.65119	-119.45301
21	FR2-1-21	579696	147081	46.65187	-119.45877
22	FR2-1-22	579776	147081	46.65186	-119.45772
23	FR2-1-23	579856	147081	46.65185	-119.45667
24	FR2-1-24	579937	147081	46.65184	-119.45562
25	FR2-1-25	580017	147081	46.65183	-119.45457
26	FR2-1-26	579656	147151	46.65250	-119.45928
27	FR2-1-27	579736	147151	46.65249	-119.45823
28	FR2-1-28	579816	147151	46.65248	-119.45718
29	FR2-1-29	579896	147151	46.65247	-119.45613
30	FR2-1-30	579977	147151	46.65246	-119.45509
31	FR2-1-31	579696	147220	46.65312	-119.45874
32	FR2-1-32	579776	147220	46.65311	-119.45770
33	FR2-1-33	579856	147220	46.65310	-119.45665
34	FR2-1-34	579937	147220	46.65309	-119.45560
35	FR2-1-35	580056	147061	46.65164	-119.45407
36	FR2-1-36	579656	147290	46.65375	-119.45926
37	FR2-1-37	579736	147290	46.65374	-119.45821
38	FR2-1-38	579816	147290	46.65373	-119.45716
39	FR2-1-39	579947	147261	46.65346	-119.45546
40	FR2-1-40	580059	147277	46.65359	-119.45399
1	IU6-4-1	582334	141963	46.60551	-119.42522
2	IU6-4-2	582582	141954	46.60540	-119.42199
3	IU6-4-3	582753	141954	46.60538	-119.41975
4	IU6-4-4	582924	141954	46.60535	-119.41752
5	IU6-4-5	582325	142102	46.60676	-119.42531

Sample #	Sample ID	Easting	Northing	Latitude	Longitude
6	IU6-4-6	582496	142102	46.60674	-119.42308
7	IU6-4-7	582667	142102	46.60672	-119.42084
8	IU6-4-8	582838	142102	46.60670	-119.41861
9	IU6-4-9	583010	142102	46.60668	-119.41637
10	IU6-4-10	583181	142102	46.60666	-119.41414
11	IU6-4-11	583352	142102	46.60664	-119.41190
12	IU6-4-12	583550	142137	46.60692	-119.40931
13	IU6-4-13	582410	142250	46.60808	-119.42417
14	IU6-4-14	582582	142250	46.60806	-119.42193
15	IU6-4-15	582753	142250	46.60804	-119.41970
16	IU6-4-16	582924	142250	46.60802	-119.41746
17	IU6-4-17	583095	142250	46.60800	-119.41523
18	IU6-4-18	583266	142250	46.60798	-119.41299
19	IU6-4-19	583438	142250	46.60796	-119.41076
20	IU6-4-20	582325	142399	46.60943	-119.42526
21	IU6-4-21	582496	142399	46.60941	-119.42302
22	IU6-4-22	582667	142399	46.60939	-119.42079
23	IU6-4-23	582838	142399	46.60937	-119.41855
24	IU6-4-24	583010	142399	46.60934	-119.41632
25	IU6-4-25	583181	142399	46.60932	-119.41408
26	IU6-4-26	583352	142399	46.60930	-119.41185
27	IU6-4-27	582068	142547	46.61079	-119.42858
28	IU6-4-28	582239	142547	46.61077	-119.42635
29	IU6-4-29	582410	142547	46.61075	-119.42411
30	IU6-4-30	582582	142547	46.61073	-119.42188
31	IU6-4-31	582753	142547	46.61071	-119.41964
32	IU6-4-32	582924	142547	46.61069	-119.41741
33	IU6-4-33	583095	142547	46.61067	-119.41518
34	IU6-4-34	583266	142547	46.61065	-119.41294
35	IU6-4-35	582325	142695	46.61210	-119.42520
36	IU6-4-36	582496	142695	46.61208	-119.42297
37	IU6-4-37	582667	142695	46.61205	-119.42074
38	IU6-4-38	582838	142695	46.61203	-119.41850
39	IU6-4-39	582410	142843	46.61342	-119.42406
40	IU6-4-40	582582	142843	46.61340	-119.42183

Table C.2. Raw sampling results for pilot study decision units (CALC-DVZ-AFRI-104)

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
7	OL-14-2R	7/31/2014 8:03	60	18.94	2.96	5.31	2.46
8	OL-14-2R	7/31/2014 8:04	60	18.5	2.99	6.09	2.5
9	OL-14-2R	7/31/2014 8:05	60	22.75	3.14	5.09	2.59
10	OL-14-10R	7/31/2014 8:08	60	16.01	3.06	7.53	2.63
11	OL-14-10R	7/31/2014 8:09	60	16.21	3.05	5.72	2.56
12	OL-14-10R	7/31/2014 8:10	60	17.54	3.09	5.15	2.57
13	OL-14-19R	7/31/2014 8:13	60	486.95	11.06	41.91	8.81
14	OL-14-19R	7/31/2014 8:14	60	481.63	10.89	35.08	8.62
15	OL-14-19R	7/31/2014 8:15	60	487.73	11.12	47.69	8.9
16	OL-14-27R	7/31/2014 8:18	60	269.7	8.12	33.39	6.57
17	OL-14-27R	7/31/2014 8:19	60	277.83	8.28	37.79	6.73
18	OL-14-27R	7/31/2014 8:20	60	190.8	6.9	20.28	5.55
19	OL-14-35R	7/31/2014 8:23	60	937.68	15.13	35.18	11.78
20	OL-14-35R	7/31/2014 8:24	60	985.4	15.69	35.06	12.2
21	OL-14-35R	7/31/2014 8:25	60	1000.75	15.89	49.78	12.45
22	OL-14-37R	7/31/2014 8:28	60	41.31	3.84	< LOD	4.58
23	OL-14-37R	7/31/2014 8:29	60	43	3.92	< LOD	4.67
24	OL-14-37R	7/31/2014 8:30	60	42.49	3.87	< LOD	4.58
25	OL-14-36R	7/31/2014 8:33	60	450.74	10.43	118.84	8.92
26	OL-14-36R	7/31/2014 8:34	60	462.71	10.77	110.2	9.12
27	OL-14-36R	7/31/2014 8:35	60	459.48	10.7	109.09	9.05
28	OL-14-32R	7/31/2014 8:38	60	344.83	9.51	33.15	7.61
29	OL-14-32R	7/31/2014 8:39	60	362.04	9.72	32.82	7.76
30	OL-14-32R	7/31/2014 8:40	60	358.46	9.61	34.04	7.68
31	OL-14-28R	7/31/2014 8:43	60	500.57	11.44	55.24	9.21
32	OL-14-28R	7/31/2014 8:44	60	493.8	11.18	51.76	8.98
33	OL-14-28R	7/31/2014 8:45	60	491.84	11.07	56.59	8.93
34	OL-14-23R	7/31/2014 8:48	60	301.48	8.48	18.27	6.68
35	OL-14-23R	7/31/2014 8:49	60	307	8.54	28.21	6.81
36	OL-14-23R	7/31/2014 8:50	60	323.03	8.73	29.04	6.97
37	OL-14-20R	7/31/2014 8:53	60	201.99	7.3	24.1	5.9
38	OL-14-20R	7/31/2014 8:54	60	212.47	7.48	22.62	6.01
39	OL-14-20R	7/31/2014 8:55	60	221.48	7.59	19.73	6.05
40	OL-14-16R	7/31/2014 8:59	60	418.11	10.21	46.81	8.22
41	OL-14-16R	7/31/2014 9:00	60	426.58	10.29	41.95	8.23
43	OL-14-16R	7/31/2014 9:02	60	412.55	10.27	57.45	8.36
44	OL-14-7R	7/31/2014 9:05	60	35.56	3.42	< LOD	4.12
45	OL-14-7R	7/31/2014 9:06	60	29.8	3.24	7.25	2.69
46	OL-14-7R	7/31/2014 9:07	60	31.84	3.32	5.84	2.73
48	OL-14-3R	7/31/2014 9:12	60	21.57	3.2	< LOD	3.87
49	OL-14-3R	7/31/2014 9:13	60	17.19	3.02	4.17	2.49
50	OL-14-3R	7/31/2014 9:14	60	18.62	3.07	< LOD	3.74
52	OL-14-11R	7/31/2014 9:19	60	51.48	4.1	8.07	3.35
53	OL-14-11R	7/31/2014 9:20	60	57.86	4.41	8.37	3.58
54	OL-14-11R	7/31/2014 9:22	60	68.24	4.63	< LOD	5.46
55	OL-14-8R	7/31/2014 9:24	60	20.89	3.09	5.2	2.57
56	OL-14-8R	7/31/2014 9:26	60	21.9	3.13	< LOD	3.72
57	OL-14-8R	7/31/2014 9:27	60	20.26	3.07	< LOD	3.7
58	OL-14-4R	7/31/2014 9:30	60	16.14	2.81	6.39	2.39
59	OL-14-4R	7/31/2014 9:31	60	17.59	2.83	4.14	2.34
60	OL-14-4R	7/31/2014 9:32	60	18.31	2.89	3.62	2.37
61	OL-14-5R	7/31/2014 9:37	60	15.31	2.88	< LOD	3.56

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
62	OL-14-5R	7/31/2014 9:38	60	16.66	2.92	< LOD	3.58
63	OL-14-5R	7/31/2014 9:39	60	18.68	2.97	< LOD	3.6
64	OL-14-12R	7/31/2014 9:42	60	29.99	3.48	7.2	2.9
65	OL-14-12R	7/31/2014 9:43	60	24.48	3.28	8.45	2.79
66	OL-14-12R	7/31/2014 9:44	60	26.26	3.34	8.98	2.84
67	OL-14-17R	7/31/2014 9:47	60	377.37	9.69	41.28	7.79
68	OL-14-17R	7/31/2014 9:48	60	382.77	9.73	42.98	7.84
69	OL-14-17R	7/31/2014 9:50	60	299.98	8.87	22.89	7.03
70	OL-14-24R	7/31/2014 9:52	60	382.59	9.75	23.07	7.68
71	OL-14-24R	7/31/2014 9:53	60	389.98	9.77	30.08	7.75
72	OL-14-24R	7/31/2014 9:54	60	395.86	9.82	27.6	7.77
79	OL-14-6R	7/31/2014 10:16	60	13.56	2.83	< LOD	3.49
80	OL-14-6R	7/31/2014 10:17	60	15.85	2.92	< LOD	3.52
81	OL-14-6R	7/31/2014 10:18	60	14.96	2.88	3.73	2.38
82	OL-14-14R	7/31/2014 10:21	60	18.16	3.19	< LOD	3.88
83	OL-14-14R	7/31/2014 10:22	60	13.24	3	6.52	2.59
84	OL-14-14R	7/31/2014 10:23	60	15.67	3.11	6.83	2.66
85	OL-14-13R	7/31/2014 10:27	60	21.36	3.29	4.24	2.69
86	OL-14-13R	7/31/2014 10:28	60	20.88	3.24	5.31	2.68
87	OL-14-13R	7/31/2014 10:29	60	19.31	3.19	4.42	2.62
88	OL-14-25R	7/31/2014 10:32	60	24.52	3.4	7.55	2.87
89	OL-14-25R	7/31/2014 10:33	60	31.18	3.63	6.24	2.99
90	OL-14-25R	7/31/2014 10:34	60	40.25	3.91	< LOD	4.61
91	OL-14-29R	7/31/2014 10:36	60	37.62	3.73	5.66	3.04
92	OL-14-29R	7/31/2014 10:37	60	35.16	3.63	8.64	3.03
93	OL-14-29R	7/31/2014 10:39	60	35.17	3.64	8.74	3.04
94	OL-14-38R	7/31/2014 10:41	60	45.5	3.99	7.22	3.25
95	OL-14-38R	7/31/2014 10:43	60	45.29	4.01	6.85	3.26
96	OL-14-38R	7/31/2014 10:44	60	43.35	3.97	5.45	3.2
97	OL-14-33R	7/31/2014 10:46	60	29.64	3.19	6.12	2.64
98	OL-14-33R	7/31/2014 10:47	60	29.97	3.2	7.37	2.68
99	OL-14-33R	7/31/2014 10:48	60	31.4	3.25	5.52	2.67
100	OL-14-39R	7/31/2014 10:51	60	143.26	6.36	16.53	5.13
101	OL-14-39R	7/31/2014 10:52	60	139.14	6.32	19.74	5.15
102	OL-14-39R	7/31/2014 10:53	58.35	148.77	6.56	20.15	5.33
103	OL-14-30R	7/31/2014 10:56	60	49.41	4.06	4.91	3.26
104	OL-14-30R	7/31/2014 10:57	60	49.96	4.02	6.37	3.26
105	OL-14-30R	7/31/2014 10:59	60	52.41	4.17	7.8	3.4
109	OL-14-21R	7/31/2014 11:06	60	31.13	3.52	4.55	2.86
110	OL-14-21R	7/31/2014 11:07	60	32.51	3.57	< LOD	4.3
111	OL-14-21R	7/31/2014 11:08	59.58	29.85	3.52	5.13	2.87
115	OL-14-9R	7/31/2014 11:28	60	19.8	3.21	4.39	2.64
116	OL-14-9R	7/31/2014 11:29	58.6	17.57	3.13	3.95	2.58
117	OL-14-9R	7/31/2014 11:30	60	19.06	3.15	< LOD	3.89
118	OL-14-18R	7/31/2014 11:33	60	114.86	5.72	13.43	4.61
119	OL-14-18R	7/31/2014 11:34	60	117.28	5.83	10.78	4.65
120	OL-14-18R	7/31/2014 11:35	60	122.13	5.97	11.34	4.77
121	OL-14-26R	7/31/2014 11:38	60	119.06	5.84	12.62	4.69
122	OL-14-26R	7/31/2014 11:39	60	121.64	5.9	9.03	4.68
123	OL-14-26R	7/31/2014 11:40	59.8	119.38	5.83	11.84	4.67
124	OL-14-34R	7/31/2014 11:43	60	615.73	12.41	71.01	10
125	OL-14-34R	7/31/2014 11:44	52.96	608.69	13.42	73.36	10.85
126	OL-14-34R	7/31/2014 11:45	58.92	599.37	12.49	83.84	10.17
127	OL-14-40R	7/31/2014 11:48	60	1116.89	17.06	109.66	13.65

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
128	OL-14-40R	7/31/2014 11:49	60	1105.57	16.92	99.54	13.49
129	OL-14-40R	7/31/2014 11:50	60	1111.67	16.95	105.19	13.54
130	OL-14-31R	7/31/2014 11:53	60	890.99	14.68	< LOD	16.6
131	OL-14-31R	7/31/2014 11:54	60	886.84	14.55	< LOD	16.61
132	OL-14-31R	7/31/2014 11:55	60	937.1	15.22	< LOD	17.42
133	OL-14-22R	7/31/2014 11:57	60	26.61	3.4	5.98	2.82
134	OL-14-22R	7/31/2014 11:59	60	27.12	3.39	< LOD	4.11
135	OL-14-22R	7/31/2014 12:00	60	27.88	3.39	< LOD	4.09
136	OL-14-15R	7/31/2014 12:02	60	243.55	8	26.27	6.43
137	OL-14-15R	7/31/2014 12:03	48.49	254.83	9.16	17.99	7.25
138	OL-14-15R	7/31/2014 12:04	60	252.99	8.14	23.17	6.49
139	OL-14-1R	7/31/2014 12:07	60	20.86	3.2	4.51	2.64
140	OL-14-1R	7/31/2014 12:08	60	19.81	3.14	< LOD	3.83
141	OL-14-1R	7/31/2014 12:09	60	19.78	3.14	4.5	2.59
118	OL32-7	7/15/2014 8:32	60	14.32	3.05	4.05	2.54
120	OL32-7	7/15/2014 8:33	60	15.02	3.09	< LOD	3.78
121	OL32-7	7/15/2014 8:34	60	12.61	3.01	< LOD	3.7
122	OL32-6	7/15/2014 8:37	60	39.54	3.88	< LOD	4.69
123	OL32-6	7/15/2014 8:38	60	44.85	4.02	6.93	3.27
124	OL32-6	7/15/2014 8:39	60	42.01	3.93	7.05	3.21
125	OL32-5	7/15/2014 8:41	60	25.61	3.61	5.37	2.99
126	OL32-5	7/15/2014 8:42	60	24.79	3.56	< LOD	4.27
127	OL32-5	7/15/2014 8:44	60	22.51	3.47	< LOD	4.2
128	OL32-4	7/15/2014 8:46	60	22.56	3.09	4.57	2.55
129	OL32-4	7/15/2014 8:47	60	22.79	3.09	5.38	2.56
130	OL32-4	7/15/2014 8:48	60	24.38	3.16	4.64	2.6
131	OL32-3	7/15/2014 8:51	60	175.29	6.92	28.95	5.68
132	OL32-3	7/15/2014 8:52	60	170.22	6.76	24.02	5.5
133	OL32-3	7/15/2014 8:53	60	175.19	6.87	26.63	5.61
134	OL32-2	7/15/2014 8:56	60	224.5	7.82	42.36	6.49
135	OL32-2	7/15/2014 8:57	60	223.05	7.92	33.07	6.47
136	OL32-2	7/15/2014 8:58	60	217.52	7.82	34.85	6.42
137	OL32-1	7/15/2014 9:01	60	301.45	8.78	< LOD	10.25
138	OL32-1	7/15/2014 9:02	60	306.01	8.92	10.93	6.95
139	OL32-1	7/15/2014 9:03	60	309.33	9.07	13.43	7.09
141	OL32-8	7/15/2014 9:07	60	176.46	6.92	22.27	5.6
142	OL32-8	7/15/2014 9:08	60	176.88	7.01	21.12	5.66
143	OL32-8	7/15/2014 9:09	60	175.87	6.92	21.62	5.6
145	OL32-15	7/15/2014 9:12	60	120.17	5.67	21	4.67
146	OL32-15	7/15/2014 9:13	60	120.3	5.57	12.42	4.47
147	OL32-15	7/15/2014 9:14	60	119.92	5.51	21.74	4.55
148	OL32-9	7/15/2014 9:16	60	177.7	6.91	21.46	5.59
149	OL32-9	7/15/2014 9:17	60	184.59	6.93	16.61	5.54
150	OL32-9	7/15/2014 9:18	60	188.3	6.97	22.12	5.63
151	OL32-16	7/15/2014 9:21	60	193.1	7.48	12.48	5.91
152	OL32-16	7/15/2014 9:22	60	198.73	7.56	9.38	5.93
153	OL32-16	7/15/2014 9:23	60	196	7.58	16.85	6.04
154	OL32-10	7/15/2014 9:25	60	68.15	4.75	< LOD	5.66
155	OL32-10	7/15/2014 9:27	60	55.04	4.3	6.27	3.47
156	OL32-10	7/15/2014 9:28	60	43.81	3.98	8.04	3.28
157	OL32-17	7/15/2014 9:30	60	32.92	3.69	6.55	3.03
158	OL32-17	7/15/2014 9:31	60	36.09	3.77	5.42	3.06
159	OL32-17	7/15/2014 9:32	60	37.05	3.82	6.97	3.13
161	OL32-11	7/15/2014 9:34	60	195.01	7.3	18.74	5.84

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
162	OL32-11	7/15/2014 9:36	60	191.94	7.24	24.87	5.87
163	OL32-11	7/15/2014 9:37	60	205.25	7.48	20.09	5.99
164	OL32-18	7/15/2014 9:39	60	22.11	3.22	< LOD	3.95
165	OL32-18	7/15/2014 9:40	60	20.54	3.14	< LOD	3.84
166	OL32-18	7/15/2014 9:42	60	20.12	3.11	4.5	2.56
167	OL32-12	7/15/2014 9:44	60	20.05	3.2	< LOD	3.94
168	OL32-12	7/15/2014 9:45	60	19.5	3.18	5.85	2.66
169	OL32-12	7/15/2014 9:46	60	22.31	3.27	4.9	2.69
170	OL32-19	7/15/2014 9:49	60	16.52	3.03	< LOD	3.74
171	OL32-19	7/15/2014 9:50	60	19.44	3.15	4.2	2.59
172	OL32-19	7/15/2014 9:51	60	19.2	3.12	< LOD	3.8
173	OL32-13	7/15/2014 9:53	60	21.1	3.33	5.29	2.77
174	OL32-13	7/15/2014 9:54	60	20.68	3.3	4.7	2.73
175	OL32-13	7/15/2014 9:56	60	23.8	3.41	4.88	2.8
176	OL32-20	7/15/2014 9:58	60	28.51	3.69	5.3	3.03
177	OL32-20	7/15/2014 9:59	60	27.6	3.63	6.18	3.01
178	OL32-20	7/15/2014 10:00	60	33.5	3.8	< LOD	4.51
180	OL32-21	7/15/2014 10:02	60	13.11	2.74	3.93	2.29
181	OL32-21	7/15/2014 10:04	60	13.59	2.77	< LOD	3.43
182	OL32-21	7/15/2014 10:05	60	12.21	2.71	< LOD	3.35
183	OL32-14	7/15/2014 10:07	60	31.11	3.65	8.52	3.07
184	OL32-14	7/15/2014 10:09	60	34.34	3.74	5.48	3.06
185	OL32-14	7/15/2014 10:10	60	33.54	3.7	7.69	3.08
192	OL32-24	7/15/2014 10:36	60	43.69	4.15	7.78	3.41
193	OL32-24	7/15/2014 10:37	60	47.13	4.26	< LOD	5.1
194	OL32-24	7/15/2014 10:38	60	43.85	4.15	5.12	3.35
195	OL32-23	7/15/2014 10:41	60	30.57	3.45	8.47	2.89
196	OL32-23	7/15/2014 10:42	60	33.25	3.57	< LOD	4.32
197	OL32-23	7/15/2014 10:43	60	36.86	3.69	< LOD	4.41
198	OL32-22	7/15/2014 10:46	60	23.88	3.3	5.27	2.73
199	OL32-22	7/15/2014 10:47	60	23.24	3.25	< LOD	3.97
200	OL32-22	7/15/2014 10:48	60	21.49	3.22	6.22	2.69
201	OL32-25	7/15/2014 10:50	60	100.57	5.5	8.52	4.39
202	OL32-25	7/15/2014 10:51	60	97.88	5.38	8.23	4.28
203	OL32-25	7/15/2014 10:53	60	94.67	5.3	< LOD	6.28
204	OL32-29	7/15/2014 10:55	60	379.3	9.87	98.72	8.42
205	OL32-29	7/15/2014 10:56	60	391.84	10.27	101.59	8.76
206	OL32-29	7/15/2014 10:57	60	395.28	10.31	92.13	8.71
207	OL32-33	7/15/2014 11:00	60	65.09	4.58	7.88	3.7
208	OL32-33	7/15/2014 11:01	60	62.16	4.49	7.66	3.63
209	OL32-33	7/15/2014 11:02	60	66.49	4.58	7.31	3.69
210	OL32-37	7/15/2014 11:05	60	480.63	10.96	< LOD	12.74
211	OL32-37	7/15/2014 11:06	60	593.01	12.04	17.53	9.34
212	OL32-37	7/15/2014 11:07	60	599.79	12.29	16.43	9.53
213	OL32-38	7/15/2014 11:10	60	25.6	3.22	6.84	2.69
214	OL32-38	7/15/2014 11:11	60	31	3.46	5.38	2.83
215	OL32-38	7/15/2014 11:12	60	29.73	3.38	4.57	2.75
216	OL32-39	7/15/2014 11:15	60	276.26	8.42	29.21	6.76
217	OL32-39	7/15/2014 11:16	60	324.84	9.18	26.87	7.3
218	OL32-39	7/15/2014 11:17	60	317.28	9.06	27.54	7.21
219	OL32-40	7/15/2014 11:20	60	371.89	9.69	23.54	7.64
220	OL32-40	7/15/2014 11:21	60	370.57	9.72	19.54	7.63
221	OL32-40	7/15/2014 11:22	60	373.88	9.83	24.75	7.76
222	OL32-36	7/15/2014 11:27	60	105.48	6.27	18.25	5.17

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
223	OL32-36	7/15/2014 11:28	60	109.17	6.33	22.11	5.27
224	OL32-36	7/15/2014 11:29	60	104.11	6.27	20.65	5.21
225	OL32-35	7/15/2014 11:32	60	165.99	6.7	37.44	5.63
226	OL32-35	7/15/2014 11:33	60	166.07	6.77	40.92	5.73
227	OL32-35	7/15/2014 11:34	60	167.85	6.8	39.33	5.73
228	OL32-34	7/15/2014 11:37	60	4146.66	32.81	395.02	26.22
229	OL32-34	7/15/2014 11:38	60	4098.7	32.69	426.99	26.23
230	OL32-34	7/15/2014 11:39	60	4316.18	34	423	27.21
233	OL32-30	7/15/2014 11:42	60	47.14	3.98	< LOD	4.77
234	OL32-30	7/15/2014 11:43	60	42	3.82	8.08	3.15
235	OL32-30	7/15/2014 11:44	60	44.13	3.87	5.31	3.12
236	OL32-26	7/15/2014 11:47	60	183.86	7.27	12.65	5.75
237	OL32-26	7/15/2014 11:48	60	180.86	7.17	16.37	5.72
238	OL32-26	7/15/2014 11:49	60	182.3	7.2	20.56	5.8
239	OL32-31	7/15/2014 11:51	60	960.62	15.68	63.66	12.37
240	OL32-31	7/15/2014 11:52	60	946.01	15.52	70.1	12.29
241	OL32-31	7/15/2014 11:53	60	935.7	15.38	67.79	12.17
242	OL32-27	7/15/2014 11:56	39.47	153.63	8.06	16.7	6.48
243	OL32-27	7/15/2014 11:57	60	155.92	6.48	12.55	5.15
244	OL32-27	7/15/2014 11:58	60	156.42	6.34	12.59	5.05
245	OL32-32	7/15/2014 12:01	60	705.25	13.77	50.72	10.89
246	OL32-32	7/15/2014 12:02	60	721.38	13.78	36.09	10.8
247	OL32-32	7/15/2014 12:03	60	712.23	13.71	40.18	10.77
248	OL32-28	7/15/2014 12:05	60	38.76	3.87	9.26	3.22
249	OL32-28	7/15/2014 12:06	60	37.4	3.8	9.98	3.19
250	OL32-28	7/15/2014 12:07	60	38.97	3.89	9.53	3.24
29	FR2-1-21	7/25/2014 9:28	60	15.75	2.81	3.49	2.31
30	FR2-1-21	7/25/2014 9:29	60	16.43	2.81	< LOD	3.38
31	FR2-1-21	7/25/2014 9:30	60	16	2.79	< LOD	3.35
32	FR2-1-22	7/25/2014 9:33	60	19.08	3.01	< LOD	3.62
33	FR2-1-22	7/25/2014 9:34	60	16.25	2.88	4.43	2.38
34	FR2-1-22	7/25/2014 9:35	60	20.64	3.08	< LOD	3.69
35	FR2-1-23	7/25/2014 9:38	60	23.85	3.57	5.99	2.97
36	FR2-1-23	7/25/2014 9:40	60	25.72	3.66	5.69	3.03
37	FR2-1-23	7/25/2014 9:41	60	22.92	3.53	6.77	2.97
38	FR2-1-24	7/25/2014 9:44	60	23.85	3.36	5.86	2.78
39	FR2-1-24	7/25/2014 9:45	60	28.06	3.52	< LOD	4.22
40	FR2-1-24	7/25/2014 9:46	60	20.52	3.24	9.29	2.79
41	FR2-1-25	7/25/2014 9:49	60	14.16	3.05	4.57	2.54
42	FR2-1-25	7/25/2014 9:51	60	17.45	3.16	< LOD	3.81
43	FR2-1-25	7/25/2014 9:52	60	18.15	3.22	< LOD	3.92
44	FR2-1-30	7/25/2014 9:55	60	17.5	3.18	< LOD	3.87
45	FR2-1-30	7/25/2014 9:56	60	17.62	3.26	< LOD	3.99
46	FR2-1-30	7/25/2014 9:57	60	18.45	3.27	< LOD	3.99
47	FR2-1-29	7/25/2014 10:01	60	71.52	4.9	15.18	4.08
48	FR2-1-29	7/25/2014 10:02	60	76.47	4.98	14.77	4.12
49	FR2-1-29	7/25/2014 10:03	60	76.21	4.97	16.58	4.14
50	FR2-1-28	7/25/2014 10:06	60	12.83	2.59	< LOD	3.21
51	FR2-1-28	7/25/2014 10:07	60	13.93	2.62	< LOD	3.17
52	FR2-1-28	7/25/2014 10:08	60	12.6	2.56	3.2	2.12
53	FR2-1-27	7/25/2014 10:12	60	17.34	2.93	5.27	2.45
54	FR2-1-27	7/25/2014 10:13	60	19.98	3.05	3.82	2.5
55	FR2-1-27	7/25/2014 10:14	60	21.55	3.07	< LOD	3.68
56	FR2-1-26	7/25/2014 10:17	60	15.08	2.96	< LOD	3.63

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
57	FR2-1-26	7/25/2014 10:18	60	15.92	2.86	3.83	2.36
58	FR2-1-26	7/25/2014 10:19	60	17.41	2.89	< LOD	3.49
59	FR2-1-31	7/25/2014 10:22	60	20.8	3.18	< LOD	3.83
60	FR2-1-31	7/25/2014 10:23	60	17.05	3.01	4.11	2.49
61	FR2-1-31	7/25/2014 10:24	60	19.93	3.14	< LOD	3.81
62	FR2-1-32	7/25/2014 10:27	60	16	2.76	< LOD	3.3
63	FR2-1-32	7/25/2014 10:28	60	16.85	2.8	< LOD	3.37
64	FR2-1-32	7/25/2014 10:29	60	15.72	2.74	< LOD	3.32
65	FR2-1-33	7/25/2014 10:32	60	18.7	2.92	6.03	2.46
66	FR2-1-33	7/25/2014 10:33	60	23.71	3.12	4.28	2.56
67	FR2-1-33	7/25/2014 10:34	60	22.11	3.05	< LOD	3.71
68	FR2-1-34	7/25/2014 10:37	60	55.36	4.28	13.71	3.58
69	FR2-1-34	7/25/2014 10:38	60	58.85	4.36	12.79	3.62
70	FR2-1-34	7/25/2014 10:39	60	54.29	4.24	15.59	3.59
71	FR2-1-35	7/25/2014 10:44	60	39.27	4.04	17.33	3.54
72	FR2-1-35	7/25/2014 10:45	60	44.07	4.19	14.56	3.59
73	FR2-1-35	7/25/2014 10:47	60	43.59	4.2	13.46	3.58
74	FR2-1-40	7/25/2014 10:50	60	24	3.49	4.57	2.86
75	FR2-1-40	7/25/2014 10:51	60	23.83	3.47	6.62	2.89
76	FR2-1-40	7/25/2014 10:52	60	27.46	3.63	< LOD	4.33
77	FR2-1-39	7/25/2014 10:56	60	17.19	3.12	< LOD	3.81
78	FR2-1-39	7/25/2014 10:57	60	20.1	3.23	4.1	2.65
79	FR2-1-39	7/25/2014 10:58	60	19.37	3.19	< LOD	3.83
80	FR2-1-38	7/25/2014 11:00	60	19.19	3.2	< LOD	3.93
81	FR2-1-38	7/25/2014 11:01	60	17.58	3.09	< LOD	3.78
82	FR2-1-38	7/25/2014 11:02	60	17.98	3.07	4.51	2.55
83	FR2-1-37	7/25/2014 11:05	60	17.41	3.02	< LOD	3.69
84	FR2-1-37	7/25/2014 11:06	60	19.24	3.12	< LOD	3.83
85	FR2-1-37	7/25/2014 11:07	60	16.52	2.99	< LOD	3.63
86	FR2-1-36	7/25/2014 11:10	60	21.08	3.12	5.18	2.59
87	FR2-1-36	7/25/2014 11:11	60	19.66	3.11	7.15	2.64
88	FR2-1-36	7/25/2014 11:12	60	21.5	3.17	4.67	2.61
254	FR2-1-13	7/22/2014 10:39	60	74.31	4.78	11.24	3.9
255	FR2-1-13	7/22/2014 10:40	60	78.08	4.89	6.83	3.9
256	FR2-1-13	7/22/2014 10:41	60	85.29	5	< LOD	5.92
257	FR2-1-20	7/22/2014 10:44	60	16.01	3.08	< LOD	3.73
258	FR2-1-20	7/22/2014 10:45	60	17.18	3.2	< LOD	3.85
259	FR2-1-20	7/22/2014 10:46	60	16.19	3.13	4	2.58
260	FR2-1-19	7/22/2014 10:49	60	11.35	3.03	8.41	2.66
261	FR2-1-19	7/22/2014 10:50	60	15.09	3.23	< LOD	3.96
262	FR2-1-19	7/22/2014 10:51	60	15.26	3.2	6.3	2.72
263	FR2-1-18	7/22/2014 10:53	60	23.25	3.42	5.59	2.86
264	FR2-1-18	7/22/2014 10:54	60	23.37	3.42	4.59	2.82
265	FR2-1-18	7/22/2014 10:55	60	24.65	3.43	< LOD	4.22
266	FR2-1-17	7/22/2014 10:58	60	24.67	3.29	< LOD	4.03
267	FR2-1-17	7/22/2014 10:59	60	25.27	3.31	5.24	2.73
268	FR2-1-17	7/22/2014 11:00	60	23.2	3.23	5.05	2.66
270	FR2-1-16	7/22/2014 11:03	60	22.9	3.39	< LOD	4.13
271	FR2-1-16	7/22/2014 11:04	60	24.56	3.46	5.7	2.87
272	FR2-1-16	7/22/2014 11:06	60	23.44	3.41	4.71	2.8
273	FR2-1-15	7/22/2014 11:08	60	13.91	2.63	< LOD	3.22
274	FR2-1-15	7/22/2014 11:10	60	13.59	2.6	< LOD	3.18
275	FR2-1-15	7/22/2014 11:11	60	13.46	2.62	< LOD	3.23
276	FR2-1-14	7/22/2014 11:14	60	24.57	3.38	< LOD	4.13

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
277	FR2-1-14	7/22/2014 11:15	60	21.91	3.33	4.52	2.73
278	FR2-1-14	7/22/2014 11:16	60	26.55	3.48	< LOD	4.21
279	FR2-1-7	7/22/2014 11:18	60	17.86	3.17	4.13	2.62
280	FR2-1-7	7/22/2014 11:20	60	18.42	3.15	< LOD	3.82
281	FR2-1-7	7/22/2014 11:21	60	16.81	3.1	5.44	2.59
282	FR2-1-1	7/22/2014 11:23	60	90.54	5.14	11.64	4.17
283	FR2-1-1	7/22/2014 11:24	60	96.37	5.23	6.99	4.16
284	FR2-1-1	7/22/2014 11:25	60	101.44	5.33	8.84	4.25
285	FR2-1-2	7/22/2014 11:28	60	479.05	10.65	28.37	8.38
286	FR2-1-2	7/22/2014 11:29	60	472.1	10.66	28.08	8.39
287	FR2-1-2	7/22/2014 11:30	60	468.84	10.62	32.24	8.39
288	FR2-1-8	7/22/2014 11:33	60	23.76	3.29	6.49	2.75
289	FR2-1-8	7/22/2014 11:35	60	26.61	3.39	5.17	2.79
290	FR2-1-8	7/22/2014 11:36	60	28.89	3.46	7.04	2.88
291	FR2-1-3	7/22/2014 11:38	60	253.27	7.98	< LOD	9.28
292	FR2-1-3	7/22/2014 11:39	60	233.88	7.79	< LOD	9.09
293	FR2-1-3	7/22/2014 11:41	60	212.74	7.43	< LOD	8.59
294	FR2-1-9	7/22/2014 11:43	60	32.71	3.73	< LOD	4.53
295	FR2-1-9	7/22/2014 11:44	30.68	30.35	5.31	< LOD	6.53
296	FR2-1-9	7/22/2014 11:45	60	29.49	3.62	< LOD	4.37
297	FR2-1-4	7/22/2014 11:48	60	1291.6	17.95	117.75	14.32
298	FR2-1-4	7/22/2014 11:49	60	1299.75	17.88	118.22	14.27
299	FR2-1-4	7/22/2014 11:50	60	1316.99	18.12	114.54	14.43
300	FR2-1-10	7/22/2014 11:53	60	18.99	3.77	5.19	3.14
301	FR2-1-10	7/22/2014 11:54	60	15.25	3.35	5.29	2.82
302	FR2-1-10	7/22/2014 11:55	60	21.38	3.61	< LOD	4.38
303	FR2-1-5	7/22/2014 11:58	60	60.82	4.6	10	3.77
304	FR2-1-5	7/22/2014 11:59	60	62.35	4.62	11.38	3.81
305	FR2-1-5	7/22/2014 12:00	60	58.64	4.58	14.42	3.84
306	FR2-1-11	7/22/2014 12:03	60	193.42	7.51	19.54	6.02
307	FR2-1-11	7/22/2014 12:05	60	175.86	7.25	13.06	5.76
308	FR2-1-11	7/22/2014 12:06	60	183.3	7.46	18.76	5.99
309	FR2-1-6	7/22/2014 12:09	60	50.91	4.35	9.98	3.6
310	FR2-1-6	7/22/2014 12:10	60	50.1	4.33	13.53	3.65
311	FR2-1-6	7/22/2014 12:11	60	52.84	4.38	12.71	3.67
312	FR2-1-12	7/22/2014 12:13	31.32	16.16	4.52	< LOD	5.45
313	FR2-1-12	7/22/2014 12:14	60	17.99	3.17	< LOD	3.85
314	FR2-1-12	7/22/2014 12:15	60	16.33	3.13	< LOD	3.76
28	IU6-4-39	7/17/2014 8:30	60	65.4	4.59	13.19	3.81
29	IU6-4-39	7/17/2014 8:31	60	68.52	4.69	10.94	3.84
30	IU6-4-39	7/17/2014 8:32	60	69.47	4.77	9.47	3.87
31	IU6-4-35	7/17/2014 8:36	60	134.12	6.31	21.44	5.18
32	IU6-4-35	7/17/2014 8:37	60	144.01	6.4	22.57	5.24
33	IU6-4-35	7/17/2014 8:38	60	150.66	6.48	19.73	5.26
34	IU6-4-27	7/17/2014 8:45	60	23.43	3.06	3.89	2.5
35	IU6-4-27	7/17/2014 8:47	60	24.62	3.07	6.18	2.56
36	IU6-4-27	7/17/2014 8:48	60	26.56	3.17	< LOD	3.82
37	IU6-4-28	7/17/2014 8:52	60	35.74	3.78	6.82	3.11
38	IU6-4-28	7/17/2014 8:53	60	33.15	3.77	8.41	3.14
39	IU6-4-28	7/17/2014 8:54	60	34.79	3.81	6.2	3.12
40	IU6-4-29	7/17/2014 8:59	60	264.3	8.64	15.43	6.8
41	IU6-4-29	7/17/2014 9:00	60	257.92	8.6	18.75	6.81
42	IU6-4-29	7/17/2014 9:02	60	260.1	8.59	21.8	6.84
43	IU6-4-21	7/17/2014 9:06	60	53.53	4.04	14.5	3.42

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
44	IU6-4-21	7/17/2014 9:07	60	57.02	4.07	11.34	3.37
45	IU6-4-21	7/17/2014 9:08	60	59	4.15	12.83	3.46
46	IU6-4-20	7/17/2014 9:12	60	313.93	9.43	35.03	7.59
47	IU6-4-20	7/17/2014 9:13	60	326.78	9.53	32.74	7.64
48	IU6-4-20	7/17/2014 9:15	60	338.99	9.75	26.19	7.74
49	IU6-4-13	7/17/2014 9:19	60	762.74	14.74	111.93	12.04
50	IU6-4-13	7/17/2014 9:20	60	752	14.53	113.74	11.9
51	IU6-4-13	7/17/2014 9:21	60	759.65	14.73	109.15	12.02
52	IU6-4-14	7/17/2014 9:25	60	350.28	8.88	39.44	7.15
53	IU6-4-14	7/17/2014 9:26	60	341.94	8.89	45.58	7.22
54	IU6-4-14	7/17/2014 9:27	60	334.02	8.75	45.59	7.12
55	IU6-4-7	7/17/2014 9:31	60	307.6	8.91	26.63	7.1
56	IU6-4-7	7/17/2014 9:33	60	317.79	8.91	27.66	7.1
57	IU6-4-7	7/17/2014 9:34	60	320.9	8.9	42.84	7.23
58	IU6-4-6	7/17/2014 9:38	60	104.1	4.98	10.48	4
59	IU6-4-6	7/17/2014 9:39	60	118.85	5.21	9.7	4.15
60	IU6-4-6	7/17/2014 9:40	60	120.77	5.28	7.61	4.17
61	IU6-4-5	7/17/2014 9:44	60	24.62	3.37	< LOD	4.1
62	IU6-4-5	7/17/2014 9:45	60	24.54	3.37	< LOD	4.06
63	IU6-4-5	7/17/2014 9:47	60	23.41	3.37	4.5	2.77
64	IU6-4-1	7/17/2014 9:50	60	21.89	3.2	6.01	2.67
65	IU6-4-1	7/17/2014 9:51	60	22.85	3.23	< LOD	3.92
66	IU6-4-1	7/17/2014 9:52	60	20.44	3.12	5.46	2.6
67	IU6-4-2	7/17/2014 9:58	60	50.13	4.14	6.42	3.35
68	IU6-4-2	7/17/2014 9:59	60	48.86	4.04	6.07	3.27
69	IU6-4-2	7/17/2014 10:00	60	48.61	3.97	5.75	3.21
70	IU6-4-3	7/17/2014 10:04	60	20.74	3.46	< LOD	4.29
71	IU6-4-3	7/17/2014 10:05	60	21.36	3.52	< LOD	4.21
72	IU6-4-3	7/17/2014 10:06	60	19.56	3.42	< LOD	4.25
73	IU6-4-8	7/17/2014 10:10	60	34.82	3.79	4.68	3.06
74	IU6-4-8	7/17/2014 10:11	60	34.04	3.76	< LOD	4.56
75	IU6-4-8	7/17/2014 10:12	60	30.29	3.6	9.1	3.03
78	IU6-4-15	7/17/2014 10:17	60	42.17	3.99	5.27	3.23
79	IU6-4-15	7/17/2014 10:18	60	43.65	4.02	7.84	3.3
80	IU6-4-15	7/17/2014 10:19	60	43.26	4.01	6.32	3.26
81	IU6-4-22	7/17/2014 10:24	60	37.49	3.84	10.64	3.24
82	IU6-4-22	7/17/2014 10:25	60	38.08	3.92	7.94	3.23
83	IU6-4-22	7/17/2014 10:26	60	41.54	3.97	7.41	3.26
84	IU6-4-30	7/17/2014 10:30	60	31.23	3.78	< LOD	4.55
85	IU6-4-30	7/17/2014 10:31	60	34.13	3.96	< LOD	4.81
86	IU6-4-30	7/17/2014 10:32	60	35.7	3.97	< LOD	4.77
87	IU6-4-36	7/17/2014 10:36	60	322.41	9.24	26.27	7.34
88	IU6-4-36	7/17/2014 10:37	60	326.43	9.25	38.85	7.47
89	IU6-4-36	7/17/2014 10:38	60	330.97	9.34	38.14	7.53
96	IU6-4-40	7/17/2014 11:04	60	21.16	3.11	< LOD	3.77
97	IU6-4-40	7/17/2014 11:05	60	19.81	3.08	3.97	2.53
98	IU6-4-40	7/17/2014 11:06	60	22.9	3.25	< LOD	3.89
99	IU6-4-38	7/17/2014 11:10	60	40.06	4.01	< LOD	4.83
100	IU6-4-38	7/17/2014 11:11	60	39.73	3.96	< LOD	4.78
101	IU6-4-38	7/17/2014 11:13	60	38.67	3.89	6.84	3.18
102	IU6-4-37	7/17/2014 11:16	60	18.46	3.15	< LOD	3.85
103	IU6-4-37	7/17/2014 11:17	60	17.96	3.18	4.74	2.64
104	IU6-4-37	7/17/2014 11:18	60	16.98	3.14	4.02	2.58
192	IU6-4-33	7/22/2014 8:26	60	47.14	4.04	5.39	3.25

Reading No.	Sample ID	Time	Scan Duration (s)	Lead (mg/kg)	Lead 2σ Error	Arsenic (mg/kg)	Arsenic 2σ Error
193	IU6-4-33	7/22/2014 8:27	60	56.03	4.28	< LOD	5.12
194	IU6-4-33	7/22/2014 8:28	60	59.75	4.36	< LOD	5.2
195	IU6-4-32	7/22/2014 8:33	60	22.06	3.23	5.55	2.67
196	IU6-4-32	7/22/2014 8:34	60	23.16	3.22	3.96	2.62
197	IU6-4-32	7/22/2014 8:35	60	23.05	3.2	4.11	2.62
198	IU6-4-31	7/22/2014 8:39	60	21.7	3.31	5.63	2.75
199	IU6-4-31	7/22/2014 8:40	60	20.89	3.25	4.23	2.66
200	IU6-4-31	7/22/2014 8:41	60	22.56	3.31	5.85	2.76
201	IU6-4-23	7/22/2014 8:45	60	32.67	3.61	5.81	2.95
202	IU6-4-23	7/22/2014 8:46	60	35.1	3.63	< LOD	4.37
203	IU6-4-23	7/22/2014 8:47	60	33.45	3.61	< LOD	4.35
204	IU6-4-24	7/22/2014 8:51	60	368.12	9.95	36.86	7.97
205	IU6-4-24	7/22/2014 8:52	60	381.36	9.82	44.04	7.92
206	IU6-4-24	7/22/2014 8:53	60	379.28	9.84	51.57	8
207	IU6-4-25	7/22/2014 8:57	60	19.07	2.9	4.81	2.4
208	IU6-4-25	7/22/2014 8:58	60	19.33	2.98	4.65	2.47
209	IU6-4-25	7/22/2014 9:00	60	21.09	3.02	5.04	2.49
211	IU6-4-18	7/22/2014 9:04	60	22.12	3.34	< LOD	4.05
212	IU6-4-18	7/22/2014 9:05	60	21.46	3.26	4.75	2.69
213	IU6-4-18	7/22/2014 9:06	60	18.71	3.19	6.91	2.69
214	IU6-4-17	7/22/2014 9:10	60	21.06	3.31	22.43	3.17
215	IU6-4-17	7/22/2014 9:12	60	17.95	3.23	25.02	3.18
216	IU6-4-17	7/22/2014 9:13	60	18.99	3.25	21.02	3.1
217	IU6-4-16	7/22/2014 9:16	60	12.66	2.95	7.58	2.55
218	IU6-4-16	7/22/2014 9:18	60	17.13	3.12	5.3	2.6
219	IU6-4-16	7/22/2014 9:19	60	18.99	3.18	5.96	2.67
220	IU6-4-9	7/22/2014 9:22	60	20	3.37	< LOD	4.13
221	IU6-4-9	7/22/2014 9:23	60	16.55	3.22	6.91	2.75
222	IU6-4-9	7/22/2014 9:25	60	16.36	3.23	5.49	2.71
223	IU6-4-4	7/22/2014 9:28	60	15.38	3	9.28	2.62
224	IU6-4-4	7/22/2014 9:29	31.11	18.5	4.61	6.15	3.87
225	IU6-4-4	7/22/2014 9:30	60	20.1	3.15	5.71	2.63
226	IU6-4-10	7/22/2014 9:36	60	26.09	3.31	< LOD	3.95
227	IU6-4-10	7/22/2014 9:37	60	28.81	3.4	< LOD	4.09
228	IU6-4-10	7/22/2014 9:38	60	31.73	3.49	< LOD	4.16
229	IU6-4-11	7/22/2014 9:42	60	21.34	3.33	4.5	2.75
230	IU6-4-11	7/22/2014 9:43	60	24.8	3.48	< LOD	4.25
231	IU6-4-11	7/22/2014 9:44	60	23.15	3.4	5.12	2.81
232	IU6-4-12	7/22/2014 9:49	60	20.81	3.31	< LOD	4.05
233	IU6-4-12	7/22/2014 9:50	60	18.5	3.2	4.61	2.64
234	IU6-4-12	7/22/2014 9:51	60	19.61	3.29	< LOD	4.01
235	IU6-4-19	7/22/2014 9:55	60	19.47	3.31	< LOD	4.08
236	IU6-4-19	7/22/2014 9:56	60	19.49	3.18	3.97	2.61
237	IU6-4-19	7/22/2014 9:57	60	23.08	3.34	< LOD	4.01
239	IU6-4-26	7/22/2014 10:02	60	22.43	3.43	< LOD	4.15
240	IU6-4-26	7/22/2014 10:03	60	21.27	3.4	< LOD	4.15
241	IU6-4-26	7/22/2014 10:04	60	19.84	3.37	< LOD	4.12
242	IU6-4-34	7/22/2014 10:08	60	201.38	6.99	28.16	5.68
243	IU6-4-34	7/22/2014 10:09	60	206.27	7.14	26.34	5.78
244	IU6-4-34	7/22/2014 10:10	60	195.95	7.02	37.46	5.83

Table C.3. Summary of results for decision unit OL-14 (CALC-DVZ-AFRI-106). Concentration is the average of the three replicate results (Table C.1). “SD” is the standard deviation of the three replicates. The 2σ Error is the average reported counting error of the three replicates. Shaded cell indicates the MDL was used in place of non-detectable result for calculation purposes. “#DIV/0!” in the St. dev. column indicates that only one of the three replicates was detectable, and the one result was used as the average concentration. Statistics for the data set are included at the bottom of the table summary.

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
OL-14-1R	20.2	0.6	3.2	4.5	0.0	3.0
OL-14-2R	20.1	2.3	3.0	5.5	0.5	2.5
OL-14-3R	19.1	2.2	3.1	4.2	#DIV/0!	3.4
OL-14-4R	17.3	1.1	2.8	4.7	1.5	2.4
OL-14-5R	16.9	1.7	2.9	3.90	NA	3.6
OL-14-6R	14.8	1.2	2.9	3.7	#DIV/0!	3.1
OL-14-7R	32.4	2.9	3.3	6.5	1.0	3.2
OL-14-8R	21.0	0.8	3.1	5.2	#DIV/0!	3.3
OL-14-9R	18.8	1.1	3.2	4.2	0.3	3.0
OL-14-10R	16.6	0.8	3.1	6.1	1.2	2.6
OL-14-11R	59.2	8.5	4.4	8.2	0.2	4.1
OL-14-12R	26.9	2.8	3.4	8.2	0.9	2.8
OL-14-13R	20.5	1.1	3.2	4.7	0.6	2.7
OL-14-14R	15.7	2.5	3.1	6.7	0.2	3.0
OL-14-15R	250.5	6.1	8.4	22.5	4.2	6.7
OL-14-16R	419.1	7.1	10.3	48.7	7.9	8.3
OL-14-17R	353.4	46.3	9.4	35.7	11.1	7.6
OL-14-18R	118.1	3.7	5.8	11.9	1.4	4.7
OL-14-19R	485.4	3.3	11.0	41.6	6.3	8.8
OL-14-20R	212.0	9.8	7.5	22.2	2.2	6.0
OL-14-21R	31.2	1.3	3.5	4.8	0.4	3.3
OL-14-22R	27.2	0.6	3.4	6.0	#DIV/0!	3.7
OL-14-23R	310.5	11.2	8.6	25.2	6.0	6.8
OL-14-24R	389.5	6.6	9.8	26.9	3.6	7.7
OL-14-25R	32.0	7.9	3.6	6.9	0.9	3.5
OL-14-26R	120.0	1.4	5.9	11.2	1.9	4.7
OL-14-27R	246.1	48.1	7.8	30.5	9.1	6.3
OL-14-28R	495.4	4.6	11.2	54.5	2.5	9.0
OL-14-29R	36.0	1.4	3.7	7.7	1.8	3.0
OL-14-30R	50.6	1.6	4.1	6.4	1.4	3.3
OL-14-31R	905.0	27.9	14.8	3.90	NA	16.9
OL-14-32R	355.1	9.1	9.6	33.3	0.6	7.7
OL-14-33R	30.3	0.9	3.2	6.3	0.9	2.7
OL-14-34R	607.9	8.2	12.8	76.1	6.8	10.3
OL-14-35R	974.6	32.9	15.6	40.0	8.5	12.1
OL-14-36R	457.6	6.2	10.6	112.7	5.3	9.0
OL-14-37R	42.3	0.9	3.9	3.90	NA	4.6
OL-14-38R	44.7	1.2	4.0	6.5	0.9	3.2
OL-14-39R	143.7	4.8	6.4	18.8	2.0	5.2
OL-14-40R	1111.4	5.7	17.0	104.8	5.1	13.6
Average	214			21		
Standard Deviation	284			26		
RSD	132%			125%		
Maximum	1111			113		
Minimum	14.8			3.7		

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
#ND	0			3		
# > SC	13			14		

Table C.4. Summary of results for decision unit OL-32 (CALC-DVZ-AFRI-106). Concentration is the average of the three replicate results (Table C.1). “SD” is the standard deviation of the three replicates. The 2σ Error is the average reported counting error of the three replicates. Shaded cell indicates the MDL was used in place of non-detectable result for calculation purposes. “#DIV/0!” in the St. dev. column indicates that only one of the three replicates was detectable, and the one result was used as the average concentration. Statistics for the data set are included at the bottom of the table summary.

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
OL32-1	305.60	3.96	8.92	12.18	1.77	8.10
OL32-2	221.69	3.68	7.85	36.76	4.93	6.46
OL32-3	173.57	2.90	6.85	26.53	2.47	5.60
OL32-4	23.24	0.99	3.11	4.86	0.45	2.57
OL32-5	24.30	1.61	3.55	5.37	#DIV/0!	3.82
OL32-6	42.13	2.66	3.94	6.99	0.08	3.72
OL32-7	13.98	1.24	3.05	4.05	#DIV/0!	3.34
OL32-8	176.40	0.51	6.95	21.67	0.58	5.62
OL32-9	183.53	5.38	6.94	20.06	3.01	5.59
OL32-10	55.67	12.18	4.34	7.16	1.25	4.14
OL32-11	197.40	6.97	7.34	21.23	3.22	5.90
OL32-12	20.62	1.49	3.22	5.38	0.67	3.10
OL32-13	21.86	1.69	3.35	4.96	0.30	2.77
OL32-14	33.00	1.68	3.70	7.23	1.57	3.07
OL32-15	120.13	0.19	5.58	18.39	5.18	4.56
OL32-16	195.94	2.82	7.54	12.90	3.75	5.96
OL32-17	35.35	2.16	3.76	6.31	0.80	3.07
OL32-18	20.92	1.05	3.16	4.50	#DIV/0!	3.45
OL32-19	18.39	1.62	3.10	4.20	#DIV/0!	3.38
OL32-20	29.87	3.18	3.71	5.74	0.62	3.52
OL32-21	12.97	0.70	2.74	3.93	#DIV/0!	3.02
OL32-22	22.87	1.24	3.26	5.75	0.67	3.13
OL32-23	33.56	3.16	3.57	8.47	#DIV/0!	3.87
OL32-24	44.89	1.94	4.19	6.45	1.88	3.95
OL32-25	97.71	2.95	5.39	8.38	0.21	4.98
OL32-26	182.34	1.50	7.21	16.53	3.96	5.76
OL32-27	155.32	1.49	6.96	13.95	2.38	5.56
OL32-28	38.38	0.85	3.85	9.59	0.36	3.22
OL32-29	388.81	8.41	10.15	97.48	4.85	8.63
OL32-30	44.42	2.58	3.89	6.70	1.96	3.68
OL32-31	947.44	12.52	15.53	67.18	3.26	12.28
OL32-32	712.95	8.09	13.75	42.33	7.55	10.82
OL32-33	64.58	2.21	4.55	7.62	0.29	3.67
OL32-34	4187.18	114.26	33.17	415.00	17.42	26.55
OL32-35	166.64	1.05	6.76	39.23	1.74	5.70
OL32-36	106.25	2.62	6.29	20.34	1.95	5.22
OL32-37	557.81	66.93	11.76	16.98	0.78	10.54
OL32-38	28.78	2.82	3.35	5.60	1.15	2.76
OL32-39	306.13	26.14	8.89	27.87	1.21	7.09

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
OL32-40	372.11	1.67	9.75	22.61	2.73	7.68
Average	260			27		
Standard Deviation	668			66		
RSD	257%			243%		
Maximum	4187			415		
Minimum	13.0			3.9		
#ND	0			0		
# > SC	8			13.00		

Table C.5. Summary of results for decision unit OL-FR2-1 (CALC-DVZ-AFRI-106). Concentration is the average of the three replicate results (Table C.1). “SD” is the standard deviation of the three replicates. The 2σ Error is the average reported counting error of the three replicates. Shaded cell indicates the MDL was used in place of non-detectable result for calculation purposes. “#DIV/0!” in the St. dev. column indicates that only one of the three replicates was detectable, and the one result was used as the average concentration. Statistics for the data set are included at the bottom of the table summary.

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
FR2-1-1	96.12	5.45	5.23	9.16	2.34	4.19
FR2-1-2	473.33	5.21	10.64	29.56	2.32	8.39
FR2-1-3	233.30	20.27	7.73	3.90	NA	8.99
FR2-1-4	1302.78	12.96	17.98	116.84	2.00	14.34
FR2-1-5	60.60	1.86	4.60	11.93	2.26	3.81
FR2-1-6	51.28	1.41	4.35	12.07	1.86	3.64
FR2-1-7	17.70	0.82	3.14	4.79	0.93	3.01
FR2-1-8	26.42	2.57	3.38	6.23	0.96	2.81
FR2-1-9	30.85	1.67	4.22	3.90	NA	5.14
FR2-1-10	18.54	3.09	3.58	5.24	0.07	3.45
FR2-1-11	184.19	8.81	7.41	17.12	3.54	5.92
FR2-1-12	16.83	1.01	3.61	3.90	NA	4.35
FR2-1-13	79.23	5.58	4.89	9.04	3.12	4.57
FR2-1-14	24.34	2.33	3.40	4.52	#DIV/0!	3.69
FR2-1-15	13.65	0.23	2.62	3.90	NA	3.21
FR2-1-16	23.63	0.85	3.42	5.21	0.70	3.27
FR2-1-17	24.38	1.07	3.28	5.15	0.13	3.14
FR2-1-18	23.76	0.78	3.42	5.09	0.71	3.30
FR2-1-19	13.90	2.21	3.15	7.36	1.49	3.11
FR2-1-20	16.46	0.63	3.14	4.00	#DIV/0!	3.39
FR2-1-21	16.06	0.34	2.80	3.49	#DIV/0!	3.01
FR2-1-22	18.66	2.23	2.99	4.43	#DIV/0!	3.23
FR2-1-23	24.16	1.43	3.59	6.15	0.56	2.99
FR2-1-24	24.14	3.78	3.37	7.58	2.43	3.26
FR2-1-25	16.59	2.13	3.14	4.57	#DIV/0!	3.42
FR2-1-26	16.14	1.18	2.90	3.83	#DIV/0!	3.16
FR2-1-27	19.62	2.13	3.02	4.55	1.03	2.88
FR2-1-28	13.12	0.71	2.59	3.20	#DIV/0!	2.83
FR2-1-29	74.73	2.79	4.95	15.51	0.95	4.11
FR2-1-30	17.86	0.52	3.24	3.90	NA	3.95
FR2-1-31	19.26	1.96	3.11	4.11	#DIV/0!	3.38
FR2-1-32	16.19	0.59	2.77	3.90	NA	3.33
FR2-1-33	21.51	2.56	3.03	5.16	1.24	2.91

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
FR2-1-34	56.17	2.38	4.29	14.03	1.43	3.60
FR2-1-35	42.31	2.64	4.14	15.12	1.99	3.57
FR2-1-36	20.75	0.96	3.13	5.67	1.31	2.61
FR2-1-37	17.72	1.39	3.04	3.90	NA	3.72
FR2-1-38	18.25	0.84	3.12	4.51	#DIV/0!	3.42
FR2-1-39	18.89	1.51	3.18	4.10	#DIV/0!	3.43
FR2-1-40	25.10	2.05	3.53	5.60	1.45	3.36
Average	81			9.8		
Standard Deviation	214			18		
RSD	266%			185%		
Maximum	1303			117		
Minimum	13.1			3.2		
#ND	0			7		
# > SC	2			2		

Table C.6. Summary of results for decision unit OL-IU6-4 (CALC-DVZ-AFRI-106). Concentration is the average of the three replicate results (Table C.1). “SD” is the standard deviation of the three replicates. The 2σ Error is the average reported counting error of the three replicates. Shaded cell indicates the MDL was used in place of non-detectable result for calculation purposes. “#DIV/0!” in the St. dev. column indicates that only one of the three replicates was detectable, and the one result was used as the average concentration. Statistics for the data set are included at the bottom of the table summary.

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
IU6-4-1	21.7	1.2	3.2	5.7	0.4	3.1
IU6-4-2	49.2	0.8	4.1	6.1	0.3	3.3
IU6-4-3	20.6	0.9	3.5	3.9	NA	4.3
IU6-4-4	18.0	2.4	3.6	7.0	1.9	3.0
IU6-4-5	24.2	0.7	3.4	4.5	#DIV/0!	3.6
IU6-4-6	114.6	9.1	5.2	9.3	1.5	4.1
IU6-4-7	315.4	7.0	8.9	32.4	9.1	7.1
IU6-4-8	33.1	2.4	3.7	6.9	3.1	3.6
IU6-4-9	17.6	2.0	3.3	6.2	1.0	3.2
IU6-4-10	28.9	2.8	3.4	3.9	NA	4.1
IU6-4-11	23.1	1.7	3.4	4.8	0.4	3.3
IU6-4-12	19.6	1.2	3.3	4.6	#DIV/0!	3.6
IU6-4-13	758.1	5.5	14.7	111.6	2.3	12.0
IU6-4-14	342.1	8.1	8.8	43.5	3.5	7.2
IU6-4-15	43.0	0.8	4.0	6.5	1.3	3.3
IU6-4-16	16.3	3.3	3.1	6.3	1.2	2.6
IU6-4-17	19.3	1.6	3.3	22.8	2.0	3.2
IU6-4-18	20.8	1.8	3.3	5.8	1.5	3.1
IU6-4-19	20.7	2.1	3.3	4.0	#DIV/0!	3.6
IU6-4-20	326.6	12.5	9.6	31.3	4.6	7.7
IU6-4-21	56.5	2.8	4.1	12.9	1.6	3.4
IU6-4-22	39.0	2.2	3.9	8.7	1.7	3.2
IU6-4-23	33.7	1.2	3.6	5.8	#DIV/0!	3.9
IU6-4-24	376.3	7.1	9.9	44.2	7.4	8.0
IU6-4-25	19.8	1.1	3.0	4.8	0.2	2.5
IU6-4-26	21.2	1.3	3.4	3.9	NA	4.1
IU6-4-27	24.9	1.6	3.1	5.0	1.6	3.0

Sample ID	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
IU6-4-28	34.6	1.3	3.8	7.1	1.1	3.1
IU6-4-29	260.8	3.2	8.6	18.7	3.2	6.8
IU6-4-30	33.7	2.3	3.9	3.9	NA	4.7
IU6-4-31	21.7	0.8	3.3	5.2	0.9	2.7
IU6-4-32	22.8	0.6	3.2	4.5	0.9	2.6
IU6-4-33	54.3	6.5	4.2	5.4	#DIV/0!	4.5
IU6-4-34	201.2	5.2	7.1	30.7	6.0	5.8
IU6-4-35	142.9	8.3	6.4	21.2	1.4	5.2
IU6-4-36	326.6	4.3	9.3	34.4	7.1	7.4
IU6-4-37	17.8	0.8	3.2	4.4	0.5	3.0
IU6-4-38	39.5	0.7	4.0	6.8	#DIV/0!	4.3
IU6-4-39	67.8	2.1	4.7	11.2	1.9	3.8
IU6-4-40	21.3	1.5	3.1	4.0	#DIV/0!	3.4
Average	101			14		
Standard Deviation	153			20		
RSD	151%			137%		
Maximum	758			112		
Minimum	16.3			3.9		
#ND	0			4		
# > SC	7.00			9.00		

Table C.7. Daily QA field check results (CALC-DVZ-AFRI-104)

QA Summary		Lead (mg/kg)			Arsenic (mg/kg)		
Sample ID	n	Average	SD	RSD	Average	SD	RSD
			OL-14				
OL-14-M2-1	7	39.7	1.9	4.7%	15.7	1.3	8.0%
OL-IU6-4-M-4	7	199.1	2.7	1.3%	27.8	2.1	7.6%
OL-IU6-H-2	7	851.6	6.4	0.7%	237.5	6.2	2.6%
SRM 2 (1)	3	167.4	1.9	1.1%	28.2	1.7	6.0%
SRM 2 (2)	3	166.7	8.1	4.9%	28.0	2.6	9.3%
SRM 2 (3)	3	170.8	2.5	1.4%	28.9	1.2	4.3%
Blank (1)	3	ND	NA	NA	ND	NA	NA
Blank (2)	3	ND	NA	NA	ND	NA	NA
			OL-32				
OL-14-M2-1	7	43.4	4.7	10.7%	11.7	1.3	11.1%
OL-IU6-4-M-4	7	197.2	2.2	1.1%	29.6	2.1	7.0%
OL-IU6-H-2	7	1283.5	9.2	0.7%	340.3	7.2	2.1%
SRM 2 (1)	3	168.6	4.7	2.8%	28.5	4.9	17.1%
SRM 2 (2)	3	168.2	5.2	3.1%	25.7	1.1	4.2%
SRM 2 (3)	3	166.1	2.2	1.3%	29.5	1.0	3.3%
Blank (1)	3	ND	NA	NA	ND	NA	NA
Blank (2)	3	ND	NA	NA	ND	NA	NA
Blank (3)	3	ND	NA	NA	ND	NA	NA
Blank (3)	3	3.9	#DIV/0!	#DIV/0!	ND	NA	NA
			OL-FR2-1				
OL-14-M2-1	7	37.9	5.6	14.7%	12.4	1.8	14.5%
OL-IU6-4-M-4	7	199.1	8.1	4.1%	30.0	3.1	10.2%
OL-IU6-H-2	7	1249.2	39.5	3.2%	353.1	13.1	3.7%
SRM 2 (1)	3	171.1	4.1	2.4%	25.1	2.5	9.8%
SRM 2 (2)	3	168.3	3.2	1.9%	26.4	3.6	13.8%

QA Summary		Lead (mg/kg)			Arsenic (mg/kg)		
SRM 2 (3)	3	169.1	5.5	3.3%	30.7	0.5	1.6%
SRM 2 (4)	3	169.3	3.0	1.8%	28.7	1.9	6.5%
Blank (1)	3	ND	NA	NA	ND	NA	NA
Blank (2)	3	ND	NA	NA	ND	NA	NA
Blank (3)	3	ND	NA	NA	ND	NA	NA
OL-IU6-4							
OL-14-M2-1	7	45.9	2.6	5.6%	13.2	2.2	17.0%
OL-IU6-4-M-4	7	198.3	2.4	1.2%	27.0	2.1	7.9%
OL-IU6-H-2	7	1171.0	8.4	0.7%	335.4	10.4	3.1%
OL-14-M2-1	7	43.5	1.7	4.0%	14.3	2.0	14.1%
OL-IU6-4-M-4	7	199.8	3.9	2.0%	32.4	3.3	10.2%
OL-IU6-H-2	7	1042.9	14.1	1.3%	258.0	11.8	4.6%
SRM 2 (1)	3	170.7	6.0	3.5%	26.7	2.3	8.8%
SRM 2 (2)	3	174.4	1.5	0.8%	28.7	0.5	1.8%
SRM 2 (3)	3	173.8	3.4	2.0%	28.6	4.5	15.9%
SRM 2 (4)	3	169.1	5.5	3.3%	30.7	0.5	1.6%
Blank (1)	3	ND	NA	NA	ND	NA	NA
Blank (2)	3	ND	NA	NA	ND	NA	NA
Blank (3)	3	ND	NA	NA	ND	NA	NA
Blank (4)	3	ND	NA	NA	ND	NA	NA
Blank (4)	3	ND	NA	NA	ND	NA	NA

Table C.8. Results for MDL calculation (CALC-DVZ-AFRI-105)

Date	Duration (s)	Units	Sample	Lead (mg/kg)	Arsenic (mg/kg)	Lead 2σError	Arsenic 2σError
7/7/2014 15:10	60.17	mg/kg	OL-14-L-1	19.3	4.9	3.18	2.63
7/7/2014 15:18	60.30	mg/kg	OL-14-L-2	17.8	7.9	3.13	2.67
7/7/2014 15:26	60.34	mg/kg	OL-14-L-3	19.1	5.0	3.12	2.58
8/1/2014 14:31	60.23	mg/kg	OL-14-L-4	18.5	6.0	3.12	2.62
7/9/2014 13:57	60.12	mg/kg	OL-14-L-5	18.0	6.9	3.12	2.63
7/9/2014 14:07	60.22	mg/kg	OL-14-L-6	20.1	4.4	3.21	2.64
7/9/2014 14:15	60.29	mg/kg	OL-14-L-7	18.1	6.1	3.13	2.63
Student T-Value for n=7 ⇒ 3.143 (n-1= 6 degrees of freedom) MDL= (SD) x (T-value)			Average	18.7	5.9		
			Standard Deviation	0.84	1.23		
			MDL	2.6	3.9		

Appendix D

Data Collected “For Information Only” as Part of the 100-OL-1 Operable Unit Pilot Study

Appendix D

Data Collected “For Information Only” as Part of the 100-OL-1 Operable Unit Pilot Study

This appendix contains the results of supplemental field sampling. This includes an additional set of 40 gridded sample results collected at OL-14 and results for samples collected in transects at OL-14 and OL-IU6-4. This sampling was done to supplement the quality assurance (QA) validated data contained in Appendix C, and to assist in data interpretation. Therefore, these additional results were not QA validated. This data was used for information only, and should not be used for any decision making purposes.

Table D.1. “For Information Only” Results for OL-14. The notation “#DIV/0!” in the concentration column indicates that all three replicate results were less than the quantification limit of the XRF instrument. #DIV/0 in the “SD” (standard deviation) column indicates that only 1 of the 3 replicates was quantifiable by the instrument.

Sample ID	Latitude	Longitude	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
OL-14-26	46.71088	119.49383	27.4	1.4	3.5	7.5	1.4	2.9
OL-14-25	46.71089	119.49479	31.0	2.5	3.6	6.6	1.4	3.0
OL-14-30	46.71147	119.49417	29.3	1.4	3.3	6.3	2.0	2.8
OL-14-31	46.71145	119.49334	252.1	8.7	8.5	61.3	6.8	7.2
OL-14-32	46.71144	119.49237	1410.9	2.9	19.2	121.9	22.7	15.3
OL-14-33	46.71143	119.49141	687.4	92.9	13.7	55.4	12.9	10.9
OL-14-37	46.71201	119.49188	543.0	3.8	11.5	81.6	3.3	9.4
OL-14-36	46.71202	119.49285	473.0	12.2	10.5	38.6	2.6	8.4
OL-14-35	46.71203	119.49381	51.4	1.0	4.0	13.6	1.9	3.4
OL-14-34	46.71204	119.49477	19.0	0.5	3.0	4.3	#DIV/0!	3.3
OL-14-38	46.71260	119.49428	89.1	2.4	5.2	13.0	4.2	4.2
OL-14-40	46.71318	119.49475	29.7	2.5	3.3	5.4	1.6	3.2
OL-14-39	46.71260	119.49332	65.4	13.1	4.6	#DIV/0!	#DIV/0!	5.4
OL-14-27	46.71087	119.49287	611.8	17.9	13.0	135.4	4.7	10.9
OL-14-28	46.71086	119.49190	268.6	15.8	8.9	14.3	#DIV/0!	9.2
OL-14-29	46.71085	119.49094	424.2	25.9	10.4	12.8	#DIV/0!	10.8
OL-14-24	46.71028	119.49047	740.2	17.1	14.3	58.3	1.4	11.3
OL-14-19	46.70971	119.49096	397.5	5.4	10.0	49.0	2.3	8.1
OL-14-23	46.71028	119.49143	190.0	4.7	7.1	34.8	2.8	5.9
OL-14-18	46.70971	119.49193	152.1	3.3	6.4	16.5	1.7	5.1
OL-14-22	46.71029	119.49240	850.0	13.4	15.0	72.4	14.6	11.9
OL-14-17	46.70972	119.49289	173.4	4.1	6.7	10.8	1.0	5.3
OL-14-21	46.71030	119.49336	814.8	2.2	14.4	90.6	9.7	11.6
OL-14-16	46.70974	119.49481	11.5	1.0	2.8	3.6	#DIV/0!	3.1
OL-14-20	46.71031	119.49432	31.3	1.1	3.6	6.6	0.2	2.9
OL-14-1	46.70741	119.49100	29.8	2.6	3.6	5.8	0.5	2.9
OL-14-5	46.70798	119.49051	42.1	6.9	3.8	7.7	1.2	3.1
OL-14-4	46.70799	119.49148	61.3	6.7	4.5	10.1	0.5	4.2
OL-14-3	46.70800	119.49244	29.8	0.8	3.5	5.0	0.3	2.9
OL-14-2	46.70801	119.49340	20.2	1.5	3.2	4.3	0.2	3.0
OL-14-6	46.70859	119.49484	15.5	1.5	3.0	5.4	0.9	2.5

Sample ID	Latitude	Longitude	Lead (mg/kg)	Lead SD	Lead 2σ Error	Arsenic (mg/kg)	Arsenic SD	Arsenic 2σ Error
OL-14-7	46.70858	119.49387	17.7	1.0	3.1	5.1	1.1	3.0
OL-14-8	46.70858	119.49291	34.4	1.7	3.7	#DIV/0!	#DIV/0!	4.4
OL-14-9	46.70857	119.49195	52.7	0.4	4.4	6.4	1.3	3.5
OL-14-10	46.70856	119.49098	110.9	1.1	5.3	13.3	2.0	4.3
OL-14-15	46.70913	119.49049	579.7	14.5	12.1	44.9	11.0	9.6
OL-14-14	46.70914	119.49145	46.3	3.8	4.1	10.6	1.1	3.4
OL-14-13	46.70915	119.49242	166.0	0.5	6.7	14.7	2.7	5.3
OL-14-12	46.70915	119.49338	17.9	1.3	3.0	5.0	0.1	2.9
OL-14-11	46.70919	119.49438	17.5	2.6	3.1	4.8	1.0	3.0

Table D.2. Results of transect samples collected at OL-14 and OL-IU6-4

x (ft)	y (ft)	Transect 1	Lead (mg/kg)	Arsenic (mg/kg)	Transect 2	Lead (mg/kg)	Arsenic (mg/kg)	Transect 3	Lead (mg/kg)	Arsenic (mg/kg)
0	0	OL-14-T1-G0	938	119	OL-14-T2-G0	20	5	OL-IU6-4-G0	192	33
-0.5	0	OL-14-T1-A-0.5	641	99	OL-14-T2-A-0.5	54	11	OL-IU6-4-A-0.5	218	30
-1	0	OL-14-T1-A-1	713	85	OL-14-T2-A-1	53	9	OL-IU6-4-A-1	447	44
-2	0	OL-14-T1-A-2	578	48	OL-14-T2-A-2	60	8	OL-IU6-4-A-2	541	33
-4	0	OL-14-T1-A-4	696	72	OL-14-T2-A-4	58	9	OL-IU6-4-A-4	628	91
-8	0	OL-14-T1-A-8	1010	139	OL-14-T2-A-8	30	ND	OL-IU6-4-A-8	372	115
-12	0	OL-14-T1-A-12	884	52	OL-14-T2-A-12	98	10	OL-IU6-4-A-12	182	38
-16	0	OL-14-T1-A-16	535	42	OL-14-T2-A-16	157	13	OL-IU6-4-C-0.5	157	33
0	0.5	OL-14-T1-B-0.5	779	95	OL-14-T2-B-0.5	88	10	OL-IU6-4-C-1	240	35
0	1	OL-14-T1-B-1	370	30	OL-14-T2-B-1	60	12	OL-IU6-4-C-2	251	22
0	2	OL-14-T1-B-2	422	72	OL-14-T2-B-2	209	49	OL-IU6-4-C-4	483	46
0	4	OL-14-T1-B-4	130	23	OL-14-T2-B-4	453	67	OL-IU6-4-C-8	600	38
0	8	OL-14-T1-B-8	98	13	OL-14-T2-B-8	160	27	OL-IU6-4-C-12	850	128
0	12	OL-14-T1-B-12	172	18	OL-14-T2-B-12	302	21	OL-IU6-4-B-0.5	418	75
0	16	OL-14-T1-B-16	915	144	OL-14-T2-B-16	50	7	OL-IU6-4-B-1	299	48
0.5	0	OL-14-T1-C-0.5	620	66	OL-14-T2-C-0.5	125	21	OL-IU6-4-B-2	218	62
1	0	OL-14-T1-C-1	1442	137	OL-14-T2-C-1	82	20	OL-IU6-4-B-4	277	34
2	0	OL-14-T1-C-2	393	49	OL-14-T2-C-2	40	10	OL-IU6-4-B-8	361	38
4	0	OL-14-T1-C-4	1094	154	OL-14-T2-C-4	185	36	OL-IU6-4-B-12	343	57
8	0	OL-14-T1-C-8	840	93	OL-14-T2-C-8	42	6	OL-IU6-4-D-0.5	237	60
12	0	OL-14-T1-C-12	132	10	OL-14-T2-C-12	136	8	OL-IU6-4-D-1	193	17
16	0	OL-14-T1-C-16	66	12	OL-14-T2-C-16	44	10	OL-IU6-4-D-2	256	30
0	-0.5	OL-14-T1-D-0.5	532	67	OL-14-T2-D-0.5	202	26	OL-IU6-4-D-4	598	26
0	-1	OL-14-T1-D-1	227	30	OL-14-T2-D-1	165	ND	OL-IU6-4-D-8	195	29
0	-2	OL-14-T1-D-2	122	19	OL-14-T2-D-2	151	9	OL-IU6-4-D-12	335	17
0	-4	OL-14-T1-D-4	225	17	OL-14-T2-D-4	108	ND			
0	-8	OL-14-T1-D-8	50	11	OL-14-T2-D-8	46	11			
0	-12	OL-14-T1-D-12	104	13	OL-14-T2-D-12	235	33			
0	-16	OL-14-T1-D-16	142	24	OL-14-T2-D-16	119	27			
		Average	513	61	Average	122	18	Average	356	47
		Maximum	1442	154	Maximum	453	67	Maximum	850	128
		Minimum	50	10	minimum	20	5	minimum	157	17
		Standard Deviation	372	46	Standard Deviation	95	15	Standard Deviation	176	28
		RSD	72.5%	75.5%	RSD	77.9%	81.1%	RSD	49.5%	60.2%
		n	29	29		29	26		25	25

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