UNIFORM FEDERAL POLICY

QUALITY ASSURANCE PROJECT PLAN

For

The Characterization of Lead in Soil at the Lead Sweetening Area and Ethyl Blending Area

WILCOX OIL SUPERFUND SITE

Bristow, Creek County, Oklahoma

October 12, 2017

Revision 2

Prepared for:

U.S. EPA Region 6

Dallas, Texas

Prepared by: Technology Integration and Information Branch (TIIB), Office of Superfund Remediation and Technology Innovation (OSRTI), Washington, DC 20460

and

ICF, 9300 Lee Highway, Fairfax, VA 22031 USA

Contract No.: EP-W-14-001; OSRTI Technical Assessment, Support, Outreach and Training

Technical Direction No.: Task Order TO 006/TD 013

9956689

QAPP Worksheet #1 & 2: Title and Approval Page

(UFP-QAPP Manual Section 2.1)
(EPA 2106-G-05 Section 2.2.1)

1. **Project Identifying Information**
   a. **Site name/project name:** Wilcox Oil Superfund Site, Characterization of Lead at Two Sites
   b. **Site location/number:** Bristow, Creek County, Oklahoma (06GG/0604942, OU 1)
   c. **Contract/Work assignment number:** EP-W-14-001/TO 006, Technical Directive 013

2. **Lead Organization:** EPA OSRTI TIIB

Prepared by: Deana Crumbing, EPA OSRTI TIIB

Deana M. Crumbing

Date

3. **Federal Regulatory Agency**

Approved by: Katrina Higgins-Coltrain, EPA Region 6, RPM and Project Lead

EPA Region 6 Remedial Project Manager Date

Approved by: David Charters, Quality Assurance Manager, EPA OSRTI

EPA OSRTI Quality Assurance Manager Date

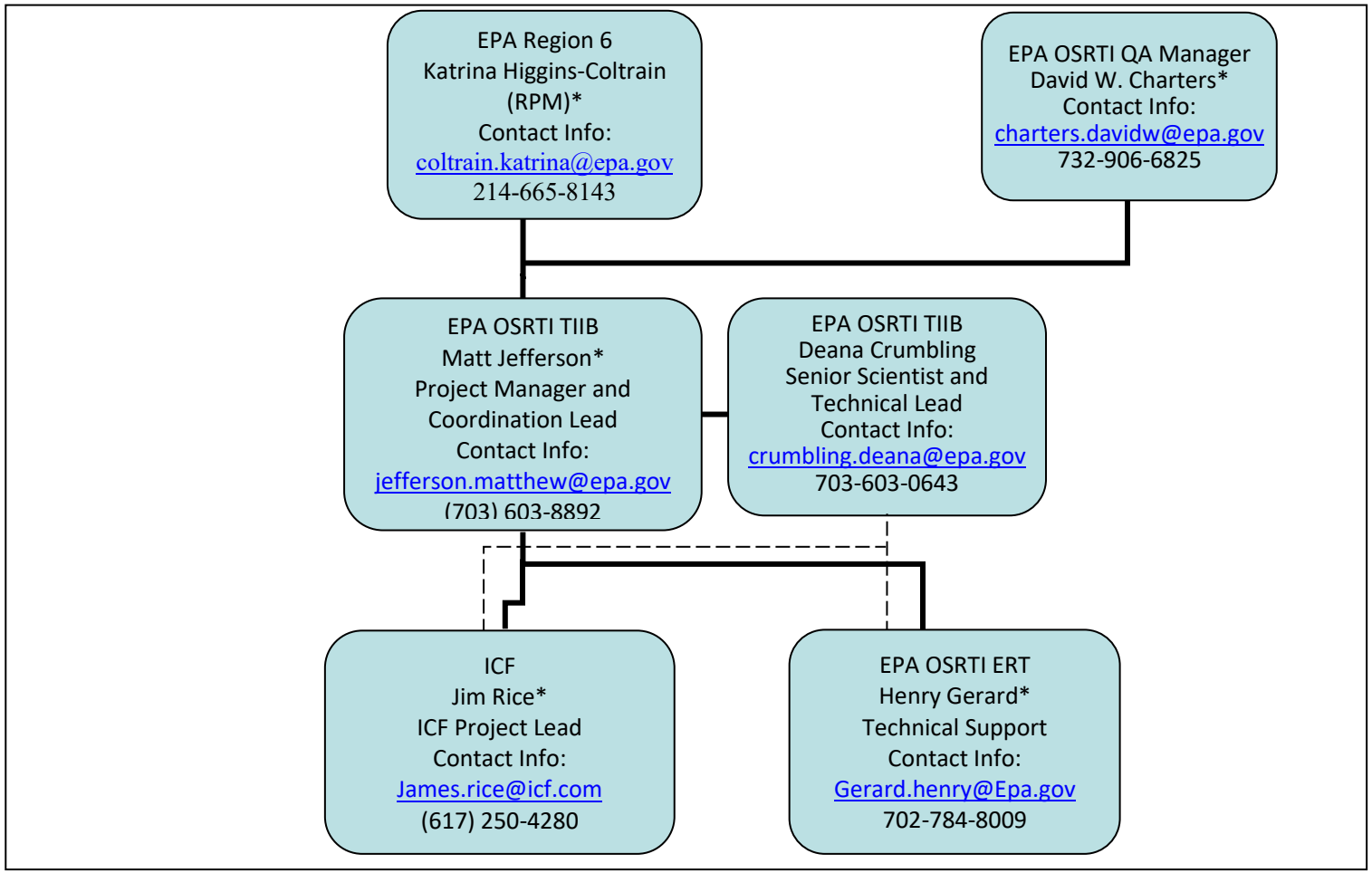
4. **State Regulatory Agency:** Oklahoma Department of Environmental Quality (ODEQ) is an observer, assisting EPA with planning and implementing Long-term Sampling and Response Plan at Wilcox Oil. ODEQ is not a signatory for the QAPP.
5. **Other Stakeholders:** Not Applicable
6. **List plans and reports from previous investigations relevant to this project:** Not Applicable

Signatures indicate that officials have reviewed the QAPP and concur with its implementation it as written.

QAPP Worksheet #3 & 5: Project Organization and QAPP Distribution
(UFP-QAPP Manual Section 2.3 and 2.4)
(EPA 2106-G-05 Section 2.2.3 and 2.2.4)

The most current and approved copy of the QAPP will be delivered to recipients using email or a web-based system in use by EPA at the time of submittal.

*QAPP recipient Lines of authority _____ Lines of Communication ----------



QAPP Worksheet #4, 7 & 8: Personnel Qualifications and Sign-off Sheet
(UFP-QAPP Manual Sections 2.3.2 – 2.3.4)
(EPA 2106-G-05 Section 2.2.1 and 2.2.7)

ORGANIZATION: EPA OSRTI

Name Signature/Date	Project Title/Role	Education/Experience	Specialized Training/Certifications
Matt Jefferson	**HQ Coordination Lead, Project Manager for Study.** Responsible for providing management and technical oversight during all field, laboratory, and analysis activities. Coordinates with EPA Region 6 RPM to ensure project goals are being met. Review and sign-off on QAPPs and any future modifications to the plans; provides quality-related direction to the Project QA Manager; and has authority to suspend affected project or lab activities if approved quality requirements are not adequately met. Operational support as needed.	BS, MS Environmental Engineering, 20 years RPM experience in several regions	EPA TOCOR, XRF Radiation Safety, XRF operation, 40-hour HAZWOPER
Deana Crumbling	**Technical Lead, Senior Scientist.** Assist with study design and QAPP preparation; sample processing and analysis team lead; technical and operational support to sample prep and field teams, Niton instrument analysis leader, lead evaluator of the study data using statistics and any other suitable tools; conduit of experimental results to other EPA parties interested in XRF application to risk assessment and site cleanups.	BS, biochemistry; MS, environmental science; 20+ years as analytical chemist	XRF Radiation Safety, 40-hour HAZWOPER

ORGANIZATION: EPA Region 8 Superfund

Name Signature/Date	Project Title/Role	Education/Experience	Specialized Training/Certifications
Katrina Higgins-Coltrain	**EPA Region 6 RPM for the Wilcox Oil Site.** Project proponent with overall responsibility for the lead delineation project to support project specific needs (Remedial Investigation). Approves all project level decisions and coordinates Region 6 contractor and OSRTI actions.	MS Geology, 20 years as an RPM	EPA TOM, 40-hour HAZWOPER
EPA Region 6 START Contractor support staff	**Field and Logistics Support**. START contractor may be on site conducting other work during part of the lead delineation and available to help support general field logistics. As required for task.	various	Field health and safety training

ORGANIZATION: ICF (Contractor to OSRTI)

Name Signature/Date	Project Title/Role	Education/Experience	Specialized Training/Certifications
Jim Rice	**Field Sampling Team Lead and Technical Support.** Assists with preparation of QAPP and SOPs, Field Sample Team Lead; technical support to Sample Prep and XRF instrument analysis team. Provides initial level of quality assurance through adherence to the QAPP, self-check, and good laboratory practice; liaison with off-site geostatistical analysis staff	BS, MS Geology, 25 years conducting site investigations and supporting technology analysis and transfer. Field QA officer under EPA RAC, ARCS and other agency cleanup contracts.	XRF Radiation Safety, 40-Hour OSHA Hazardous Waste Site Worker Training; OSHA Supervisor Training, 8 Hour OSHA Refresher Training; First Aid and CPR
Paul Zarella	**Technical Support.** Provides support for preparation of QAPP and SOPs, oversees field activities, conducts XRF analysis and supports the project as needed in field or lab.	BA, MSc Geology, 3 years planning and implementing site investigations, GIS and chemical data analysis.	XRF Radiation Safety, 40-Hour OSHA Hazardous Waste Site Worker Training; 8 Hour OSHA Refresher Training;

ORGANIZATION: EPA OSRTI ERT

Name Signature/Date	Project Title/Role	Education/Experience	Specialized Training/Certifications
Henry Gerard	**Technical Support, Health and Safety.** Technical and field support for sample collection, sample processing and XRF analysis using ERT's Olympus XRF. Provide initial level of quality assurance through adherence to the QAPP, self-check, and good laboratory practice. POC for all field safety issues.	Degrees in Chemistry and Biology, extensive experience in field analytical implementation	XRF Radiation Safety, lead for the USEPA ERTG-XRF Subgroup.
Other ERT support staff and/or SERAS Contractor support	**Technical Support.** Additional staff to be assigned to the project as needed to support field sample collection, sample processing, and XRF analysis.	various	As required for task. Any staff operating the XRF will have taken the XRF Radiation Safety Training course.
David W. Charters	EPA OSRTI Quality Assurance Manager. Review/approve QAPP prepared by OSRTI TIIB		

***Signatures indicate personnel have read and agree to implement this QAPP as written**

QAPP Worksheet #6: Communication Pathways
(UFP-QAPP Manual Section 2.4.2)
(EPA 2106-G-05 Section 2.2.4)

Mobile phone numbers are included here for all EPA OSRTI TIIB staff because most of the communication needs will be in the field.

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Project Objectives, Site access and Logistics	EPA Region 6 Remedial Project Manager	Katrina Higgins-Coltrain	214-665-8143	As the proponent of the study RPM will communicate project needs to the OSRTI TIIB team. Coordinates with START contractor and site contacts to support logistics for TIIB team.
Quality Management/Quality Assurance Officer	EPA OSRTI	David W. Charters	732-906-6825	QAO will remain independent of direct project involvement and day-to-day operations. The QAO will ensure implementation of the quality assurance elements outlined in this QAPP. The QAO will be the point of contact with the Project Manager for quality matters.
Manage all Project Phases	EPA OSRTI TIIB	Matt Jefferson	703 209-4784	Project manager will manage project personnel, and serve as liaison to the Region 6 team. Manage day to day operations of the project. Reports to Region 6 RPM issues with cost, schedule, etc.

Coordination and communication of fieldwork activities	ICF	Field Sampling Team leader Jim Rice	978 590-5852	Field team leader will communicate relevant field information to the project manager, technical lead, and team members.
Field data and quality control reports				Field team leader will generate and report data and documents as required by this UFP QAPP along with quality control reports to the Site project manager.
Coordination of sampling supplies for field activities				The Field Team Leader will ensure all sample containers and appropriate shipping materials (such as coolers and bags) are mobilized before field sampling begins and throughout the project.
Internal chain-of-custody records and sampling documentation				Internal chain-of-custody records and sampling documentation will be submitted to the field lab at the end of each day that samples are collected.
Minor deviations from QAPP procedures identified during field activities	ICF	Field Sampling Team leader Jim Rice	978 590-5852	The Field Team Leader will verbally request a field change for any minor changes in sampling procedures that occur as a result of conditions in the field. Approval from Tech Lead is required before the change is initiated. This request will be documented in the field log book.

QAPP amendments	EPA OSRTI TIIB	Technical Lead Deana Crumbling	571 215-6947	Any changes to the QAPP prior to field work will require the Technical Lead to prepare an addendum that will be approved by the PM and EPA RPM before any changes are implemented.
QAPP – routine communications regarding analyses during implementation	EPA OSRTI TIIB	Technical Lead Deana Crumbling	571 215-6947	Primary point of contact to ensure that field analytical activities comply with the QAPP so that resulting data will meet data quality objectives.
QAPP changes during project execution (sample prep and analysis)	EPA OSRTI TIIB	Technical Lead Deana Crumbling	crumbling.deana@epa.gov 571 215-6947	Communicates the need for, and content of revisions to RPM and Region ~~8~~ 6 RPM for approval. Advises project teams of changes.
Data verification issues, e.g., incomplete records	EPA OSRTI TIIB	Technical Lead Deana Crumbling	crumbling.deana@epa.gov 571 215-6947	Communicates issues to RPM and Quality Manager for resolution
Data review corrective actions	EPA OSRTI TIIB	Technical Lead Deana Crumbling	crumbling.deana@epa.gov 571 215-6947	Communicates issues to RPM and Quality Manager for resolution

QAPP Worksheet #9a: Project Planning Session Summary
(UFP-QAPP Manual Section 2.5.1 and Figures 9-12)
(EPA 2106-G-05 Section 2.2.5)

Project Name: Characterization of Lead in Soil at the Lead Sweetening Area and Ethyl Blending Area, Wilcox Oil Superfund Site **Project Manager:** Katrina Higgins-Coltrain	**Site Name:** Wilcox Oil **Site Location:** Bristow, OK

Date of Session: Monday, June 3, 2016
Systematic Planning Meeting Purpose: Conference Call scoping meeting for all areas of Wilcox Site (included discussion of EBA and LSA)

Name	Title	Affiliation	Phone #	E-mail Address
Katrina Higgins-Coltrain	Remedial Project Manager	EPA R6	214-665-8143	coltrain.katrina@epa.gov
Phil Turner	Risk Assessor	EPA R6	214-665-2706	turner.philip@epa.gov
Teri Mcmillan	Project Manager	EA Engineering	505 224-9013	tmcmillan@eaest.com
Tom Kady	ERT	EPA ERT	732-735-5822	Kady.Thomas@epa.gov
Matthew Jefferson	Environmental Engineer	EPA TIIB	703-603-8892	jefferson.matthew@epa.gov
Deana Crumbling	Staff scientist	EPA TIIB	703-603-0643	Crumbling.Deana@epa.gov
Ed Gilbert	Hydrogeologist	EPA TIIB	703-603-8883	Gilbert.edward@Epa.gov
Jim Rice	Geologist	ICF	617-250-4280	James.Rice@icf.com
Todd Downham	Project Manager	Oklahoma DEQ	405-702-5136	Todd.Downham@deq.ok.gov
Barry Forsyth	EPA Liaison	USFWS	214 665 8467	Forsythe.Barry@epa.gov

Key Decisions: EBA and LSA will be part of Phase 1 (Mobilization 1) delineation. EPA OSRTI TIIB Field Team will utilize XRF (30-point incremental composite soil sampling and other techniques) to identify the areas where Pb concentrations in soil (0 to 24 inches) exceed 200 ppm, the preliminary remediation goal.
Action Items: OSRTI will prepare a work plan and QAPP for the Pb delineation.

QAPP Worksheet #9b

Systematic Planning Meeting Participants Sheet

Project Name: Characterization of Lead in Soil at the Lead Sweetening Area and Ethyl Blending Area, Wilcox Oil Superfund Site **Project Manager:** Katrina Higgins-Coltrain	**Site Name:** Wilcox Oil **Site Location:** Bristow, OK

Date of Session: Thursday July 14, 2016
Systematic Planning Meeting Purpose: In-person meeting to develop sampling strategy

Name	Title	Affiliation	Phone #	E-mail Address
Matthew Jefferson	Environmental Engineer	EPA Superfund TIIB	703-603-8892	jefferson.matthew@epa.gov
Deana Crumbling	Staff scientist	EPA Superfund TIIB	703-603-0643	Crumbling.Deana@epa.gov
Jim Rice	Geologist	ICF	617-250-4280	James.Rice@icf.com

Key Decisions: Decision is made to sample along transects using sampling units (SUs) of 9 to16 points within 4 to 9 square feet, and then develop definitive DUs to confirm < 200 ppm. Recon and SU sampling at EBA to identify potential source areas prior to DU sampling. Sampling will require developing an equipment list.
Action Items: OSRTI will begin developing SFP, Decision Logic Diagrams and QAPP. Develop sampling equipment list.

QAPP Worksheet #9c

Systematic Planning Meeting Participants Sheet

Project Name: Characterization of Lead in Soil at the Lead Sweetening Area and Ethyl Blending Area, Wilcox Oil Superfund Site **Project Manager:** Katrina Higgins-Coltrain	**Site Name:** Wilcox Oil **Site Location:** Bristow, OK

Date of Session: Wednesday, August 24, 2016
Systematic Planning Meeting Purpose: Field reconnaissance to observe site conditions.

Name	Title	Affiliation	Phone #	E-mail Address
Matthew Jefferson	Environmental Engineer	EPA Superfund TIIB	(703) 603-8892	jefferson.matthew@epa.gov
Deana Crumbling	Staff scientist	EPA Superfund TIIB	703-603-0643	Crumbling.Deana@epa.gov

Key Decisions: Identified additional potential source area and some logistical concerns including a number of fences that prevent access along the west side of the EBA and east and southern boundaries of the LSA – investigation will not end at fences, unless access prevents it. Two buildings are present at EBA, on with dirt floor - we will sample the floor of the eastern building
Action Items: Incorporate these considerations into the FSP and QAPP.

QAPP Worksheet #9d

Systematic Planning Meeting Participants Sheet

Project Name: Characterization of Lead in Soil at the Lead Sweetening Area and Ethyl Blending Area, Wilcox Oil Superfund Site **Project Manager:** Karina Higgins-Coltrain	**Site Name:** Wilcox Oil **Site Location:** Bristow, OK

Dates of Discussion: August 14 - 18, 2017
Purpose of Discussions: The R6 RPM raised concerns that there may be a disruption of the federal government October 1, 2017, potentially interrupting the Pb characterization field work deployment. Consultation among the parties required to evaluate change in schedule.

Name	Title	Affiliation	Phone #	E-mail Address
Katrina Higgins-Coltrain	Remedial Project Manager	EPA R6	214-665-8143	coltrain.katrina@epa.gov
Matthew Jefferson	Environmental Engineer	EPA TIIB	703-603-8892	jefferson.matthew@epa.gov
Henry Girard	ERT	EPA ERT	702-784-8009	Gerard.henry@epa.gov
Deana Crumbling	Technical Lead, Senior Scientist	EPA TIIB	703-603-0643	Crumbling.Deana@epa.gov
Dan Powell	Chief, Technology Integration & Information Branch	EPA TIIB	703-603-7196	Powell.dan@epa.gov
Jim Rice	Geologist	ICF	617-250-4280	James.Rice@icf.com

Key Decisions: TIIB's Wilcox field effort would be moved from Sept 17 – Oct 7 to Oct 22 to Nov 11, 2017.

Action Items: Deana to finish QAPP revisions. David Charters (OSRTI/ERT QA Manager) will serve as the QAPP reviewer and approver.

QAPP Worksheet #9e (Placeholder)
Systematic Planning Meeting Participants Sheet

Project Name: Characterization of Lead in Soil at the Lead Sweetening Area and Ethyl Blending Area, Wilcox Oil Superfund Site **Project Manager:** Karina Higgins-Coltrain	**Site Name:** Wilcox Oil **Site Location:** Bristow, OK

Date of Session: TBD
Systematic Planning Meeting Purpose: Systematic Planning meeting to review CSM for EBA and LSA and identify path to closure of these sites. Proposed attendees below

Name	Title	Affiliation	Phone #	E-mail Address
Katrina Higgins-Coltrain	Remedial Project Manager	EPA R6	214-665-8143	coltrain.katrina@epa.gov
Phil Turner	Risk Assessor	EPA R6	214-665-2706	turner.philip@epa.gov
Teri Mcmillan	Project Manager	EA Engineering	505 224-9013	tmcmillan@eaest.com
Tom Kady	ERT	EPA ERT	732-735-5822	Kady.Thomas@epa.gov
Matthew Jefferson	Environmental Engineer	EPA Superfund TIIB	703-603-8892	jefferson.matthew@epa.gov
Henry Girard	ERT	EPA ERT	702-784-8009	Gerard.henry@Epa.gov
Deana Crumbling	Staff scientist	EPA Superfund TIIB	703-603-0643	Crumbling.Deana@epa.gov
Jim Rice	Geologist	ICF	617-250-4280	James.Rice@icf.com
Todd Downham	Project Manager	Oklahoma DEQ	(O) 405-702-5136	Todd.Downham@deq.ok.gov
Barry Forsyth	EPA Liason	USFWS	214 665 8467	Forsythe.Barry@epa.gov

Key Decisions: TBD
Action Items: TBD

QAPP Worksheet #10: Conceptual Site Model
(UFP-QAPP Manual Section 2.5.2)
(EPA 2106-G-05 Section 2.2.5)

Conceptual Site Model (CSM) for the Areas to be sampled during the Study

Wilcox Oil Company is an inactive and abandoned oil refinery located in Creek County, Oklahoma in the northeast section of the town of Bristow, Oklahoma (Figures 10-1 and 10-2).

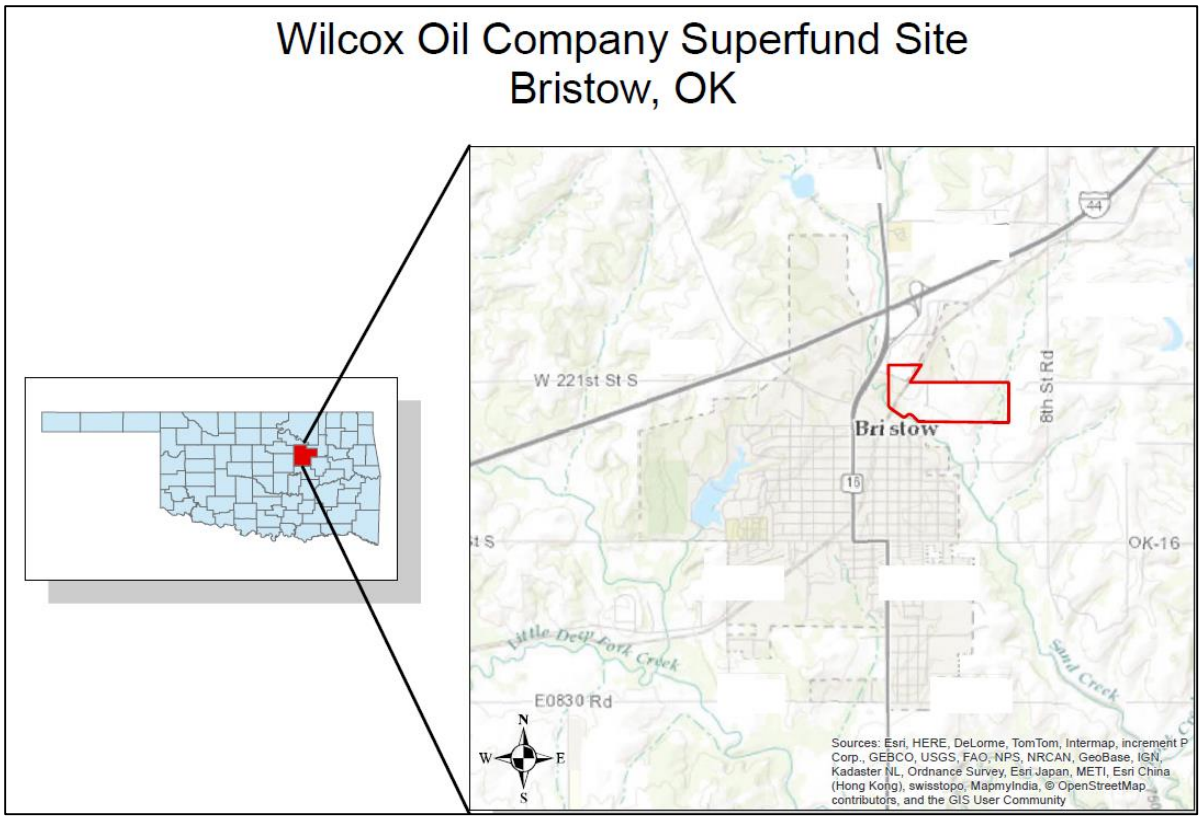


Figure 10-1. Location of Wilcox Oil Site.

The site encompasses approximately 140 to 150 acres and includes five areas: the Wilcox Process Area, the Loraine Process Area, the Loading Dock Area, the North Tank Farm, and the East Tank Farm. Several preliminary investigations have occurred at the site beginning in 1994. In 2015, Lockheed Martin assisted the Environmental Protection Agency/ Environmental Response Team (EPA/ERT) and EPA Region 6 to perform a direct sensing investigation to qualitatively address the nature and extent of contamination at several sites using direct sensing tools including the rapid optical screening tool (ROST) and X-Ray fluorescence (XRF). Details of the site history and previous investigations can be found in the reports from these investigations (Lockheed Martin, 2016).

Within the Wilcox Process Area, the two areas containing lead as the contaminant of potential concern (COC) in soil include:

- Lead Sweetening Area (LSA)
- Ethyl Blending Area (EBA)

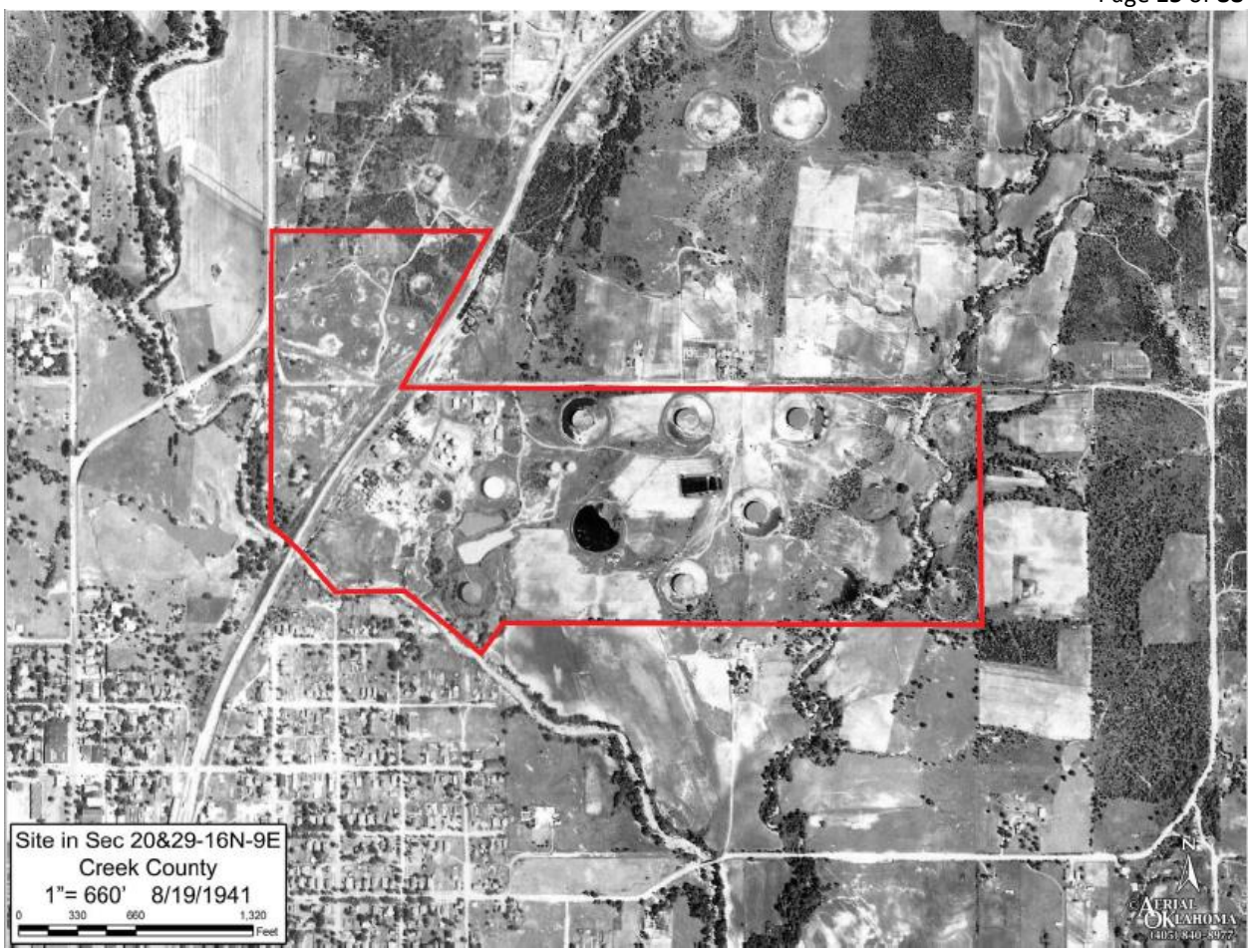


Figure 10-2. 1941 aerial photo of refinery footprint.

The **Lead Sweetening Area (LSA)** is located in the central portion of the Wilcox property. Historical maps indicate the area contained acid tanks, agitators, treaters, nearby "run down" tanks, and condensate tanks. The area was also called the "Doctor Process Area" (Figure 10-3).

The ERT report (Lockheed Martin, 2016) states that the chemicals used in the doctor sweetening process included sodium plumbite (Na2PbO2), sodium hydroxide (NaOH), and elemental sulfur or sulfonic acid to produce lead sulfide precipitate. The lead sulfide adsorbs mercaptan compounds that darken gasoline and give an offensive odor (Lachman, 1931). The ERT investigation identified phenolic compounds in the subsurface soils which were associated with the process. Crystals were observed on the surface in this area and XRF analysis showed that they contained very high lead content (percent levels above the calibration range). Vertical contamination of lead was investigated at five boring locations using single *in situ* XRF readings. In four of the locations, lead was found above 200 ppm in the upper foot of soil only, and at the remaining location it was detected at a maximum depth of 4 feet. Groundwater samples from the area show elevated lead concentrations (up to 151,000 mg/L - near Tank 34), and are believed to reflect perched water zones.

The LSA is currently very sandy with minimal plant growth and contains areas of sparkling sands/salts. Erosion is noted from this area to the south toward Sand Creek, and the tributary to Sand Creek to the east. Areas of dense trees, shrubs, poison ivy, and tall grasses surround the open sandy area. A metal fence extends through the eastern side of the investigation area, and there is a nearby elongated pond.

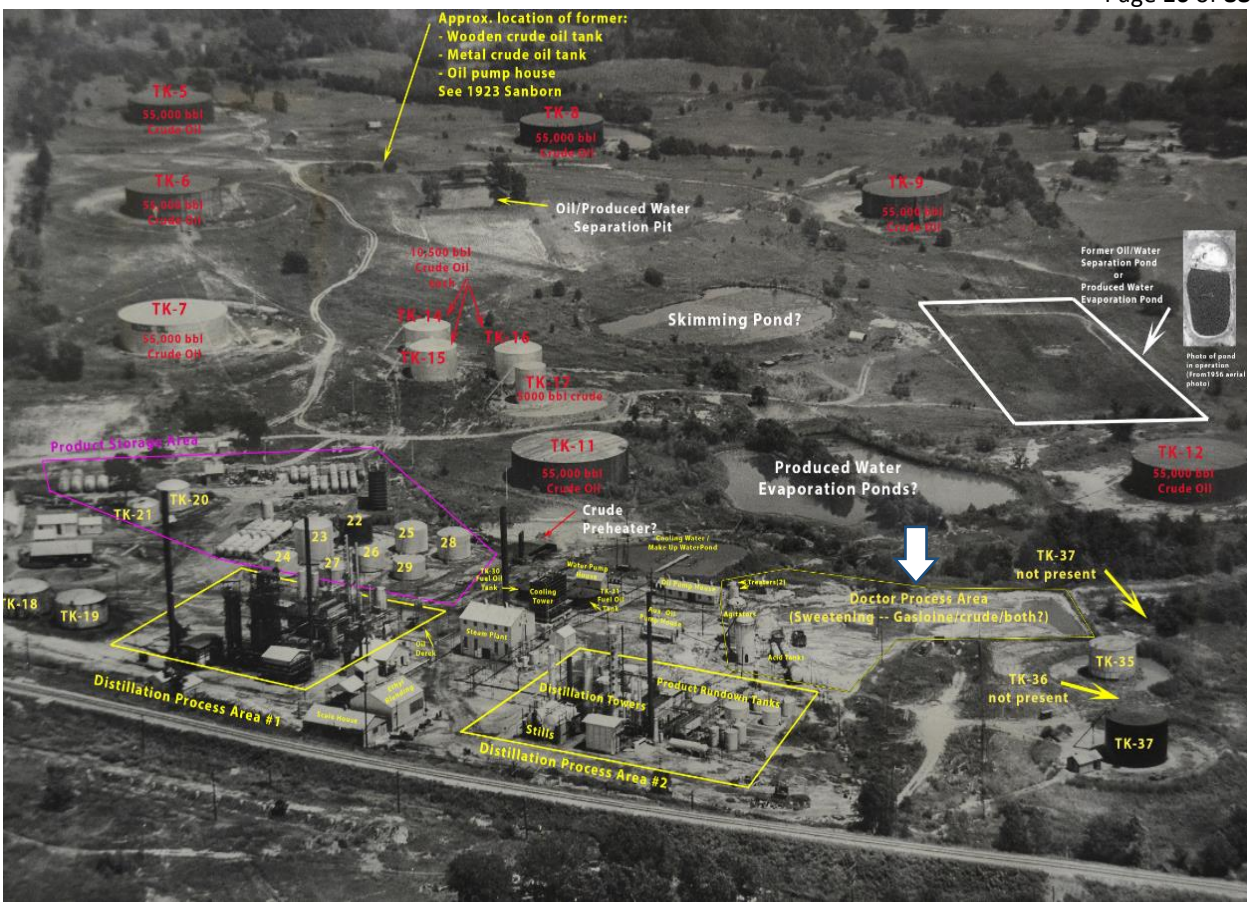


Figure 10-3. Lead Sweetening Area (large white arrow).

Much of the infrastructure has been removed in the intervening years, and unmanaged vegetation has grown up throughout the area (Figure 10-4).

Modeling of the 2015 XRF data produced a contour map of lead concentration (Figure 10-5). The estimated area of concentration greater than 200 ppm is approximately 6 acres (600 feet north-south and 500 feet east-west) and the high concentration area, greater than 10,000 ppm, is approximately 0.6 acres (approximately 250 feet north-south and 100 feet east-west). Most of the soil lead measurements were taken with a handheld XRF at the ground surface, and there is limited data regarding the vertical extent of lead contamination. The subsurface sample near the center of the area analyzed showed high concentrations (greater than 5,000 ppm at a depth of 1 foot).

Figure 10-4. 2017 Google Earth image of the Lead Sweetening Area (LSA, yellow pin), and the Ethyl Blending Area structures (white arrow) by railroad track.

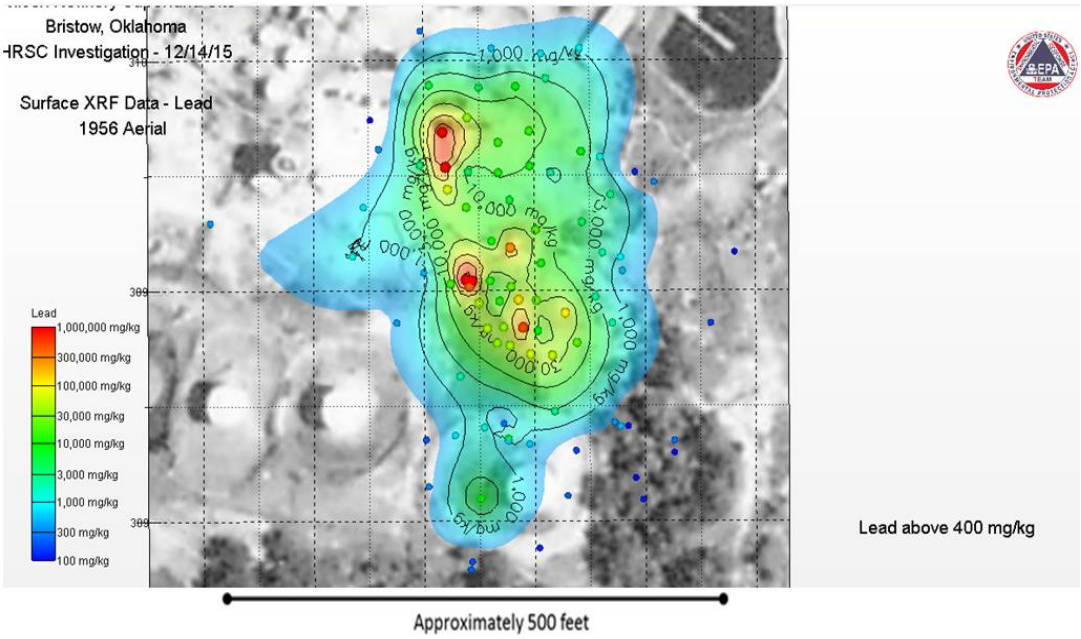


Figure 10-5. Geostatistical kriging iso-concentration lines produced from 2015 *in situ* XRF readings in the LSA (Kady, 2015).

The **Ethyl Blending Area (EBA)** is located in the Upper Wilcox Process Area in the northwest corner of the Wilcox Refinery. The area currently contains an intact main building measuring approximately 45 by 40 feet, with a sign reading "Ethyl Blending" and was presumably used to blend liquid tetraethyl lead (TEL) into the final gasoline product. TEL, which was TEL blended with the lead scavengers 1,2-dibromoethane and 1,2-dichloroethane, is normally supplied as ethyl fluid and contained a reddish dye to distinguish treated from untreated gasoline. Historical maps and photographs show no other permanent buildings within approximately 100 feet, but a rectangular feature (possible fence, slab or foundation) appears to be present on the southwest side of the building. Recent aerial photographs indicate the area is relatively flat and currently contains several large trees.

Historical aerial photographs show that between 1941 and 1956 the building was expanded to the northwest and the addition appears to have a lower roofline possibly indicating a storage area approximately 20 by 50 feet. Lighter colored ground on the southeast side of the building indicates surface disturbance. Access to the building includes a road parallel to the railroad and fence line that terminates at the northwest side (rear) of the building, and a larger road to the east that services several buildings in the area. A site visit by EPA staff in August 2016 found the area densely grown up with brush and poison ivy. Two structures are present. The main building is solidly enclosed with a concrete floor; one side of the building is very close to the railroad tracks. The adjacent structure is little more than a shed with open sides and with a dirt floor under which trucks may have stopped to load/unload. Rusted drums and fragments of equipment are present in and around the buildings. Small bore steel piping is still visible along sides of the buildings. There is at least one concrete basin that holds rain water.

The ERT investigation included screening surface soils with XRF at approximately 25 locations in the EBA. There is limited discussion of the EBA results in the SERAS report, but a contour map of lead concentration was prepared (Figure 10-6).

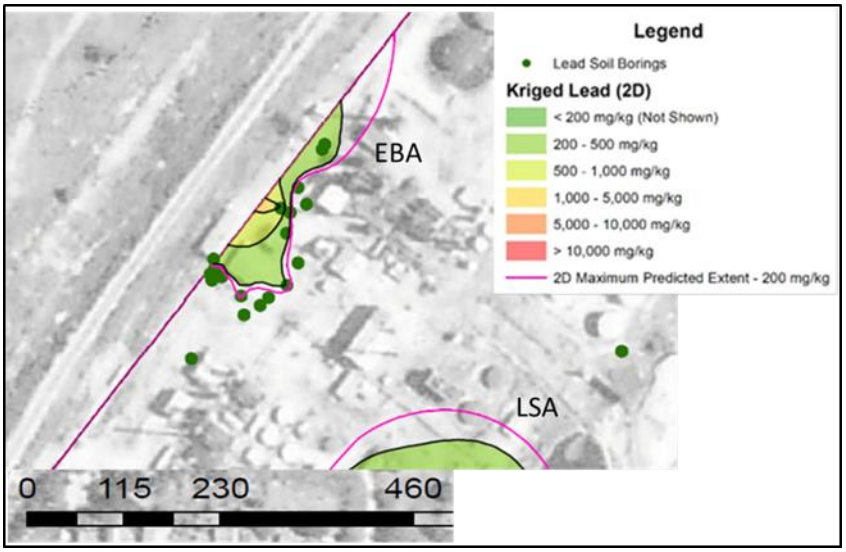


Figure 10-6. Geostatistical kriging iso-concentration lines from 2015 *in situ* XRF readings around the EBA structures.

The map shows a possible area of lead contamination above the 200 ppm screening level near the building along the railroad track. The area greater than 200 ppm extends less than 100 feet to the east, but appears to be elongated several hundred feet in the north-south direction. Most readings were between 100 and 600 ppm. The maximum concentration is 1,449 ppm.

The problem to be addressed by the project: Region 6 is conducting a remedial investigation at the site in several phases (mobilizations) and has prioritized the site investigations based on potential risk.

Surface and near surface soils with lead concentration of greater than 200 ppm present a potential risk for direct contact and soil migration, and are priority sites. The RPM would like to identify the boundaries where lead exceeds 200 ppm in soils at both of these sites. There are two potential exposure zones to be delineated, 0 to 6 inches (human exposure) and 0 to 24 inches (ecological exposure). Deeper soils (greater than 2 feet) will not be investigated in this task, but one of the outcomes will be to identify potential areas where deeper soil investigation may be needed. The results of this study will be used to plan the next steps which may include risk management or removal actions.

QAPP Worksheet #11: Project/Data Quality Objectives
(UFP-QAPP Manual Section 2.6.1)
(EPA 2106-G-05 Section 2.2.6)

Statement of the Problem

Metals contamination related to industrial activities affects many areas in the U.S. Traditional soil and sediment investigations for metal contamination have relied on the collection of discrete samples, followed by analysis of grab subsamples in a distant laboratory. However, this strategy generally produces data sets that contain high degrees of data variability due to soil heterogeneity at the spatial scales of sample collection (100-300 grams) and metals analysis (0.5 to 1 gram). Since risk and cleanup decisions are made at much larger spatial scales (10s to 100s tons), statistical evaluations of soil data are needed to manage the chance of decision errors in risk and cleanup decisions. As a consequence of the high degree of data variability, very large numbers of discrete samples are required, incurring high costs and long time frames.

Incremental sampling is an alternative technique for collecting soil and sediment samples for contaminant analysis. Although new to remediation practitioners, incremental sampling has long been practiced in the mining and agricultural industries using the theory and practices outlined by Pierre Gy (USEPA 1999). Incremental sampling uses protocols for sample collection and sample processing that control soil heterogeneity so that fewer samples are required to produce statistically strong data sets. When used in conjunction with real-time sample processing and analysis, incremental sampling can reduce the costs and time frames involved in site investigation, while simultaneously producing high quality data that can support transparent and defensible decisions. This strategy has already proven its feasibility for several residential Pb sites, where incremental sampling has been paired with quality-controlled XRF analysis. This study will evaluate whether real-time XRF can be paired with 1) composite sampling of small square areas (termed sampling units, SUs) that function as sampling “points” on transects for the purpose of identifying concentration trends and locating boundaries; and 2) incremental sampling of larger-area decision units (DUs) that provide more accurate data to confirm the tentative location of excavation boundaries established by the SUs.

Historic operations at the Wilcox and Lorraine Oil refineries resulted in the release of hazardous materials to soil, sediment, surface water and groundwater. EPA Region 6 is conducting a remedial investigation to determine the nature and extent of the releases and if these releases present an unacceptable risk to human or environmental receptors. Preliminary soil screening at two of these sites, the Lead Sweetening Area (LSA) and Ethylbenzene Blending Area (EBA), identified the potential for lead at concentrations above the screening level of 200 ppm. EPA Region 6, along with cooperating agencies Oklahoma Department of Environmental Quality and US Fish and Wildlife Service, seek to identify areas where lead contamination in soil is greater than the 200 ppm screening level.

Goals of the Study and Information to be Generated

The overall goal of the study is to support the remedial investigation at the Wilcox oil site by characterizing lead concentrations at two locations. Specifically, the goals are:

1. Identify the spatial extent of lead with a concentration of greater than 200 ppm in the 0 to 6 inch interval at the EBA and LSA for risk assessment and mitigation decisions. Estimate contaminated soil volumes for possible removal.

2. Identify the spatial extent of lead with a concentration of greater than 200 ppm in the 0 to 24-inch interval at the EBA and LSA for risk assessment and mitigation decisions. Estimate contaminated soil volumes for possible removal.

3. Introduce regional EPA staff to sampling, processing and analysis techniques for Incremental Composite Sampling and XRF to rapidly and definitively identify the concentration of lead in soil. Continual improvement and procedure development for Incremental Composite Sampling and XRF analysis are important aspects of this work for OSRTI TIIB. Field methods, sample preparation procedures and analytical procedures, will be evaluated as part of the study.

4. Evaluate the relative distribution of Pb among soil particle size fractions for a few select samples. Determine whether higher Pb concentrations in finer particles are more likely to contribute to storm run-off to streams. Evaluate the particle size and Pb content of any crystalline material observed in the LSA to determine whether soil sieving at 100-mesh could remove this material and bias soil results. Retain samples of any crystalline material for potential laboratory evaluation of water solubility and/or other relevant characteristics.

Boundaries of this Study

1. This study addresses the conditions at two specific areas within the Wilcox Oil site; the LSA and the EBA. Since this is a characterization effort, the boundaries of the two contaminated areas are only generally understood at this time. Characterization activities will cross fences and other obstacles to establish the 200 ppm boundaries.

2. The data needed to support the decisions for this project will consist of XRF concentrations for Pb in two depth intervals: surface (0 to 6” depth interval) and shallow subsurface (6 to 24”). Although the data for the two depth intervals will be generated separately, the concentration of the entire 0 to 2 ft. interval can be generated mathematically if needed for risk assessment purposes.

3. The only target analyte is Pb, although data for concentrations of other metals will be automatically collected by the XRF. Pb concentrations are expected to range from <50 ppm to >300,000 ppm. The XRFs have demonstrated linearity at least to 5600 ppm. XRF linearity and accuracy are unlikely for concentrations greater than 10,000 ppm, however, accurate reporting at such high concentrations is not necessary to meet the goals of the study.

4. The process of establishing the 200-ppm Pb boundary will use soil samples sieved to 10-mesh (<2 mm particle size) to expedite sample processing. Once located, confirmation of the 200-ppm boundary will use the <100-mesh (<150 µm) soil particle size fraction, which is expected to be the most relevant particle size for risk evaluation, per the Superfund guidance for Pb-in-soil exposure (USEPA OLEM Directive 9200.1-128).

Rigor of the Sampling and Analytic Approach

The primary purpose of this study is to determine the spatial extent of lead soil contamination for two receptor groups (human and ecological). Soil that presents excessive risk will require some form of mitigation. Therefore, the data must have sufficient value to potential data users (RPMs, risk assessors, stakeholders, Superfund program managers, legal counsel, construction design etc.) to support confident decisions about site risk and optimal cleanup design. EPA policies regarding scientific integrity and data quality overwhelmingly favor sampling designs that are based on sound scientific and statistical principles, that are transparent and defensible, have undergone performance testing and peer review,

and that have error rates that are known to be acceptably low. Incremental-composite sampling (ICS) designs meet these requirements. When coupled with real-time, quality-controlled X-ray fluorescence (XRF) analysis, high density definitive Pb data can be generated rapidly and for much less cost than traditional laboratory analysis.

Reported concentrations for analytes in soil are considered definitive when the following conditions are met (USEPA 2006):

- The volume of soil over which the reported concentration value(s) apply (i.e., sample representativeness) are known, AND
- The uncertainty range around a data point (concentration), or statistics derived from a data set (such as a mean and UCL) are known, AND
- The identity of the target analyte is known.

ICS/XRF designs can rapidly generate high quality, representative, definitive data and minimize data gaps in a single mobilization using real-time adaptive decision-making. In comparison to traditional static, discrete sample/fixed lab analysis designs, ICS/XRF for many metal analytes (such as lead, arsenic and mercury) can provide higher confidence to decision-makers and stakeholders that characterization is complete and optimal mitigation options can be selected and implemented. These benefits outweigh the cost of more highly trained staff and more sophisticated procedures needed to design and implement ICS/XRF field efforts. The benefits to the project's bottom line include:

- a statistically superior and more reliable reported data result (since XRF can rapidly perform multiple analyses from the same sample at no extra cost, in contrast to the single analysis performed by traditional laboratories);
- fewer field mobilization cycles to identify and fill data gaps;
- fewer field mobilizations to complete cleanup;
- avoidance of stakeholder controversy and legal disputes due to inconsistent, ambiguous, and/or contradictory data sets (a consequence of high data variability stemming from uncontrolled soil heterogeneity); and
- reduced project lifetimes to achieve site completion, benefiting both site reuse and the workload for regulatory oversight.

These benefits far outweigh

- the additional efforts involved for proper field sample collection, sample processing and subsampling; plus
- the perceived additional effort to generate and evaluate sufficient QC data, which would normally be done by other parties as part of traditional laboratory analysis and data validation.

<u>Establishing when data is "good enough" to support confident decisions</u>

Soil contaminant data need to be accompanied by measures of its sampling and analytical variability to quality as "definitive data" (USEPA 2006). For this project, data obtained during field work will be evaluated for quality and sources of data variability in real-time. Knowing the respective contributions of sampling and analytical imprecision or bias allows proper targeting of corrective actions if an initial round of data is found to be not "good enough" to meet project goals for decision confidence and/or legal defensibility. Evaluating data quality in real-time and identifying and needed corrective actions early in field work avoids the danger of generating large amounts of data that are later found to be inadequate.

The simplest, and most objective, way to determine whether data are "good enough" is to incorporate all sources of data imprecision and known bias into a statistical confidence interval around the mean of a data set.

> The width of a statistical confidence interval is determined by an equation that takes into account the amount of data variability, how many data points are in the data set, and what level of statistical confidence is desired (such as 90 or 95%). The "upper confidence limit on the mean" (UCL) is the upper end of the confidence interval, and the "lower confidence limit on the mean" (LCL) is the lower end of the confidence interval. The higher the confidence level, the wider the interval.

Whether there is statistical confidence that a concentration result is truly below a screening level (or other type of decision threshold) is easily estimated by observing whether both the mean AND the UCL fall below the screening level (Figure 11-1).

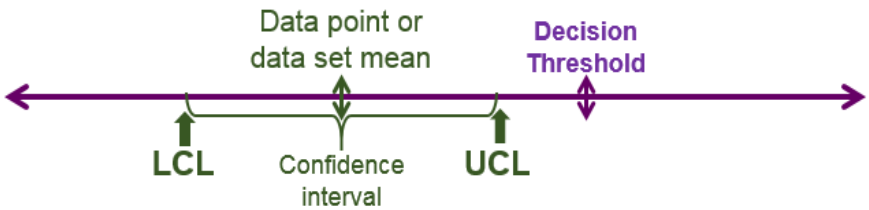


Figure 11-1. Statistical decision confidence: mean and UCL below decision threshold

Statistical confidence in the decision that a concentration result is <u>above</u> a screening level is based on observing whether both the mean AND the LCL fall <u>above</u> the screening level (Figure 11-2).

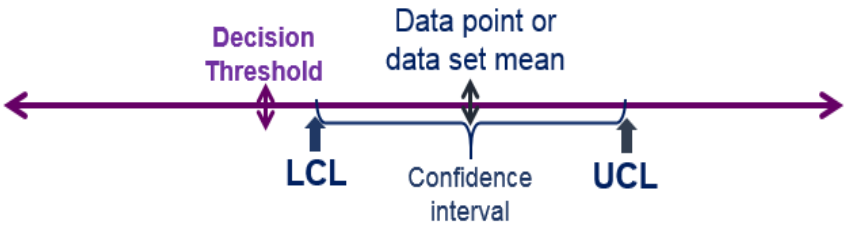


Figure 11-2. Statistical decision confidence: mean and LCL above decision threshold

When the mean and its UCL or LCL bracket the screening level, statistical uncertainty exists at the chosen level of decision confidence about whether the true concentration really is below or above the decision threshold (Figure 11-3).

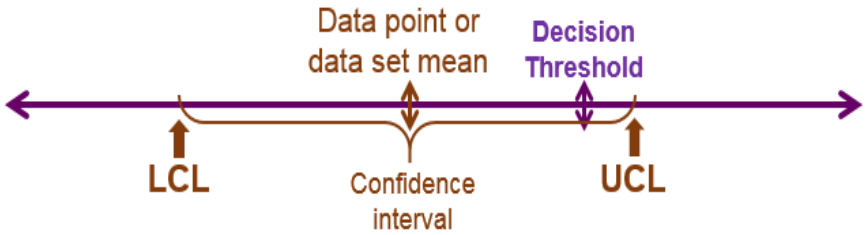


Figure 11-3. Statistical decision uncertainty: confidence interval brackets decision threshold

The most important factor determining the distance between a mean and its upper and lower confidence limits is the degree of data variability. Higher levels of data variability widen the distance covered by a confidence interval. A wider interval increases the chance that it will bracket the decision threshold so that a statistically confident decision cannot be made. In other words, too much variability (i.e., poor precision or reproducibility) can cause the data to be "not good enough" to support a confident decision, even if the mean is well below the decision threshold. This is illustrated below with the results of a set of triplicate field samples from the same DU (Figure 11-4).

Triplicate	Triplicate DU Samples Statistics			
Pb Results	Mean	Std Dev	%RSD	95% UCL
36				
145	189	179	95%	492
387				

Figure 11-4. Field triplicate samples from a single DU used to calculate a 95% UCL for the DU. This example shows the effect that high data variability has on the distance between the mean and UCL.

The benefit of real-time data is the ability to discover a problem (such as an elevated UCL that inhibits confident decisions) while there is time to take immediate corrective action so that desired decision confidence can be obtained. Corrective actions, such as sample reanalysis or recollection with improved procedures, can improve data precision and narrow the confidence interval so that the entire confidence interval falls cleanly above or below the decision threshold.

Site-specific Practices to Support the Wilcox Project's Data Quality Strategy

The following describes general QC practices to establish adequate data quality in the context of the Wilcox project. More detailed aspects of the various QC checks are covered in Worksheet #12, in the Field Work Flow Attachments, and in the attached SOP Package).

- QC to ascertain the **precision of the <u>DU</u> sampling design**
  - Periodic independent triplicate incremental samples within the same DU. Optimally, field triplicate samples will agree within 20% RSD, but replicate precision is acceptable if it is sufficient for the 1-sided 95% UCL to be <200 ppm Pb. This QC is discussed in more detail in Attachment A, Section 3, Items 3 through 7, and in Worksheet #12 in the "Representativeness" section.
  - Corrective action for inadequate DU replicate performance would involve increasing the number of increments per DU incremental sample beyond 30.
- QC to ascertain the **reliability of <u>SU composites</u>** for establishing trends along transects
  - Initially, several sets of side-by-side paired SUs (SU couplets) will be collected, starting in the center and moving outward in the LSA.
    - Optimally, couplets results will be within 30% of the highest value, but the primary determinant of couplet data quality is that they provide consistency in the trend or boundary information provided.
    - Corrective actions for inconsistent couplets include enlarging the SU area and increasing the number of increments per SU.
      - The strategy for implementing these corrective actions to perfect the SU configuration is described in detail in Attachments A (LSA Field Work Flow) and B (EBA Field Work Flow)

- After optimization of the SU configuration, on-going SU QC will take the form of periodic side-by-side couplets. The location and timing of these couplets will be determined by
  - The need for accurate information when making critical decisions (such as at the 200-ppm boundary), and
  - To fill data gaps as indicated by geostatistical modeling.

- QC to ascertain that the **performance of the XRF instrument(s)** used in the project is(are) acceptable
  - Refer to Attachment C for operational performance measures for the TIIB Niton XL3t XRF (S/N 92959); and to Attachment D for the same for the ERT Olympus X-5000 XRF (S/N 202309). These measures include
    - Calibration status for Pb (indicates whether bias could be present in the XRF's Pb results);
    - Instrument limit of detection (LOD) and quantitation limit (QL) for Pb
    - Instrument precision
  - **Pre-field deployment QC** includes (see SOP Package, XRF Procedure 02.1.1)
    - Evaluation of the XRF's calibration status and linearity, i.e., determine any Pb-reporting bias in relation to a series of certified reference materials (CRMs) that evenly span the concentration range of interest
      - Ideally, the calibration curve for an XRF will have a slope of 1.0 ± 0.5 and a y-intercept near 0
      - If an XRF's calibration curve deviates significantly from these ideals, returning the instrument to the manufacturer for recalibration should be considered
    - Determination of instrumental precision for Pb for CRMs with concentrations relevant to project decision-making
    - Determination of instrument's Limit of Detection (LOD) for Pb in CRM materials
  - **On-going performance of the XRF** will be monitored using LCS control charts (see the SOP Package, XRF Procedure 02.1.2)
    - Three concentration levels (low, mid and high) will be chosen from the group of CRMs to use as laboratory control samples (LCSs).
      - The LCS set will be run on each XRF at least 4 times per day (at startup, before and after lunch, and at shutdown), with control charting of the results. Only Pb will be charted.
      - Examples of recent control chart performance for the two XRFs to be used in this project are presented in Attachments C and D.
    - At least twice a day a silica blank (99.995% purity) will be used to monitor the XRF for build-up of dust from samples or air deposition (but will be run more frequently if the unit is deployed outdoors in dusty conditions).

- QC to ensure **the quality of Wilcox sample data generated by XRF**
  - All XRF readings are recorded in a <u>logbook</u> specific to the XRF unit and to the project.
    - This logbook is used to correct any clerical errors (such as mistyped sample IDs) that appear in the raw XRF files or in the samples' RTeX forms.
    - Verification of XRF data after field deployment is complete will involve reconciliation between the 3 data records (logbook, raw XRF output, and sample RTeX forms)

    - Completed logbooks will be scanned into pdf format for distribution to relevant parties and permanent storage as part of the Wilcox project's documentation.
- Generating XRF Pb results on individual samples will involve taking multiple readings over the sample bag and entering each reading in a real-time Excel XRF (RTeX) form (a statistical calculation sheet, see SOP Package, XRF Procedure 01.3)
    - The within-sample statistical variability (measured as relative standard deviation, RSD) for a sample with particle size <2 mm (i.e., sieved through a 10-mesh sieve) is acceptable if
        - The 95% t-UCL/LCL below/above the screening threshold, and/or
        - The precision of multiple bag readings is <30% RSD
    - If the sample bag's data variability does not meet performance expectations, potential corrective actions include
        - Taking additional readings to enlarge the per-bag data set, and/or
        - Remixing the sample bag and reanalyzing it
    - The RTeX forms are retained as a permanent record of all XRF sample readings
- Ensure that the plastic bags used as XRF "read bags" are free from significant interference for the target analyte
    - Use the Bag-Checker Tool to statistically compare CRM readings with and without 1 layer of plastic bag material (see SOP Package, XRF Procedure 02.1.3)
- XRF analyst proficiency is monitored with duplicate sample analysis
    - A previously analyzed sample bag is reanalyzed as if it were a new sample
        - The duplicate analysis is entered into the designated block in the sample's RTeX form so that a t-test is automatically performed to determine whether the 2 sets of sample results are equivalent.
        - If the calculated p-value from the RTeX's t-test is <0.05, the 2 sets of readings do not agree.
    - If disagreement is found, the sample must be remixed and analyzed a third time to determine the correct bag concentration.
    - Data records will be corrected if the initial analysis was inaccurate.
- Monitor for site- or sample-specific matrix interferences affecting the XRF readings
    - Instrument "noise" (i.e., pure analytical precision) can be measured through replicate readings taken in the same spot on the bag (i.e., repeated readings taken without moving the XRF window)
        - This QC check is performed periodically during the day on samples selected randomly, or if applicable, due to unusual behavior or appearance
        - The results are recorded in the sample's RTeX form
        - The results are used in calculations that partition sources of data variability (see the end of Worksheet #12)
    - The instrument-reported "noise" will also be monitored in the form of the sample-specific Limit of Detection (LOD), which is calculated automatically in the RTeX form
        - A sample LOD that is significantly higher than expected will trigger closer visual examination of the sample (color, particle characteristics) and possibly further testing of that sample
            - ✓ The sample may be remixed and reanalyzed by XRF

- ✓ The XRF spectrum for that sample may be compared to spectra from other site samples not showing elevated LODs to see if peak distortion can be observed
- ✓ The sample may be sent to a laboratory for further analysis, if warranted, to determine whether XRF-specific matrix interferences are present

- **Comparability analysis** to establish a quantitative statistical relationship between the XRF sample data and sample data reported by **a lab method for Pb** (such as ICP) is <u>not anticipated</u> for this project. The reasons for not doing comparability analysis:
  - The usual relationship between XRF and ICP data is that there is reduced recovery of Pb from recalcitrant mineral matrices by ICP digestion procedures. This commonly causes XRF results (which measure total Pb) to be higher than corresponding ICP results (which measure solubilizable Pb).
  - Because the Pb was released to the environment in a somewhat soluble form in both the LSA and EBA, it is expected that the XRF and ICP results would be numerically similar, since near 100% solubilization in the ICP's acid digestion could be possible.
  - If not all soil Pb is solubilizable, using XRF results to establish the 200 ppm boundaries will add an element of conservatism to decisions (i.e., erring on the side of caution with regard to risk) as compared to using ICP results, and will reduce the costs and time required for the project.
  - DU samples representing critical decisions will be archived so that ICP, bioavailability or mineralogical analyses can be performed if those tests are later determined to be advantageous.
- **Comparability evaluation** for the **two XRFs** to be used on the project (Figures 11-5 and 11-6) shows that they produce equivalent data sets, so that the Pb results from the XRF units can be used interchangeably.

Figure 11-5(a) Niton XL3t GOLDD Ultra; (b) mounted in stand

The TIIB XRF instrument used for this work will be a Niton XL3t GOLDD Ultra. This is a handheld instrument [Figure 11-5(a)] that will be used in a stand to function in "bench-top" mode [Figure 11-5(b)], although occasionally it may be used in hand-held mode to shoot very large bags, or to "chase" contamination in the EBA.

Figure 11-6. Olympus X-5000

The second XRF is ERT's Olympus X-5000, a portable bench-top model (Figure 11-6). It is anticipated that one XRF will be dedicated to the LSA, and the other to the EBA in order to avoid confusion. However, since it is established that the performance

of the Niton and the Olympus are nearly identical, the reported Pb results are entirely comparable no matter which instrument analyzes samples.

- The factors examined to draw the conclusion of direct instrument comparability for Pb are provided in Attachments C and D, and are summarized below:
  - Niton and Olympus calibration parameters are nearly the same:
    - Calibration regression slopes are 0.977 and 0.983, respectively
    - Y-intercepts are -3.1 and -4.6 ppm, respectively
    - R^2 are 0.9998 and 0.9996, respectively
  - Niton and Olympus LODs are both below 6 ppm (a longer XRF read time produces a lower LOD, the rule is that a quadrupling of the read time reduces the LOD by half):
    - Niton LOD = 5.5 ppm (30-sec read time)
    - Olympus LOD = 3.3 ppm (240-sec read time)
  - Niton and Olympus instrument/analytical precision are nearly the same despite the difference in the read time:
    - Precision at low Pb concentration (a CRM with 11 ppm Pb concentration)
      - Niton: 8.8% RSD (30-sec read time)
      - Olympus: 11.6% RSD (240-sec read time)
    - Precision at higher Pb concentration (a CRM with 300 ppm Pb concentration)
      - Niton: 1.1% RSD (30-sec read time)
      - Olympus: 1.5% RSD (240-sec read time)
  - The Niton and Olympus control charts for Pb have similar values for the mean, and the ±2 SD and ±3 SD lines (see for control chart graphics for Pb at 3 concentration levels for both instruments in Attachments C and D).

XRF data generated for the Wilcox Oil project will be considered "definitive" when the QC checks described above meet the limits provided in Worksheet #12, "Measurement Performance Criteria".

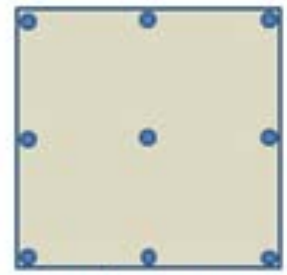
<u>General Soil Sampling Approach to Efficiently Achieve DQOs</u>

Sampling unit (SU) samples will be used to estimate approximate concentrations and trends so that more definitive **decision units (DUs**) can be placed to confirm the tentative 200-ppm boundaries indicated by the SU data. For the purpose of this QAPP, SUs and DUs are defined as follows:

Wilcox Oil Sampling Units

An SU in the Wilcox project is a very small area that is sampled with a 9 to 16 point composite.

- The SU sample result represents the <u>approximate</u> lead concentration at a "point," but the biasing effects of short-scale spatial soil heterogeneity are reduced by the compositing strategy (Figure 11-7).
- The Wilcox SUs are being used to gather spatial information on contaminant patterns and source areas.
  An SU data result is interpreted qualitatively or semi-quantitatively in relation to other SU data…is the concentration of one SU roughly higher, lower, or the same as other SUs around it?
- Linear arrangements of SUs (i.e., transects) will be used to search for the 200-ppm boundary (Figure 11-8).
- Statistical confidence in the SU's concentration estimate is not required.



2 x 2 sq.ft. SU increment configuration

Figure 11-7. SU example

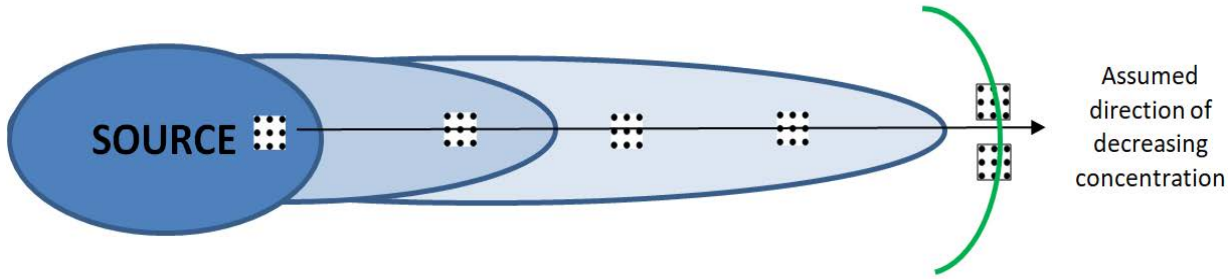


Figure 11-8. Example of an SU transect. Paired SUs (i.e., an SU couplet) will be used to confirm critical decisions, such as the tentative 200-ppm boundary (green arc).

SU couplets will be used as a field QC mechanism to establish and monitor the reliability of trend information provided by the SUs. If the initial SU configuration does not provide consistent information, different SU configurations will be tested at the start of field work until one is found. The SU configuration testing process is described in detail in Attachment A, Section 1, also see the graphical decision tree at the end of Attachment A.

Wilcox Oil Decision Units

A DU is a larger area that is sampled with a composite made of at least 30 increments in order to accurately represent the concentration of a unit volume of soil upon which a removal or exposure decision it to be made. The term for this design is "incremental sampling" or "Incremental Sampling Methodology" (ITRC 2012a).

- The larger area of a DU controls for between-sample heterogeneity at the spatial scale of decision-making. Knowledge of the spatial patterns of contamination within the DU unit volume is not needed.
- For the LSA, DUs are being used to definitively encircle the source area at the 200-ppm Pb boundary.
- For the EBA, DUs are being used to simultaneously 1) quantify Pb concentrations for exposure unit areas of compliant soil around the buildings, and 2) determine the boundaries of any Pb contamination exceeding 200 ppm. (Refer to Attachment B and its graphical decision tree).
    - DUs will be structured such that any small areas with elevated Pb due to piping leakage, spills, etc. will be excluded from DU areas. (Refer to Figure 11-9)
- Statistical confidence in the DUs' concentration results is required to demonstrate compliance with the 200-ppm action level and achieve risk assessment quality data.

Independent triplicate field samples are the field QC mechanism used for incremental sampling of DUs. This involves collecting 3 replicate (i.e., separate) samples of 30 increments each from the same DU (for a total of 90 increments in the DU), as illustrated in Figure 11-10. Triplicate field samples provide a QC measure of field sampling precision that determines whether the number of field increments is sufficient to control for the degree of within-DU field heterogeneity. This precision (i.e., variability) is also used to calculate the statistical upper confidence limit (UCL) that provides a basis for statistical confidence in the decision that a DU's concentration is below a numerical decision threshold.

Workload can be reduced by using a consensus variability term derived from a group of DUs and then the variability value to similar DUs. The consensus variability from replicated DUs is used to calculate a "predicted" UCL for those DUs having only a single incremental sample. In this way, statistical

confidence can be maintained for all DUs, but only a subset require the full effort of triplicate field samples. After the initial group of replicated DUs is done, occasional DUs are sampled with triplicate field samples as on-going QC and to monitor the reliability of the consensus variability value.

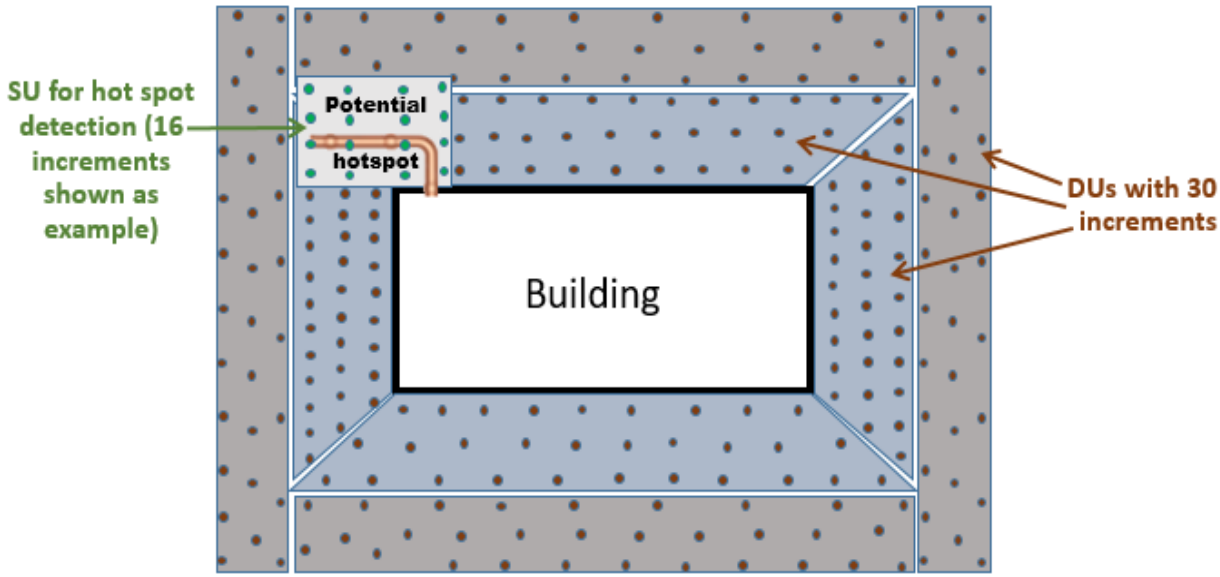


Figure 11-9. Example of DUs surrounding a building to confirm uncontaminated soil. An SU used to test a possible source area (piping) is illustrated in the upper left.

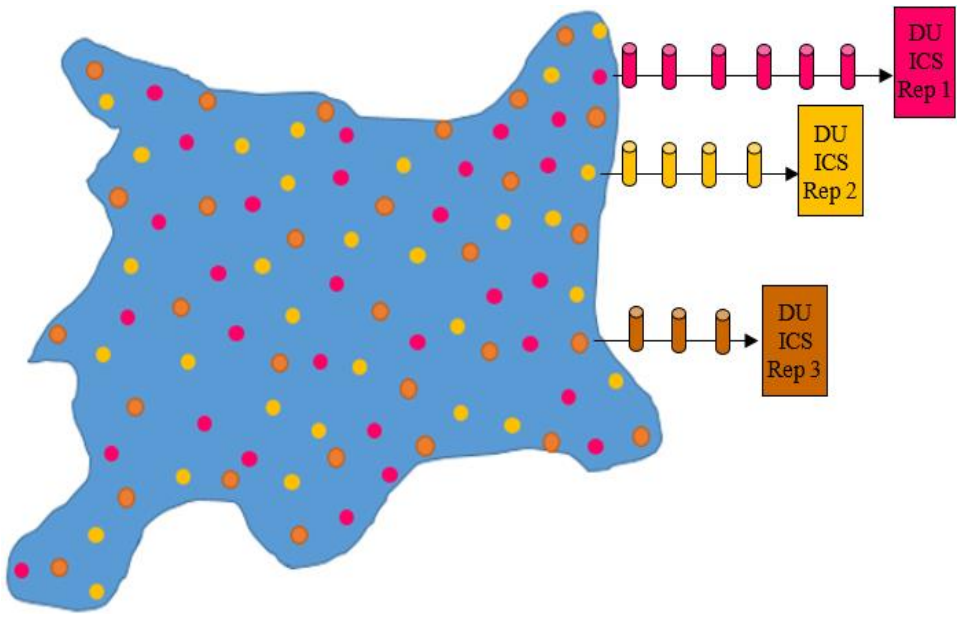


Figure 11-10. Illustration of triplicate field samples collected in a single DU.

Ecological risk assessment could be a use of these data. Different ecological receptors have different sized exposure units, but the Wilcox DUs are being structured primarily to serve compliance and mitigation goals. If individual DUs are too small to represent the exposure units for larger receptors, the

data from several smaller DUs can be combined to produce the mean and UCL for the larger combined area. This combining of DU areas is accomplished with a mathematical approach that is built into a programmed Excel spreadsheet (ITRC, 2017). Although obtaining the mean for the larger area involves simple area-weighting of the means of the individual DUs, simple weighting cannot be used to obtain the UCL for the combined mean. The UCL requires much more complex mathematics which can only be done using the specialized spreadsheet.

Decision Confidence Goals and Hot Spot Evaluation

It is desirable to keep false positive decision errors to a minimum to reduce the amount of compliant soil that is treated or removed from the site and requires disposal. It is desirable to keep false negative decision errors to a minimum to so that off-site Pb transport and receptor exposures are minimized.

- A false positive decision error for the LSA would be deciding that a boundary DU (i.e., the DU bridging the gap between the ends of two transects) exceeds the 200-ppm threshold, when in actuality it does not.
- A false negative decision error for the same would occur if a DU was considered to represent the outer edge of the >200 ppm volume, when in fact the DU's soil concentration exceeded 200 ppm and the outer boundary off the >200 ppm volume had not been identified for that location.
- A false positive decision error for the EBA would be deciding that a DU around the structures exceeds the 200-ppm threshold, when in actuality it does not.
- A false negative decision error would occur for the EBA if SUs missed a significant hot spot.

For the purposes of this project, a significant hot spot in the EBA is any SU with a concentration >200 ppm. Any SU sample or DU with a concentration >200 ppm will be investigated to determine whether there could be an above or underground migration pathway that carries Pb away from the buildings. If needed, Pb migration pathways can be "chased" using *in situ* readings with a handheld XRF.

Error Rate Goals: With the many QC checks built into both the DU/SU sampling designs and the XRF analytical protocols, the false positive and false negative decision error rates for the Wilcox project are expected to be close to zero.

- DUs:
    - The false negative decision error rate for DUs will be held to 5% or less by using the actual (or predicted) 95% UCL based on triplicate field samples within a single DU;
    - The false positive rate is difficult to quantify, but is minimized by using samples that represent the entire area of a decision unit, and by using sufficient increments as documented by the QC measured by the triplicate DU samples.
- SUs:
    - The false negative rate for individual SU samples will be held to 5% or less by using the actual 95% UCL for an SU sample bag, calculated by the RTeX spreadsheet from the replicate readings on each sample bag;
    - Both the false positive and false negative decision error rates for the representativeness of SUs will be controlled by
        - By optimizing the SU configuration and periodic QC (using SU couplet sets) that ensure that geostatistical modeling of SU results is not biased by non-representative SU results.
        - Quantifying the uncertainty in geostatistical modeling: where necessary to maintain 80% confidence in the modeled 200-ppm boundary, additional SUs will be placed at locations to fill data gaps leading to modeling uncertainty.

References for Worksheets 10 and 11

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QAPP Worksheet #12: Measurement Performance Criteria
(UFP-QAPP Manual Section 2.6.2)
(EPA 2106-G-05 Section 2.2.6)

Matrix: Soil
Analytical Group or Method: XRF (Lead)
Matrix Concentration Level: Pb: 10 – 5600 ppm and above, possibly to percent levels

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
XRF Analytical Precision (instrument only) Evaluates instrument stability and repeatability over time under the ambient operating conditions	Replicate instrument measurements: Sample bag not moved between replicate measurements. Precision calculated using the dedicated "Instrument Duplicates Calculator," or the data can be entered into a sample's RTeX form (in data blocks marked for this purpose).	• If the Instrument Duplicates Calculator is used, acceptance is that the 2nd replicate reading be within the 95% confidence interval (CI) of the first reading as described in *Procedure 2.1.1 Assessing Instrument Precision and Bias* will be used for data recording and interpretation. • If the RTeX form is used, there is no built-in calculation of acceptance criteria as in the Instrument Duplicates Calculator, but the %RSD for instrument replicate readings should be significantly less than the %RSD calculated from readings taken over the bag.
Sample Analysis Precision Evaluates analyst performance for proper mixing of sample bags prior to analysis.	A previously analyzed sample bag is reanalyzed anew. This may be done by the same person or by another person who did the first analysis.	• Acceptance criteria are built into the RTeX form with a pre-programmed t-test for a difference between means. The t-test function automatically reports the t-test p-value and whether the duplicate analyses agree at 95% confidence. • If the test fails, both bags should be remixed and reanalyzed. • For this project, the average of the final readings is considered to be the bag sample's concentration.
XRF Instrument Analytical Bias and Linearity	Pre-project: Regression analysis of 6 or more CRMs establish XRF calibration curve to 1400 ppm for Pb.	No systematic bias for XRF results vs. CRM certified Pb value (verifiable by a Wilcoxon Signed Rank paired statistical test). If bias is present, a mathematical correction of the bias might be possible. Demonstrate linearity of calibration curve to 5600 ppm Pb (highest CRM available).
XRF Measurement Precision and Instrument Stability	LCSs (selected Certified Reference Materials in XRF cups with certified values for Pb), analyzed several times/ day & plotted on paper control charts.	A set of 3 Pb LCSs (with low, mid & high concentration levels selected from the CRM set) will be used. Results within control chart limits (±2 standard deviation).

Cross-contamination check	99.995% Silica blank in XRF cup	Pure silica blank should be ND for Pb
Analytical Interferences	Interference (positive or negative bias) due to plastic bag material	No statistical difference indicating significant interference by sample reading bag plastic for any of the analytes of interest (Pb). The significant of interference is assessed using the Bag Checker spreadsheet tool (see *Procedure 2.1.3 Assessing Interference from Plastic Sample Bags*)
Analytical Sensitivity	XRF sample-specific LOD = 3 x the instrument reported standard deviation on each sample reading.	Instrument limits of detections (LODs) for Pb should be at least 20 ppm on CRM matrices. Calibration curve slope should be 1.0 +/- 0.1 for Pb CRMs.
Completeness	Real-time decision-making detects when data are missing or data gaps exist	100% (no missing or lost data). Missing or aberrant sample data will prompt sample reanalysis or recollection.
Field Sample Representativeness	Sample representativeness will be assessed for • SUs: by using side-by-side couplets. After testing and optimization of the SU configuration, periodic SU couplets will be used to double-check ambiguous findings or to resolve uncertainty in geostatistical modeling. • Boundary confirmation DUs: a frequency of at least 20% triplicates overall. Replication will be targeted to control decision uncertainty. The first 2 boundary DUs sampled will automatically get triplicates, and the variability information will be used to establish the Criterion Value described in Attachment A, Section 3, Item 3.	• SU couplet results will optimally be within 30% of the highest value, but the primary quality determinant will be whether the couplets provide consistent information about Pb concentration trend or the 200 ppm boundary. If couplets frequently give contradictory information, further revision of the SU configuration will be considered. • The appropriate SU configuration will be determined at the start of field work in the LSA with one of more rounds of testing. Four sets of 0-6" depth side-by-side SU couplets will be placed to span a high to low concentration range along a transect. All 8 samples will be analyzed and evaluated for information reliability. If any information given by these samples is inconsistent (e.g., one member of the couplet indicates increasing concentration and the other indicates deceasing concentration), the SU configuration will be revised and retested as described in Attachment A, Section 1. • The first 2 to 3 SUs to be collected after SU optimization will be also be couplets to ensure SU reliability, as described in Attachment A, Section 2, Item 1. • If a satisfactory SU configuration cannot be found, potentially all SU samples will need to be collected as couplets to control decision error. • DU field triplicates will optimally agree within 20% RSD. However, if

		they do not, replicate sample precision is still acceptable if it is sufficient for the 95% t-UCL to be < 200 ppm. • The Criterion Value for each single DU result must be <200 ppm
Analytical Sample Representativeness	Particle size will represent the exposure pathway	The exposure pathway evaluation will use data from the <100-mesh (150 micron) particle size per the latest Superfund guidance (EPA, 2016). Goals for analytical precision for Pb over a sample bag is <15%RSD for particle size fractions <60-mesh, and <30%RSD for <10-mesh samples.
Sample Result Uncertainty	Repeated XRF readings over the sample bag controls subsampling error to achieve 95% statistical confidence for the UCL or LCL (as applicable). A programmed Excel worksheet ("the RTeX form") provides the statistical calculation in real-time.	The reported bag result will be accompanied by the 95% statistical confidence interval. The bag conc used may either be the mean or the 95% UCL/LCL, depending on how the data result is to be used. On periodic field replicate samples, the sources of data variability will be partitioned into instrumental analysis, subsampling (within-sample heterogeneity), and field heterogeneity. See RTeX illustration and field heterogeneity equation below this table.
Project Decision Confidence False positive and false negative decision error rates	For DUs: Actual or predicted* 95% UCLs based on DU triplicate incremental samples For SUs: • Actual 95% UCL on the sample bag mean (calculated from replicate XRF readings over the bag) • SU couplet QC shows SUs are providing reliable information • Geostatistical modeling uncertainty quantitation *See Attachment 1, Section 3, Item 3.	DUs: Maximum of 5% statistical likelihood of decision error achieved by decision-making that requires the 95% DU-UCL must be <200 ppm Pb, or step-out to a new DU. SUs: An SU sample with a UCL >200 ppm is considered to exceed 200 ppm even if the bag mean is <200 ppm. The process of optimizing the SU configuration is described in Attachment A, Section 1. SU couplet QC is described in Attachment A, Section 2, Items 1 and 4. Achievement of >80% confidence in the geostatistical modeling of the 200-ppm iso-concentration line is accomplished by placing additional SUs or SU couplets to fill data gaps in locations indicated by the model.

Illustration of RTeX form (real-time statistical calculator & QC tool for XRF)

Project: Colorado Smelter, Community sampling; DMA

Property ID: FY1504

<60-mesh particle fraction read

Operator: D. Crumbling

Date: 18-May-2015

This sheet records XRF concentration results for DU bag

Read Bag lot = PO262010

As mean	As UCL	As %RSD	Pb me	Pb UCL	Pb %RSD
14.0	17.3	24.8	45.0	49.1	9.7

DU or Bag ID: S1504-FY-1218-01 **Element: As**

Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrumt Result (ppm)	Instrumt Error (as 1 Std Dev)	Note?
Sample or Location ID =						
Replicate reading 1	1323	239	30	11.57	2.35	
2	1328	240	30	11.96	2.31	
3	1331	241	30	15.10	2.34	
4	1336	242	30	19.61	2.36	
5 (optional)	1340	243	30	11.68	2.46	
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	14.0		
			SD	3.47	**Tot %RSD**	24.8
			n =	5		
		ProUCL distribution =				
	2-sided	Smple 95% t-LCL =		9.7		
	2-sided	Smple 95% t-UCL =		18.3		
	1-sided	Smple 95% t-LCL =		10.7		
	1-sided	Smple 95% t-UCL =		17.3		
1-sided Smple 95% Chebyshev LCL =				7.2		
1-sided Smple 95% Chebyshev UCL =				20.7		
subsampling error =		18.15	instrument error =		16.91	as %RSD

DU or Bag ID: S1504-FY-1218-01 **Element: Pb**

Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrumt Result (ppm)	Instrumt Error (as 1 Std Dev)	Note?
Sample or Location ID =						
Replicate reading 1	1323	239	30	45.4	2.96	
2	1328	240	30	44.5	2.89	
3	1331	241	30	46.3	2.89	
4	1336	242	30	38.3	2.82	
5 (optional)	1340	243	30	50.4	3.11	
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	45.0		
			SD	4.35	**Tot %RSD**	9.68
			n =	5		
		ProUCL distribution =				
	2-sided	Bag 95% t-LCL =		39.6		
	2-sided	Bag 95% t-UCL =		50.4		
	1-sided	Bag 95% t-LCL =		40.8		
	1-sided	Bag 95% t-UCL =		49.1		
1-sided Bag 95% Chebyshev LCL =				36.5		
1-sided Bag 95% Chebyshev UCL =				53.5		
subsampling error =		7.15	instrument error =		6.53	as %RSD

Progression of mathematical relationships to partition sources of variability to soil data

Total variability = Field variability + Subsampling variability + Analytical variability

Total variance = Field variance + Subsampling variance + Analytical variance

$$SD_{Total}^2 = SD_{LCS\text{-}instrument}^2 + SD_{analytical\ subsample}^2 + SD_{betw\text{-}IS\ samples}^2$$

$$(\text{Total \%RSD})^2 = (\text{Field \%RSD})^2 + (\text{Subsampling \%RSD})^2 + (\text{Analytical \%RSD})^2$$

$$\text{Field \%RSD} = \text{sqrt}((\text{Total \%RSD})^2 - [(\text{Subsampling \%RSD})^2 + (\text{Analytical \%RSD})^2])$$

Example of an Excel calculator that partitions variability from QC data

Park #1		
STATION_LOCATION	SAMPLE_ID	BaP
Park #1 - LabRep1/FieldRep1	15412000	210
Park #1 - LabRep2	15412008	200
Park #1 - LabRep3	15412009	210
Park #1 - FieldRep2	15412001	200
Park #1 - FieldRep3	15412002	200

BaP for Park #1			
Total Variability (Use Lab Rep1 only)			Relative Variance
Mean	SD	RSD (%)	
203.3	5.8	2.8	8.1
Processing/Subsampling + Analytical Variability			
Mean	SD	RSD (%)	
206.7	5.8	2.8	7.8
Analytical ONLY (from LCSs)			
Mean	SD	%RSD	
101.0	2.0	0.02	0.0004
Sample Processing & Subsampling Variability ONLY, as %RSD			
sqrt(Proc rel.var. - Anal rel.var.)		2.8	
Field Sampling Variability ONLY, as %RSD			
sqrt(Ttl rel.var-(Process+Anal rel.var)		0.51	

Summary	Component SDs	Component RSDs		
Field	1.0	Field only	0.51	%
Processing	5.8	Processing only	2.8	%
Analytical	2.0	Analytical only	0.02	%
		Total RSD	2.8	%

QAPP Worksheet #13: Secondary Data Uses and Limitations
(UFP-QAPP Manual Section 2.7)
(EPA 2106-G-05 Chapter 3: QAPP Elements For Evaluating Existing Data)

Data type	Source	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
Concentrations of metals in soil and the kriged (contoured) iso-concentration maps resulting from that data	ERT Investigation: Lockheed Martin SERAS contract (LMS). 2016. Trip Report: November 30 through December 16, 2015, Wilcox Oil Company Superfund Site. Draft. Work Assignment No. SERAS-277. 15 April Raw XRF Data available in Scribe database Maps and figures in report are based on kriged and contoured data.	The 2015 kriged data for the EBA establishes a preliminary area of interest for further delineation in this study. The 2015 kriged data for the LSA are being used to establish a point of comparison for positioning transects and determining step out distances for SU samples along transects.	*In situ* readings by handheld XRF may not account for small scale heterogeneity of contaminants, and grain size segregation of contaminants. The resulting data variability can produce misleading contour lines. Many samples had extremely high concentrations (% level) and were out of the effective calibration range of the instrument. Kriged and contoured data is an interpolation of concentrations between sample points and does not necessarily represent actual concentrations. There were few low concentration samples to define the 200 ppm boundary.
Screening sample locations and site features	SERAS Investigation Report (referenced above)	Selection of sample locations to establish Pb concentrations in soils.	GPS accuracy and precision; registration of air photos and changes in site features. Identifying and re-occupying previous sample locations and the 200 ppm contour intervals will be approximate.

QAPP Worksheet #14/16: Project Tasks & Schedule
(UFP-QAPP Manual Section 2.8.2)
(EPA 2106-G-05 Section 2.2.4)

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
XRF Instrument Evaluation Period	EPA TIIB	N/A	Was completed as part of prior XRF field projects	Performance summary	Summary provided in Worksheet #11 of this QAPP
XRF QC control charts and RTeXs	EPA TIIB	August 4, 2017	August 11, 2017	Updated Control Charts for Pb if needed; RTeX template adapted to Wilcox project needs	Sampling Start date **October 23, 2017**
Mobilization	EA TIIB, ICF, ERT	October 16, 2017 or earlier	One week prior to field event start date October 23, 2017	Equipment Checklists, Supplies (sent to hotel/site)	Upon completion
Sample collection-soils	ICF, ERT,	Sampling Start date October 23, 2017	est. November 11, 2017 (18 field days)	Field notes	1 week after demobilization
Sample analysis-soils	Sample Prep and Analysis Lead, Technical Lead	est. October 24, 2017	est. November 10, 2017 (18 days)	Raw RTeX spreadsheets, scanned log books, raw XRF download files	1 week after demobilization; post to shared FTP site
Geostatistical modeling of SU data	ICF	est. several days into field work starts	final day of field mobilization	Real-time electronic kriged maps of SU data to guide further sampling of the LSA and EBA	Final maps due 4 weeks after demobilization for inclusion in summary report.
Verification	EPA TIIB	1 week after demobilization	2 weeks after demobilization est. October 20 2017	Reconciled RTeX sheets; clerical corrections in XRF downloads;	3 weeks after demobilization (December 4, 2017)
Usability assessment	Project Team	October 2017	November 2017	Summary of XRF & sampling QC performance	Summary included in Draft Report
Summarize data	TIIB with support from ICF	TBD	TBD	Draft Report	December 2017 (est)

QAPP Worksheet #15: Project Action Limits and Laboratory-Specific Detection/Quantitation Limits
(UFP-QAPP Manual Section 2.6.2.3 and Figure 15)
(EPA 2106-G-05 Section 2.2.6)

Matrix: Soil
Analytical Method: Niton XRF
Concentration level (if applicable): variable from 10 ppm to over 100,000 ppm

Analyte	**CAS Number**	**Project Action Limit (i.e. Decision Criteria) (ppm)**	**Project-Required Quantitation Limit (ppm) (1/5 of decision threshold)**	**Achievable XRF Limits**	
				Instrument LOD (ppm)	**Quant Limit** (defined as the lowest conc where instrument precision is +/- 10%
Lead	7439-92-1	200	40	5.5 (with 30-sec read time)	~10 ppm (with 30-sec read time)

Matrix: Soil
Analytical Method: Olympus XRF
Concentration level (if applicable): variable from 10 ppm to over 100,000 ppm

Analyte	**CAS Number**	**Project Action Limit (i.e. Decision Criteria) (ppm)**	**Project-Required Quantitation Limit (ppm) (1/5 of decision threshold)**	**Achievable XRF Limits**	
				Instrument LOD (ppm)	**Quant Limit** (defined as the lowest conc where instrument precision is +/- 10%
Lead	7439-92-1	200	40	3.3 (with 240-sec read time)	14 (with 240-sec read time)

QAPP Worksheet #17: Sampling Design and Rationale
(UFP-QAPP Manual Section 3.1.1)
(EPA 2106-G-05 Section 2.3.1)

The release mechanism and characteristics of the contaminants are different for the EBA and LSA so different approaches will be used. Two exposure zones (0 to 6 inches for human health and 0 to 24 inch for ecological) will be addressed in each sampling rationale.

This sampling design employs two types of field composites: composites collected to represent sampling units (SUs), and incremental samples that represent decision units (DUs). Generically, an SU is any volume of soil represented by a sample. By definition, a DU is also an SU. However, a DU is a special type of SU (see text box below). So, although all DUs are SUs, not all SUs are DUs. In this QAPP, SUs are defined for the narrow purpose of gathering spatial information about concentration patterns and trends. DUs will provide confirmation of the patterns suggested by SUs. Since SUs and DUs have different purposes, they will have different numbers of increments and encompass different soil volumes (see text boxes).

> In this QAPP, a **Sampling Unit** is a mass or volume of soil for which the goal is to obtain information about the spatial distribution of contaminants (primarily trend information). These SUs will employ smaller volumes and fewer increments than the DUs because the SU soil concentration need only be approximated. SUs used in this project will be comprised of 9 to 16 increments collected from a 4-to16-square foot area for a specific depth interval.

All samples will be collected using a device (such as a corer) that includes the 0-6” depth interval. Not all sample collections will include the 6-24” subsurface interval. The decision to collect the subsurface interval will be made on-site based on the levels of Pb found in that interval, and the degree of uncertainty in drawing the boundary line and determining exposure point concentrations.

Since these are incremental samples, the bottom 18 inches (representing the 6-24” depth interval) and the top 6 inches (representing the 0-6” depth interval) of all cores from a single DU or SU will be gathered into two separate plastic storage bags. One storage bag will contain all the increments for the 0-6” depth interval, and the other will contain all the increments for the 6-24” interval.

Worksheet #17 supplies a general overview of the sampling strategy to be deployed for the lead-contaminated areas found by the 2015 ERT field efforts, namely the Lead Sweetening Area (LSA) and the Ethyl Blending Area (EBA). The detailed designs for sampling each area is covered in Attachment A (LSA Field Work Flow with decision tree graphic) and Attachment B (EBA Field Work Flow with decision tree graphic).

> A **Decision Unit** is the smallest volume of soil for which a distinct risk, cleanup or compliance decision will be. Since an accurate estimate of DU concentration is needed, DUs are sampled using a default of 30 increments. In addition, independent replicate field samples are used to provide QC and statistical confidence in the DU concentration estimate. In this study, DUs are used to confirm the 200-ppm boundary suggested by SU data, and to provide data suitable for risk assessment. A DU will cover a specific depth interval for an area ranging from 1000 to 6000 square feet. If larger DUs are needed for exposure assessment, results from smaller DUs will be combined mathematically to cover a larger area.

Lead Sweetening Area (LSA)

The LSA in known to contain an extremely high lead (Pb) concentration in its center (referred to as the “source”) with concentrations decreasing with distance from the source. The general approach will

be to determine the lateral extent of Pb concentrations >200 ppm, and whether/ where Pb has migrated vertically to the deeper soil interval (the 6 to 24-inch zone).

SU samples that represent the surface and subsurface depth intervals will be collected to determine the spatial pattern of Pb contamination. However, not all subsurface SU samples may be analyzed in those locations where Pb contamination is shown to not have migrated downward. Those samples will be archived for analysis at a later date if needed. If/where there has been downward migration, the cleanup footprint for the 6 – 24" zone will be delineated using 6-24" SU sample data.

Surface soil delineation. Prior to sampling, the approximate location of the 200 ppm boundary modeled by the 2015 ERT work will be marked in the field using GPS and flagging. Sampling will start by testing the default SU configuration (2x2 sq.ft. area and 3x3 increment arrangement) on a transect of couplet SUs that begins in the high concentration source area. These side-by-side couplet SUs will be compared for consistency (Figure 17-1).

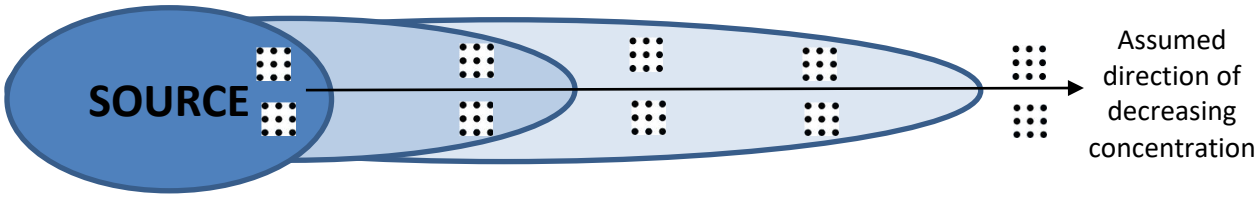


Figure 17-1. Transect to test the adequacy of SU configuration using "Test-SU Couplets"

If the performance of the default SU configuration is inadequate, the configuration will be optimized as described in Section 1 of Attachment A ("LSA Field Work Flow"). The horizontal 200 ppm boundary for surface soils (0 to 6 inches) will be delineated using the optimized SU configuration along radial transects (Figure 17-2). Except for periodic field QC checks, singlet DUs will be used along the delineation transects.

Attachment A (LSA Field Work Flow), Section 2 describes how early SU samples will be used to assess the reliability of the 2015 modeling for predicting the location of the 200-ppm boundary (the pink line in Figure 17-2).

If the 2015 modeling is found to be reliable, transects will be sampled first at the modeled 200-ppm boundary. New SUs will be placed along the transect inward or outward based on the first SU results. When an SU is believed to have found a 200-ppm border, a second SU will be placed 5 to 10 feet from the first to form an SU couplet as a QC check.

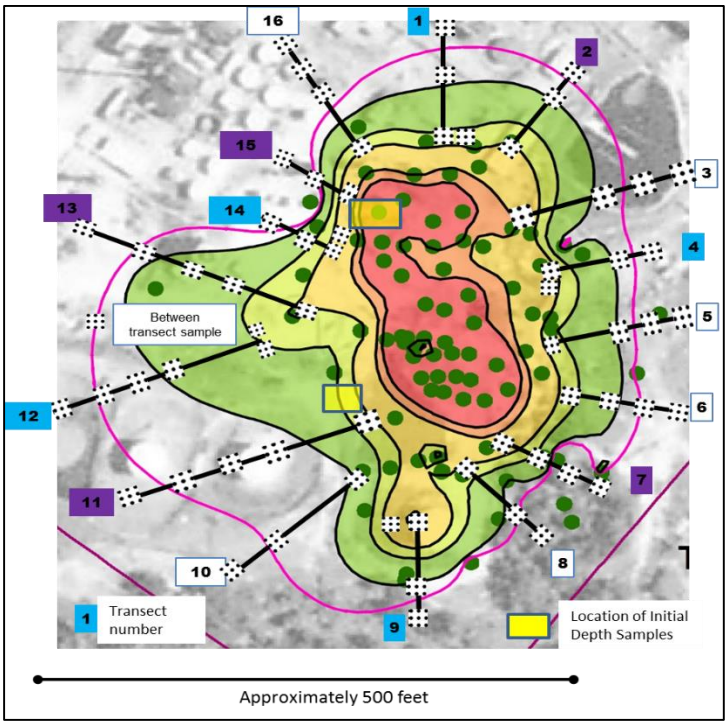


Figure 17-2. Radial transects of SUs in the LSA

If early SUs find that the 2015 modeled concentrations are not reliable, transects will be sampled from the source outward until the 200-ppm boundary is located. Early data will also be used to decide the degree of subsurface sampling needed to provide confidence in removal and risk decisions.

The anticipated maximum number of delineation transects (n = 16) are depicted in Figure 17-2. Real-time geostatistical modeling of SU data (using a contouring/kriging package such as EVS©) will guide actual placement and the number of transects needed to produce confident modeling of the 200-ppm iso-concentration line.

Once transect SUs bracket the tentative 200-ppm boundary on each transect, additional SUs may be placed between transects as needed to improve spatial coverage between transects to reduce modeling uncertainty. The location of the developing 200-ppm line will be flagged in the field.

DUs will then be placed to cover the space between transects, with the inner DU edge approximating the 200-ppm boundary modeled from the SU data (Figure 17-3). DUs will be approximately 10 feet wide.

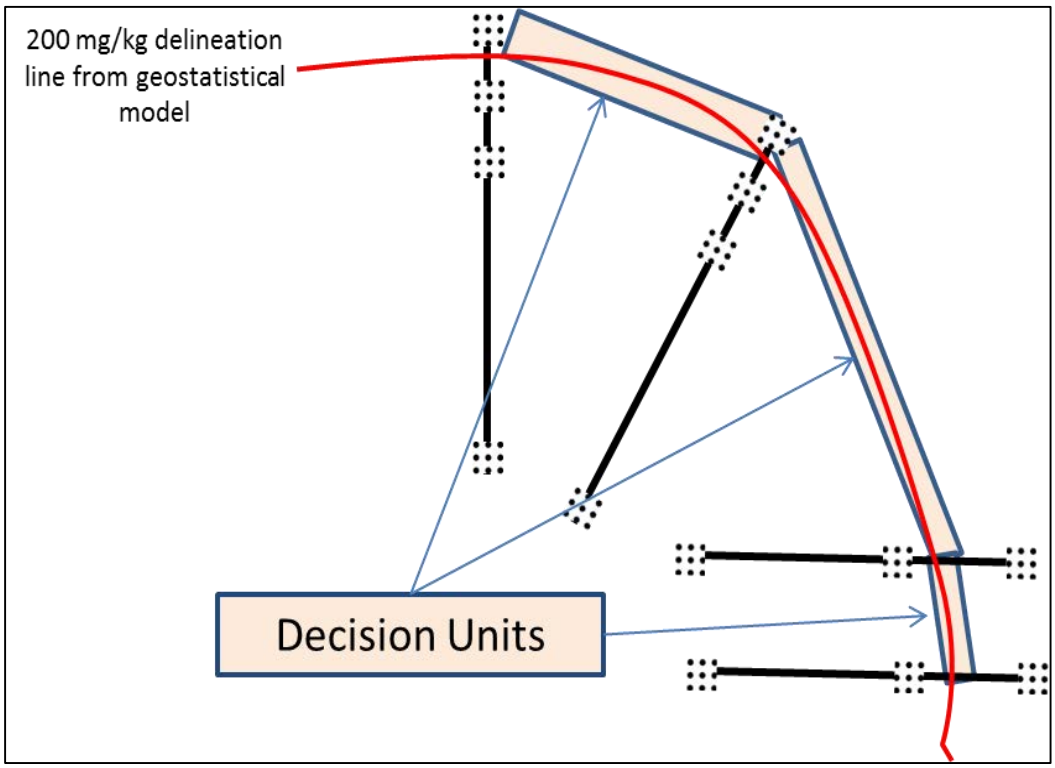


Figure 17-3. Example Decision Units to confirm the modeled 200-ppm boundary

The DU boundary will be considered confirmed when the actual or predicted 95% UCL on the DU mean is <200 ppm. A mathematical mechanism was developed to predict the 95% UCL based on a single DU-IS sample result. This mechanism will reduce the sample collection and processing workload, while ensuring sufficient decision confidence. This mathematical decision strategy to predict a DU's UCL is described in Attachment A, Section 3, Item 3.

Periodic triplicate DU-IS samples will be used as QC and for any DUs for which the conclusion of the predicted UCL is in doubt, as described in Attachment A, Section 3, Item 5.

If a DU fails the 95% UCL, the DU footprint will be moved outward and the new DU sampled, as illustrated in Figure 17-4.

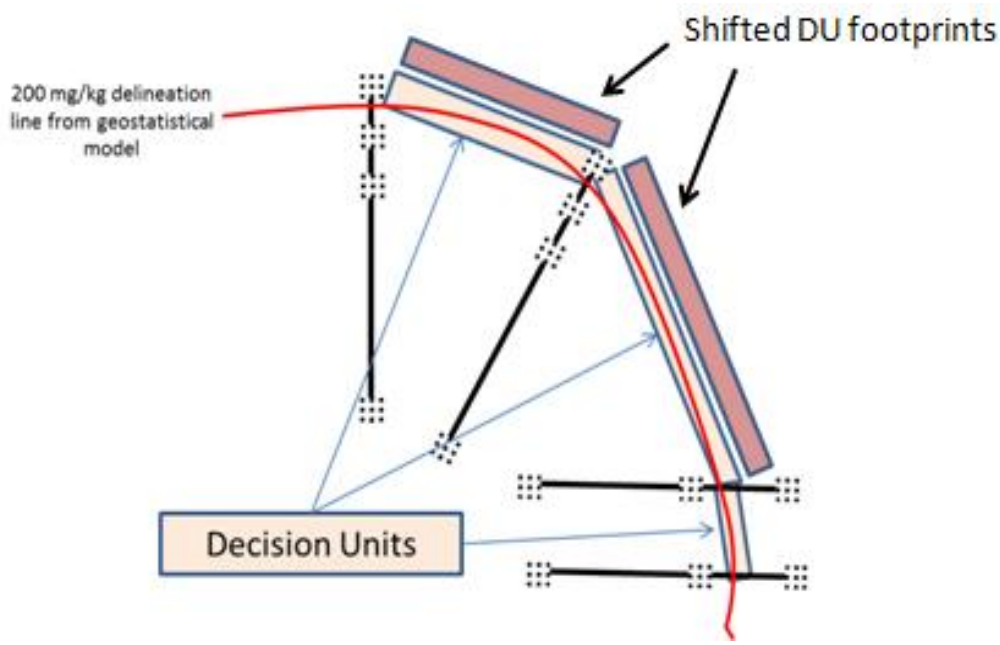


Figure 17-4. New DUs are placed outward if an initial DU's UCL is >200 ppm

Quality control checks will monitor both SU and DU precision during the investigation. These activities and the QC acceptance criteria are discussed in detail in Worksheet #12 ("Measurement Performance Criteria"), in the section for "Field Sample Representativeness."

Ethyl Blending Area

The sampling design reflects the limited knowledge and data regarding the history, source and existing conditions at this area. This approach assumes that the two buildings and their immediate proximity is the most likely source area, and concentrations decrease away from the source. However, we recognize that the ERT contour map (Figure 17-5) is based

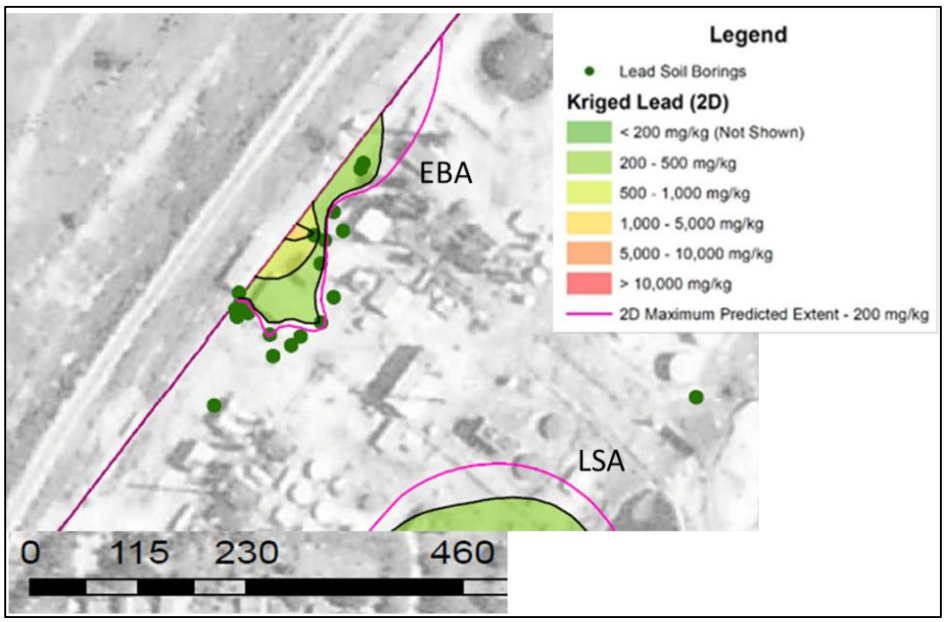


Figure 17-5. ERT 2015 contour map of Pb concentrations in the EBA

on a limited number of samples, only one of which suggests a high concentration away from the rear of the building (to the northwest).

Determination of Potential Source Areas in the EBA. The sampling strategy for determining if any significant areas are present that have lead concentrations greater than 200 ppm will begin with a visual evaluation of existing conditions for indications of potential release mechanisms. Potential source areas (PSAs) could include material storage areas, product transfer points (such as piping or valves), release areas adjacent to doors, and any stained or distressed areas near the building. The hand-held XRF may be used in *in situ* mode to test the soil surface for contamination in these areas as a means to

- test and evolve elements of the EBA's conceptual site model,
- assess the potential EBA sampling workload, and
- refine the EBA sampling strategy.

However, all PSA locations testing negative by *in situ* XRF must still be sampled with sampling units (SUs) encompassing the two depth intervals. If the lead concentration of any SU sample in a PSA location exceeds 200 ppm (as estimated by the 95% t-UCL on the SU sample's bag mean), additional SUs will be collected around it to ascertain the extent and patterns of concentrations greater than 200 ppm in that vicinity.

An area of soil with Pb concentrations >200 ppm will be considered significant if

- the volume of soil exceeding the 200-ppm Pb threshold is larger than 4 sq.ft. in either the 0-6" or 6-24" depth interval, and it has a Pb concentration greater than 400 ppm, or
- there is more than 1 SU along the side of a structure that has a concentration >200 ppm, or
- the RPM judges it significant using professional judgment.

Attachment B (EBA Field Work Flow) contains details for how the EBA investigation should progress. In general, if SU samples find that large areas of contamination >200 ppm exists in both depth intervals, 30-increment DUs (at both depth intervals) will be placed just outside the SU-identified area to confirm the 200 ppm cleanup boundary. If contamination only occurs in the surface interval, 30-point DU samples will only encompass that interval. If all SU samples show Pb levels <200 ppm, the entire side of the building will be bordered by a 10-ft wide, 30-increment DU (3 rows of 10) sampled at the 2 depth intervals and with triplicate DU-ISs. No matter what the outcome, the project manager will be supplied with exposure point concentrations for the 0-6" interval and the 0-24" interval. If applicable, a cleanup footprint and estimated cleanup volume will be supplied.

Sampling inside the east building. During field reconnaissance the field team observed that the eastern building appeared to have a dirt floor. At least one DU will be developed inside the building to sample each depth interval (0 to 6 inch and 6 to 24 inch).

Evaluation of North-South trend. The SERAS investigation data were used to develop a concentration contour map that shows an elevated area of contamination. This area will be investigated with a string of exploratory (0-6 inch depth) SUs to determine whether the elevated in situ shots recorded by the SERAS team represent areas of significant concentration. If areas of significant concentration are found, SU samples at both depth intervals of interest will be collected. If necessary, a contaminated area will be bounded by DUs to establish a 200-ppm perimeter. Step-out DUs will be used if necessary.

All samples will be processed per XRF Procedure 1.2 (see SOP Package). SU samples are sieved to 10-mesh prior to XRF analysis. DU samples may initially be sieved and analyzed at 10-mesh for exploratory purposes, but all final DU data are produced from the <100-mesh fraction. (See also Attachment B, EBA Field Work Flow).

QAPP Worksheet #18: Sampling Locations and Methods
(UFP-QAPP Manual Section 3.1.1 and 3.1.2)
(EPA 2106-G-05 Section 2.3.1 and 2.3.2)

Details of how the sampling locations will be selected are provided in Attachments A and B (the field work flow plans). The table below provides a summary of sample characteristics.

Sampling Location / ID Number	Matrix	Depth (inches bgs)	Analytical Group	Number of Samples**	Sampling SOP References	Comments
Lead Sweetening Area*	Soil	0 to 6 inches	Pb	Minimum: 30 Maximum: 60	TIIB Sample Collection 1.6 (under development)	Approximately 40 samples will be SU (9 to 16 point composites) and 8 - 20 will be DU (30 point composites)
	Soil	6 to 24 inches	Pb	Minimum: 30 Maximum: 60	TIIB Sample Collection 1.6 (under development)	Approximately 40 samples will be SU (9 to 16 point composites) and 0 to 20 will be DU (30 point composites)
Ethyl Blending Area*	Soil	0 to 6 inches	Pb	Minimum: 18 Maximum: 30	TIIB Sample Collection 1.6 (under development)	At a minimum, there will be 12 SU samples (9 to 16 point composites) and 6 30-pt DU-IS samples
	Soil	6 to 24 inches	Pb	Minimum: 18 Maximum: 30	TIIB Sample Collection 1.6 (under development)	At a minimum, there will be 12 SU samples (9 to 16 point composites) and 6 30-pt DU-IS samples

*Sample ID numbers will be assigned at the time of sampling according to the Sample ID strategy outlined in Attachment E. A map showing the approximate sampling locations for the LSA is provided in Worksheet 17, Figure 17-2.
** Because of the adaptive nature of this sampling plan, the exact number of samples cannot be determined prior to mobilization. It will depend on the extent of contamination determined in real-time based on the field laboratory results. Not all samples collected may require sample processing and analysis; however, “superfluous” samples will be retained until project completion in case data gaps are revealed that they can fill.

QAPP Worksheet #19 & 30: Sample Containers, Preservation, and Hold Times
(UFP-QAPP Manual Section 3.1.2.2)

(EPA 2106-G-05 Section 2.3.2)

Laboratory: Analysis conducted in the field at the site with 2 XRF instruments
Back-up Laboratory: None
Sample Delivery Method: Samples will be hand delivered to the analysis team from the field sampling team.

Analyte or Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
XRF Metals (Pb)	Soil	**Sample Prep:** XRF Procedure 1.2 "ISM Sample Processing" **XRF Analysis:** XRF Procedure 1.3 "Taking XRF Readings on Soil in Plastic Bags"	Not Applicable	One gallon size plastic bags for each sample collected in the field (approx. 1-4 kg)[1]	None. Samples are held at room temperature and stored in file boxes when not in use.	2 years	2 years	Real-time XRF data validation includes real-time evaluation of QC data. Final data package requires reconciliation of RTeX forms, logbooks & instrument files to check for clerical errors before study data are considered "validated."
Lab analysis of select samples	Soil	TBD, if RPM decides lab analysis is needed based on the outcome of this field effort.		Information provided in Wilcox Oil Procedure 1.4[2]	None.	2 years	2 years	Variable.

Notes: [1] These are the requirements for samples collected in the field. Samples will be processed, re-weighed and re-bagged in approved plastic bags for the XRF analysis.

[2] If the RPM determines that certain samples should be submitted for comparability analysis (such as ICP or IVBA), information on the collection, processing and containerizing of these laboratory samples is provided in *Wilcox Oil XRF Procedure 1.4. Subsampling and Analysis for Comparability Assessments.*

QAPP Worksheet #20: Field QC Summary
(UFP-QAPP Section 3.1.1 and 3.1.2)
(EPA 2106-G-05 Section 2.3.5)

Matrix	Analyte/ Analytical Group	Field Samples	Field Replicates	Matrix Spikes	Matrix Spike Duplicates	Field Blanks	Equip't Blanks	Trip Blanks	XRF Instrument Blank	XRF LCS controls	XRF Replicate Bag Readings	Total # analyses
Soil	XRF for Pb only	Variable, depending on sample result and decision logic	SUs: 2 side-by-side (couplets) DUs: 3 field DU-IS replicates at selected DUs	0	0	0	0	0	SiO_2 blank run at least 2 times per day	Group of 3 LCSs run & plotted at least 4 times per day	At least 4 readings per bag analysis; more if indicate by bag statistics	Variable, depending on sample result and decision logic

QAPP Worksheet #21: Field SOPs
(UFP-QAPP Manual Section 3.1.2)
(EPA 2106-G-05 Section 2.3.2)

Reference Number	Title, Revision Date and / or Number	Originating Organization	Topic	Modified for Project Work? (Y/N)	Comments
Wilcox Sample Collection Procedure 1.6	Incremental Sample Collection Using a Thin Walled Driven Probe/Corer	USEPA OSRTI TIIB	Collecting incremental composite soil samples up to 24 inches with thin walled tube (core/probe) sampler	No	Procedure is specific to Wilcox Oil: The 24-inch core will be separated into 0-6” and 6-24” segments.
Wilcox Sampling Equipment Decontamination Procedure 1.7	Non-disposable Equipment Decontamination	ICF	Cleaning of core samplers	No	

QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection
(UFP-QAPP Manual Section 3.1.2.4)
(EPA 2106-G-05 Section 2.3.6)

Field Equipment	Calibration Activity	Maint. Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Resp. Person	SOP Reference
Digital balance	Per manual	Per manual	Per manual	Per manual	Daily, if used	Per manual	Per manual	Field Sample Lead / Field Lab Lead	User Manual
Sieve Shaker	NA	Per Manual	NA	Per manual	Per manual	NA	Per manual	Field Lab Lead	User Manual

QAPP Worksheet #23: Project SOPs and Procedures
(UFP-QAPP Manual Section 3.2.1)
(EPA 2106-G-05 Section 2.3.4)

Reference Number	Title, Revision Date, and / or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
Wilcox Oil XRF Procedure 1.1	Operation of the TIIB Niton XL3t GOLDD Ultra (Under Development)	Definitive	Metals	Niton XL3t GOLDD Ultra XRF	USEPA OSRTI TIIB	No
Wilcox Oil XRF Procedure 1.2	ISM-XRF Sample Processing v1.0 April 2017	Definitive	Sample Prep	Not Applicable	USEPA OSRTI TIIB	No
Wilcox Oil Procedure 1.3	Taking XRF Readings on Soil in Plastic Bags v1.0 April 2017	Definitive	XRF Metals	XRF (general)	USEPA OSRTI TIIB	No
Wilcox Oil Procedure 1.7	Non-disposable Equipment Decontamination	N/A	N/A	N/A	N/A	No
Wilcox Oil XRF Procedure 2.0	The Instrument Evaluation Period v1.0 April 2017	Definitive	XRF Metals	XRF (general)	USEPA OSRTI TIIB	No
Wilcox Oil XRF Procedure 2.1	Assessing Instrument Precision and Bias v1.0 April 2017	Definitive	XRF Metals	XRF (general)	USEPA OSRTI TIIB	No
Wilcox Oil XRF Procedure 2.2	Creating and Using XRF Control Charts v1.0April 2017	Definitive	XRF Metals	XRF (general)	USEPA OSRTI TIIB	No
Wilcox Oil XRF Procedure 2.3	Using the XRF Bag Checker and Calculator Tool v1.0 April 2017	Definitive	XRF Metals	XRF (general)	USEPA OSRTI TIIB	No
Wilcox Oil XRF Procedure 2.4	Subsampling and Analysis for Comparability Assessments v1.1 August 2017	Definitive	XRF Metals	XRF (general)	USEPA OSRTI TIIB	No

QAPP Worksheet #24: Analytical Instrument Calibration
(UFP-QAPP Manual Section 3.2.2)
(EPA 2106-G-05 Section 2.3.6)

Instrument	Calibration Procedure	Calibration Range	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
Niton XL3t Gold Ultra	Energy calibration check at startup. Concentration calibration status determined prior to project, and is not altered during the project.	Concentration calibration check performed from 11 to 5600 ppm	Energy calibration done each time instrument is started	Calibration check not significantly different from previous check as established by silica blank and LCSs	Troubleshoot instrument if LCSs indicate a change in instrument calibration (see XRF Procedure 02.1.2: Creating and Using XRF Control Charts)	Deana Crumbling	TIIB XRF Procedures 02.1.1 and 02.1.2
Olympus X-5000	As above	As above	As above	As above	As above	Henry Gerard	As above

QAPP Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection
(UFP-QAPP Manual Section 3.2.3)

(EPA 2106-G-05 Section 2.3.6)

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Title/position responsible for corrective action	Reference
Niton XRF (TIIB, S/N 92959)	Clean dust from outside of instrument and stand	Run the 99.995% SiO_2 blank	Detector membrane for dust and tears	Upon receipt of the instrument; and 2 x per day during operation	SiO_2 blank is ND for Pb	Blow dust off membrane; Replace membrane if torn	Deana Crumbling or operator	Thermo Fisher Scientific Niton XL3 XRF User's Guide v. 7-0-1 Nov 2010
Olympus X-5000	As above	As above	As above	As above	As above	As above	Henry Gerard or operator	Olympus manual

QAPP Worksheet #26 & 27: Sample Handling, Custody, and Disposal
(UFP-QAPP Manual Section 3.3)
(EPA 2106-G-05 Section 2.3.3)

Sampling Organization: EPA OSRTI TIIB with ERT and ICF contractor support
Laboratory: On Site Field Laboratory
Method of sample delivery (shipper/carrier): Hand delivered from field team
Number of days from reporting until sample disposal: TBD

Activity	Organization and title or position of person responsible for the activity	SOP reference
Sample labeling	Field Sample Team Leader and designated field team samplers	None. Sample labeling scheme described in Attachment E
Chain-of-custody form completion	Field Sample Team Leader	None.
Packaging	No special packaging is required as samples will be analyzed in the field laboratory.	Not Applicable
Shipping coordination	No shipping is required as samples will be analyzed in the field laboratory.	Not Applicable
Sample receipt, inspection, & log-in	Field Laboratory Team Leader	None for field samples. For processed samples to be analyzed by XRF: *Wilcox Oil XRF Procedure 01.3:* *Taking XRF Readings On Soil In Plastic Bags*
Sample custody and storage	Field Laboratory Team Leader	None. Requirements described in addendum below.
Sample disposal	EPA Region 6, in consultation with OSRTI Project Manager	Some samples will be disposed back to the site. Other samples may be retained for additional analyses at a later time; will be determined in consultation with Region 6.

QAPP Worksheet #28: Analytical Quality Control and Corrective Action
(UFP-QAPP Manual Section 3.4 and Tables 4, 5, and 6)
(EPA 2106-G-05 Section 2.3.5)

Matrix: Soil
Analytical Group: Metals
Analytical Method/SOP: Metals by XRF (see Worksheet #23 for specific Procedures)

Matrix: Soil			**Concentration Level:** Low to High			
Analytical Group: Metals			**Analytical Method/ SOP Reference:**			
QC Procedures	**Frequency / Number**	**Method / SOP QC Acceptance Criteria**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Check XRF Calibration	Every 6 months	Curve consistent with initial curve with good linearity	Send to Manufacturer for servicing and recalibration	Deana Crumbling	Bias & Precision	Linearity up to 5600 ppm; slope (for at least 5 CRMs <1500) = 1.0+/-0.1; intercept = 0 +/- 10; r^2 >0.99
Blank analysis with 99.995% silica	If XRF used outside: before each LCS run (4 X per day) If XRF used inside: 2 x per day	Target analytes are ND	Check blank membrane for dust; check XRF platform for dust.	XRF Analyst	Accuracy/Bias	No cross-contamination; target analyte should be non-detect
Instrument Replicate analysis	Once per day, unless indicated by an unusual matrix	See XRF Procedure 2.1	Evaluate spectrum for sample-specific matrix interference	XRF Analyst	Precision/ Interference	Record in the RTeX form; instrument precision should be similar to other samples
Run Lab Control Samples (LCSs)	4 times per day (AM start up; before lunch, after lunch, and at end of day	Adapted from Westgard Rules for QC acceptance	Check cup membrane for damage or dust	XRF Analyst	Bias & Precision	See XRF Procedure 02.2 (3 concentration levels)
Paper Control Charting of LCSs (Target analytes)	100% - each chart unique to instrument, analyte, CRM, and scan time	See XRF Procedure 02.2	See XRF Procedure 02.2	XRF Analyst	Accuracy/Bias	Readings within +/- 2 SD control limits; Corrective actions as directed in SOP
Read-Bag Interference checks	Once per lot of plastic bags using 3 conc. levels of LCSs	Bag Check Calculator indicates no significant interference	See XRF Procedure 02.3	XRF Analyst	Bias & Precision	Bag Check Calculator indicates no significant interference for target analyte

QAPP Worksheet #29: Project Documents and Records
(UFP-QAPP Manual Section 3.5.1)
(EPA 2106-G-05 Section 2.2.8)

Sample Collection and Field Records			
Record	**Generation**	**Verification**	**Storage location/archival**
Field logbook or data collection sheets	Field Sample Team Leader	TIIB Project Manager	TIIB Project File
Photo documentation	Field Sample Team Leader	TIIB Project Manager	ICF Project File
Daily quality control reports	Field Sample Team Leader	TIIB Project Manager	TIIB Project File
Chain of custody	Field Sample Team Leader	TIIB Project Manager	TIIB Project File
XRF Analysis Documents and Records			
XRF-RTeX (sample analysis) forms	XRF Analyst or clerical assistant	Field Lab Team Leader	Long term XRF data storage on CD ROM @ TIIB
XRF instrument data files (.ndt files)	XRF Analyst	Field Lab Team Leader	Long term XRF data storage on CD ROM @ TIIB
Original XRF data downloads (Excel files)	XRF Analyst	Field Lab Team Leader	Long term XRF data storage on CD ROM @ TIIB
Logbooks	XRF Analyst	Field Lab Team Leader	TIIB Project File
Sample preparation logs (weights, dry times)	Sample Prep Staff	Field Lab Team Leader	TIIB Project File
Sample storage report	Field Lab Team Leader	TIIB Project Manager	TIIB Project File
Project and Data Assessment Documents and Records			
Field and lab audit checklists	Field Lab Team Leader	TIIB Project Manager	TIIB Project File
Corrective action forms	Field Lab Team Leader	TIIB Project Manager	TIIB Project File
Project Reports and Interim Work Products			
Data reduction and visualization work-products (e.g., ProUCL, Surfer, analysis)	All	TIIB Project Manager or Technical Lead	TIIB Project File
Meeting notes and collaborative work products/tools	All	TIIB Project Manager	TIIB Project File
Project reports	All	TIIB Project Manager	TIIB Project File

XRF-RTeX form = XRF Real-Time Excel = the Excel spreadsheet form used to evaluate & run statistics on XRF data from samples in real-time.
TIIB Project File may include upload to ftp or EPA SharePoint sites

QAPP Worksheet #31, 32, and 33
Planned Project Assessments Table

Assessments:

Assessment Type	Responsible Party & Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable due date
Readiness Review	EPA TIIB (Matt Jefferson) or designee	One assessment two weeks prior to mobilization	September 2017 (TBD)	Readiness Review Memorandum and Checklist (ICF)	24 hours following assessment
Field Sampling Surveillance	EPA TIIB (Matt Jefferson) or designee	One each on first day of sampling area for SU and DU sampling	September 2017 (TBD)	Notes and Team Debrief	24 hours following assessment
Soil Preparation Surveillance	EPA TIIB (Matt Jefferson) or designee	Once for each sampling area	September 2017 (TBD)	Notes and Team Debrief	24 hours following assessment
XRF Analysis Surveillance	EPA TIIB (Matt Jefferson) or designee	Once at beginning of project	September 2017 (TBD)	Notes and Team Debrief	24 hours following assessment

Assessment Response and Corrective Action:

Assessment Type	Responsibility for responding to assessment findings	Assessment Response Documentation	Timeframe for Response	Responsibility for Implementing Corrective Action	Responsible for monitoring Corrective Action implementation
Readiness Review	Field Sample Team Leader	Readiness Review Corrective Action Response	24 hours from receipt of Readiness Review Memorandum	As directed by PM	EPA TIIB (Matt Jefferson)
Field Sampling TSA	Field Sample Team Leader	Field Sampling Corrective Action Response	24 hours from receipt of Memorandum	Field Task Leader	EPA TIIB (Matt Jefferson)
Soil Preparation Surveillance	Field Lab Team Leader	On-site Analytical Corrective Action Response	24 hours from debrief	Field Lab Team Leader	EPA TIIB (Matt Jefferson)
XRF Analysis Surveillance	Field Lab Team Leader	On-site Analytical Corrective Action Response	24 hours from debrief	Field Lab Team Leader	EPA TIIB (Matt Jefferson)

Note: Any member of the field team may issue a stop work order if safety issues arise. In addition, the EPA project manager will be responsible for any other stop work orders.

QAPP WORKSHEET #34

Data Verification and Validation Inputs

Item	Description	Verification (completeness)	Validation (conformance to specifications)
Planning Documents/Records			
1	Approved QAPP and Field Sampling Plan	X	
2	Contract/Scope of Work	X	
4	Field Sampling SOPs	X	
5	Field Laboratory SOPs	X	
Field Records			
6	Field logbooks	X	X
7	Sample location files (GPS, or other)	X	X
8	Chain-of-Custody Forms	N/A	N/A
9	Sampling diagrams/surveys	X	X
10	Relevant Correspondence	X	X
11	Change orders/deviations	X	X
12	Field surveillance reports	X	X
13	Field corrective action reports	X	X
Sample Prep and XRF Data			
14	Master Sample Log in Sheet - chronology (i.e. dates and times of receipt, preparation, & analysis)	X	X
15	Internal laboratory chain-of-custody, weight/tare/duration sheets for drying, sieve shaker report sheets, sieve fraction weight sheets	X	X
16	Control Charts	X	X
17	Disaggregation Completeness Analysis Sheet	X	X
18	Plastic Bag Checker Analysis	X	X
19	Non-conformance log	X	X
20	XRF Logbooks	X	
21	XRF RTeX forms (sample measurement results and statistics)	X	X

Item	Description	Verification (completeness)	Validation (conformance to specifications)
22	CRM Standards Traceability	X	X
23	XRF Instrument evaluation period records	X	X
24	Raw data download from XRF instruments (Niton .ndt files with spectra & photos; Olympus spectra output; Excel files with numerical instrument output)	X	
25	Corrective action reports	X	X
26	Communication records	X	X

QAPP WORKSHEET #35

Data Verification Procedures

This worksheet documents procedures that will be used to verify project data. Data verification is a completeness check to confirm that all required activities were conducted, all specified records are present, and the contents of the records are complete. Data verification (as defined in the UFP-QAPP Manual, 2005) will be performed for the XRF data by after-project reconciliation of the field log books (sample collection records and XRF logbook), XRF raw data files, and RTeX sample-recording forms to ensure completeness, accuracy and preservation of all data-related records.

Records Reviewed	Requirement Documents	Process Description	Responsible Person, Organization
Field Documentation	QAPP and related Procedures (SOPs)	Verify that records are present and complete for each day of field activities. Verify that all planned samples including field QC samples were collected and that sample collection locations are documented. Verify that meteorological data were provided for each day of field activities. Verify that changes/exceptions are documented and were reported in accordance with requirements. Verify that any required field monitoring was performed and results are documented.	Daily – Field Team Leader (Matt Jefferson) At conclusion of field activities - Project QA Manager (Deana Crumbling)
Chain-of-custody forms	QAPP	None, unless off-site sample analysis requested by RPM	Deana Crumbling
Field Laboratory Data	QAPP	Verify that the field laboratory deliverables contain all records specified in the QAPP. Compare the RTeX forms to verify that results were provided for all collected samples. Review the log book to ensure all QC exceptions are described. Check for evidence that any required notifications were provided to project personnel as specified in the QAPP. Verify that necessary signatures and dates are present.	Project Technical Lead (Deana Crumbling)
Audit Reports, Corrective Action Reports	QAPP	No audits planned.	

QAPP WORKSHEET #36
Data Validation Procedures

This worksheet documents procedures that will be used to validate project data. Data validation is an analyte and sample-specific process for evaluating compliance with contract requirements, methods/SOPs, and Measurement Performance Criteria.

No samples from this study are planned for analysis by a fixed labs or submitted for EPA Standard Methods analysis; therefore, no 3rd party data validation will be performed. If the RPM decides on site to request lab analysis on selected sample(s), the RPM will be responsible for getting those data validated.

Data validation (as defined in the UFP-QAPP Manual, 2005) will be performed for the XRF data by

- pre-project evaluation of the XRF calibration status and performance for the target analyte,
- real-time evaluation of LCS results before and after running samples,
- real-time assessment of sample representativeness by evaluation of field replicates and sample analysis replicates, and
- after field work review/reconciliation of logbooks, RTeX forms and instrument data files.

The Data Usability Assessment described in Worksheet #37 will be applied to the XRF data generated for this project.

3rd Party Data Validator: None

Analytical Group/Method:	NA	NA
Data deliverable requirements:	NA	NA
Analytical specifications:	NA	NA
Measurement performance criteria:	NA	NA
Percent of data packages to be validated:	NA	NA
Percent of raw data reviewed:	NA	NA
Percent of results to be recalculated:	NA	NA
Validation procedure:	NA	NA
Validation code (*see attached table):	NA	NA
Electronic validation program/version:	NA	NA

QAPP WORKSHEET #37

Usability Assessment

This worksheet documents procedures that will be used to perform the data usability assessment. In this project, data usability will be largely assessed in real-time during data collection activities through real-time statistical evaluation of sample data and monitoring of QC checks. Real-time evaluation allows immediate identification of sampling or analytical problems that could affect data usability. A final usability assessment will performed after the field portion of the project is completed using the outputs from data verification and data validation. The final assessment will be described in the project report.

The Key personnel responsible for performing the usability assessment is Deana Crumbling (USEPA) with assistance from ICF support staff. Other project staff will participate in eh data usability assessment during the various project phases including:

- EPA Region 6 Remedial Project Manager – Katrina Higgins-Coltrain
- OSRTI TIIB Project Manager – Matt Jefferson
- Risk Assessor – Phil Turner (EPA Region 6)
- Field Sampling Leader/Geologist- Jim Rice

Summarize the data usability assessment process including statistics, equations, and computer algorithms that will be used to analyze the data:

Step 1	**Review the project's objectives and sampling design** An Adaptive Sampling Plan approach is applied for this investigation to identify the area where soils between the surface and 2 feet contain lead at concentrations greater than 200 ppm. As part of that process sample results, generated in real time, are used to define the approximate location of the 200 ppm boundaries at both sites. Decision Logic Diagrams, provided in the Work Plan, are used to guide the selection of sample locations. Geostatistical analysis using a kriging method to develop and iso-concentration contours (EVS©), is used to define the boundary line.
Step 2	**Review the data verification and data validation outputs** XRF Data • The XRF data generated during field mobilization will be validated as usable via real-time QC activities that include monitoring instrument and operator performance. This will be accomplished by real-time charting of LCS QC and real-time verification that instrument duplicate QC results are acceptable (See the relevant SOPs for more information). If QC results are not acceptable, real-time trouble-shooting and correction of any problems will be performed before data are reported. If necessary, sample data not bounded by in-control LCSs will be rerun after corrective action is successful. o All reported XRF data are required to be bounded by in-control QC results. Thus, no reported XRF data should be rejected at a later time due to QC non-conformance. • During field work, the Field Team supervisor will perform spot-checks to ensure field staff are following XRF operation and XRF data entry procedures. Any observed deviations from procedures will be addressed by the

	field supervisor or designee, and if needed, staff will be retrained. o LCS control charts (these are paper) will be inspected by the supervisor to ensure real-time charting is being performed and control chart documentation is adequate. Completed paper control charts and their accompanying "Notes/Troubleshooting" sheets will be stored in a safe location and scanned into electronic files as soon as possible. o Past and current Instrument Duplicate QC Calculator files will be checked for complete entry information. Completed files (these are electronic Excel files) should be properly stored and backed up. This may involve password protection to avoid accidental changes to a completed file. o Previous and current DU-Bag Concentration Calculators (electronic RTeX Excel spreadsheets) will be inspected to ensure that all required spreadsheet inputs are filled out, and that statistical significance was attained for each final bag sample concentration result. Completed files should be properly stored and backed up. This may involve password protection to avoid accidental changes. o Written entries in field notebooks covering the relevant time periods will be scanned into electronic files that are stored with the relevant, completed spreadsheet files so that meta information is readily accessible.
Step 3	**Verify the assumptions of the selected statistical method** The geostatistical analysis used to generate iso-concentration contours at the LSA uses a kriging methodology and is dependent on the spatial density of data points (field sample locations). The geostatistical analysis will include a qualitative (and if available, quantitative) assessment of spatial coverage to ensure the 200 ppm boundary line is adequately constrained. Real-time assessment of modeling uncertainty will be addressed by placement of additional samples in indicated locations. One assumption that will be tested and assessed during real time data evaluation is that concentration is highest at the source and decreases in a predictable pattern away from the source. Minor deviations from assumptions are not critical to statistical analysis and data interpretation. Overall measurement error will be assessed by measuring the amount of sampling error attributable to soil heterogeneity within a DU by taking three independent replicate (triplicate) DU samples. • It is critical that these field replicates be independent, which means that they are collected as 3 separate, but identical increment collections. The only difference is the increment layout, which must cover the same area, but be offset so that two increments do not fall on the exact same spot. • Ideally, the increments from all 3 field replicates will evenly cover the DU. • Each sample must have the same number of increments, and to the extent possible, the same increment mass. • Overall measurement error is calculated as the %RSD for the 3 replicate field samples. • DU samples having only a single field sample will have their UCLs predicted using a consensus %RSD derived from replicated DUs using the procedure described in Attachment A, Section 3, Item 3.

	Sufficient DUs should be selected for field replication QC so that there is confidence that either 1) all DUs have similar soil heterogeneity, or 2) soil heterogeneity varies with depth and/or by the site soil type. Field heterogeneity (as %RSD) is determined by adding the subsampling and analytical variances together and subtracting that sum from the total variance. The square root of the variance is the standard deviation (SD), which is divided by the DU mean to obtain the RSD. XRF analysis of a sample bag relies on developing a statistically robust measurement of the 95% Upper Confidence Limit (UCL) on the mean concentration of Pb in the sample, based on multiple XRF measurements of the sample. The spreadsheet used for calculation of the 95 UCL applies a well-established statistical test (Student t-test or Chebyshev test) and does not need to be verified. It should be possible to use the Student's t confidence limits, since a normal data distribution is expected for repeated XRF readings on a sieved, non-segregated bag. However, if high within-bag heterogeneity persists after corrective action efforts, it may be necessary to use the Chebyshev UCL and LCL.
Step 4	**Implement the statistical methods** • As described in Step 3 above, the EVS©, geostatistical package will be applied for determination of the initial 200 ppm boundary line at LSA. A qualitative analysis of tolerance can be perfumed by plotting the residuals at sample points. • Evaluate statistical error in DU data and calculate or predict (using the procedure in Attachment A, Section 3, Item 3) the 95% UCL for confirmatory DUs. The ideal tolerance for field triplicates is 20% RSD. If that is exceeded, replicate sample precision is still acceptable if the 95% t-UCL is < 200 ppm. • Analytical error (precision) will be quantified during analysis by using multiple XRF measurement of the sample. The tolerance for uncertainty in analytical measurements varies with particle size. For particle size fractions <60-mesh, the tolerance is 15% RSD. For <10-mesh samples, the tolerance is 30% RSD. When decision-making relies on a single bag concentration (such as decisions based on individual SU results), the 1-sided 95% Students-t UCL will be used as the estimate of the sample bag mean (the bag UCL is calculated in real-time by the RTeX form). Excessive statistical uncertainty in bag decisions due to an elevated UCL will be resolved by increasing the number of XRF readings for the bag, and/or remixing the bag. • Instrument error is provided by the XRF instrument for each reading and can be improved in many cases by using a longer read time, if necessary. It is anticipated that the XRF read time for this project can be reduced to 15-20 sec because of the analyte (Pb), expected concentrations (greater than 100 ppm), and the nature of many of the decisions (semi-quantitative decisions on coarse particle size fractions of SU samples).
Step 5	**Document data usability and draw conclusions** The written deliverable will include a data usability summary report which can be in the form of text and/or a table identifying if the data can be used as intended, considering implications of deviations and corrective actions, based on the aforementioned data quality indicators. Performance of the sampling design and limitations on data use will also be presented. The final deliverable will update the conceptual site model and document conclusions. Permanent data records in the form of RTeX forms, raw XRF output spreadsheet files, QC records and Excel data analysis and calculation files, and field and XRF logbooks will be provided.

Attachment A – LSA Field Work Flow Plan

Meet the night before to tentatively assign next day's field tasks

Anticipated work crews:

- obstacle clearing
- sample collection
- sample processing/XRF analysis
- geostatistical modeling/field communications

Preliminary Stage:

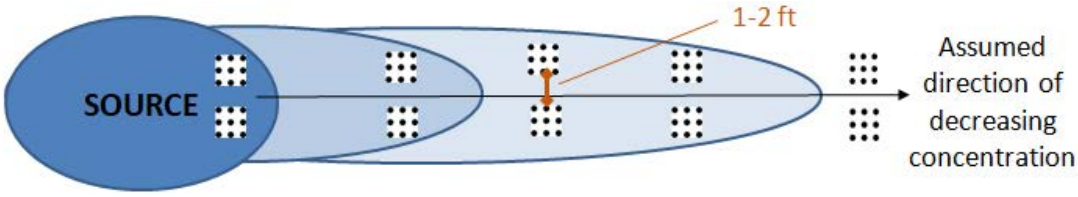
- Flag center 2 highest concentration areas per the "blue ERT kriged map" (concentrations >300K ppm), using ERT's GPS coordinates (see end of this file for the "blue map" figure)
- Flag planned transects (#1 to #16) at ERT's 1000 ppm and the 200-500 ppm line contour lines as given on the "green ERT kriged map" shown in the figure in QAPP Worksheet #17. (see end of this file for the "green map" figure)
    - The 1000 ppm line is the outer edge of the yellow-green concentration band,
    - The 500 ppm line appears to be the outer edge of the green band, and
    - The modeled 200 ppm line is the pink line.

Section 1: SU Stage #1 (SU Testing and Optimization)

The initial test of SU performance (described also in Worksheet #12 in the "Representativeness" section) will use SU side-by-side couplets, each having 9 increments over a 2 x 2 sq.ft. area (in 3 rows of 3) for a 0-6" depth interval only for one of the couplets, and both the 0-6" and 6-24" intervals for the other couplet member (to evaluate the contaminant pattern at depth). Three to four sets of couplets will span a high to low concentration range along an easily accessible transect, as illustrated by the figure below. If SU performance (agreement between the two 0-6" interval samples) is inadequate (refer to Worksheet #12 in the "Representativeness" section), the area will be enlarged and the number of increments will be increased.

Item 1. Transect Line for SU testing

- Choose a transect line that appears to cover the full concentration range while being easily accessible by the field crew.
- Test-SUs are 4 sets of side-by-side couplets (couplets should be 1-2 ft. apart as measured between adjacent sides); collect both the 0-6" and 6-24" intervals for each couplet, and place each interval into a separate bag.



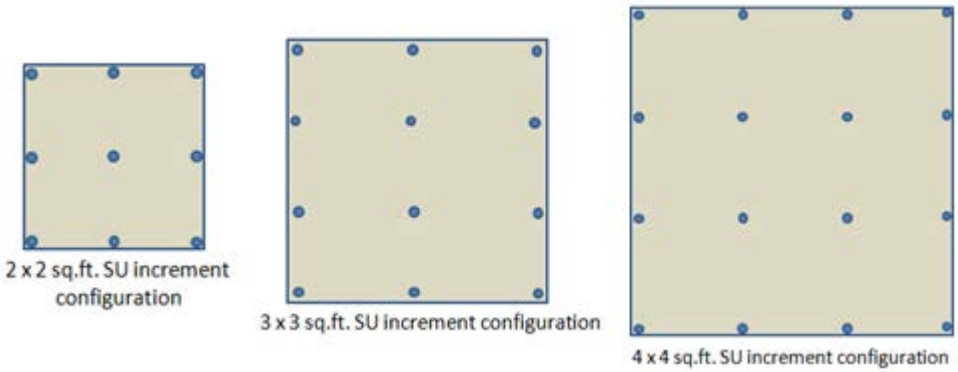
First trial transect using series of nine-point incremental samples (SUs) away from the source to test the reliability of SU configurations

- Place Test-SU Couplet #1 on the innermost SU location of test transect (refer to the "ERT green map" at the end of this file)
    - Examine the soil surface and samples from the innermost SU couplet for crystalline materials that could be Pb compounds
- Test-SU Couplets #2, 3 (and possibly 4) are placed farther out along the test transect.

- The last Test-SU Couplet should be near the pink line (modeled 200 ppm line) on the "green map"
- Test-SU samples should be delivered to the processing/XRF crew.
    - Initially, only the 0-6" interval samples are processed. The 6-24" samples are set aside until later.
    - Disaggregate and sieve 0-6" samples to <10-mesh if needed to remove vegetation or large bits of non-representative material
    - The analytical portion will be placed in a large "read bag"
    - XRF sample readings on the Test-SUs may be taken using a 15-sec XRF read time (unless the concentration is <100 ppm, in which case a 30-sec read time should be used)
    - Use the SU RTeX form for sample bag mean and statistics to control for within-sample heterogeneity
    - XRF analysis of the 0-6" interval samples for all 3 or 4 Test-SU couplets should be completed before judging the adequacy of the SU configuration
        - Using the sample bag mean as the result, is the information provided by the members of couplets consistent for deciding whether a trend exists?
        - If yes, complete analysis of the 6-24" Test-SU samples. Is the trend information consistent in the subsurface samples (i.e., if there is Pb >200 ppm in any subsurface samples, is there a pattern of decreasing concentration with distance from the center of the LSA)?
        - Using the sample bag mean as the result, evaluate the concentration difference between the members of couplets using the Excel SU Couplet Evaluator (see screen shot below):
            - Is the lowest concentration member within 40% of the highest concentration member?
            - Ex. If the highest concentration member is 600 ppm, is the concentration for the lower member of the couplet > 360 ppm?

SU Couplet Evaluator				
SU Identifier	Highest couplet conc	Lowest couplet conc	minus 40% of highest	Is the lowest within 40%?
A	600	450	360	yes
B	400	200	240	no

Item 2. If the 3x3 increment/2x2 ft^2 area configuration for the 0-6" interval is inadequate (indications of concentration trend is inconsistent among any of the 4 couplets or between-couplets), use the degree of inconsistency to decide whether to go to the 3x4 increment/3x3 ft^2 or 4x4 increment/4x4 ft^2 configuration.



- If initial SU performance is <u>markedly</u> inadequate, the SU configuration will be changed to 4 x 4 sq.ft. area and 16 increments (4 rows of 4).

    - If performance is only marginally inadequate, the area will be enlarged to 3 x 3 sq.ft. and 12 increments (3 rows of 4)
- Another 3 to 4 sets of test couplets should be collected using the new configuration to confirm adequate performance.
    - Repeat testing with the new SU configuration along the test transect, but offset slightly from the previous SU sampling locations
    - Evaluate agreement between couplet members as described before
    - Also evaluate the degree of agreement between the first and second SU sets
        - This gives a sense of the degree of short-scale heterogeneity (lateral noise), which influences the ability to reliably detect a concentration trend
- The 6-24" interval samples from an unsuccessful SU configuration can be discarded back to the site.

Section 2: SU Stage #2 (Delineation data collection)

After optimizing the SU configuration, SU sampling along transects will begin near the outer borders identified as being near 200 ppm by the kriged *in situ* XRF Pb results from the 2015 field work (see ERT-produced figures at the end of this file).

Depth consideration

If the Test-SU transect found that subsurface contamination (i.e., Pb >200 ppm in the 6-24" depth interval) was not present (except perhaps at the very highest concentrations in the LSA center), SU sampling at the outer boundary does not need to include the 6-24" interval.

- However, if there is any doubt about where subsurface contamination ends, SU samples should include the deeper interval in locations where there is uncertainty about the presence of subsurface Pb.
- If any subsurface Pb levels >200 ppm are found, the areal extent of the contaminated 6-24" interval must be delineated using SUs and geostatistical modeling.
- Since the 0-6" interval is likely to be much higher than the 6-24" interval, SUs sampled solely to determine the extent of subsurface contamination do not require processing and analysis of the 0-6" interval.

Item 1. If there were only 3 Test-SU couplets performed in Section 1, collect a couplet at the first SU location of the first delineation transect as additional confirmation of the selected configuration.

- If all SU results from the first SU location exceed 200 ppm (as measured by the 95% UCL on the XRF bag analysis), the next SU location will be further out along the transect.
    - The subsequent SUs can be singlets.
- If all SU results from the first location are less than 200 ppm, the next SU will be located further in toward the center of the LSA.
    - The subsequent SUs can be singlets.
- If the SUs are not giving consistent information, another SU configuration should be considered.
- When the putative 200 ppm boundary has been bracketed, place a second SU next to the decisive SU (to make a couplet) to confirm that conclusion
    - This step of confirming a decision indicated by one SU by coupling with a second SU should be performed for >75% of the SU transects.

Item 2. SU singlets will be used along the rest of the transects, except when confirming the final SU of a transect.

- Sieving to 10-mesh will be done as needed:
    - LSA soils that are nearly all sand and finer grain sizes, with no stones or with little aggregated material present, do not need to be sieved since nearly all material would pass through.

- XRF sample readings may be taken using a 15-sec XRF read time (unless the concentration is <100 ppm, in which case a 30-sec read time should be used)

Item 3. Place the 1st SU of subsequent transects on the 200-400 ppm contour line shown in the ERT "green map" (if there is confidence in the contouring accuracy of the map) or place it near the suspected 200 ppm line indicated by on-going data collection.

- Based on the sample results, move inward or outward along the transect to place the next SU. The goal is to have an SU above 200 ppm and at least 1 SU below 200 ppm along each transect.
    - Distance to the next SU placement along a transect will use professional judgment based on the actual SU concentrations found and any pattern developing as data collection moves forward.
    - Inward placement of SUs will stop once there is confidence that concentrations further along the transect will all be >200 ppm Pb.

Item 4. When a group of SU transect data has been completed, provide the data to the geostatistical operator for concentration contour modeling.

- Additional SUs/SU couplets or whole transects may be placed between existing transects to increase spatial coverage where professional judgment finds excessive uncertainty in the geostatistical modeling.

Item 5. When convenient for the sample collection crew, SU samples (both 0-6" and 6-24") should be collected from the two locations flagged as the highest *in situ* concentrations ERT found (refer to the "green map").

- Both the surface and subsurface samples at each of the 2 locations should be examined visually for Pb crystallization
- Both the surface and subsurface samples at each location should be analyzed to evaluate the relationship between surface and subsurface Pb concentrations.
- If the subsurface Pb concentrations are <200 ppm at both high concentration locations, and other subsurface analyses performed to that point also show subsurface concentrations <200 ppm, processing and analysis of other subsurface samples may be put on hold, depending on the consistency of subsurface sample results:
    - The consistency of Pb concentrations in the subsurface samples will be examined to determine whether enough subsurface data is available to determine the Pb concentration in the subsurface interval outside of any subsurface "hot spot" >200 ppm. This information is needed for mathematically combining data from the 0-6" and 6-24" intervals to generate 0-24" interval concentrations for ecological risk assessment purposes.
        - Consistency in Pb concentrations throughout all or most of the subsurface indicates that fewer subsurface samples will require analysis
        - Inconsistent subsurface Pb concentrations will require analysis of more subsurface samples.
        - Again, geostatistical modeling may assist to determine when sufficient data has been generated to support decisions.

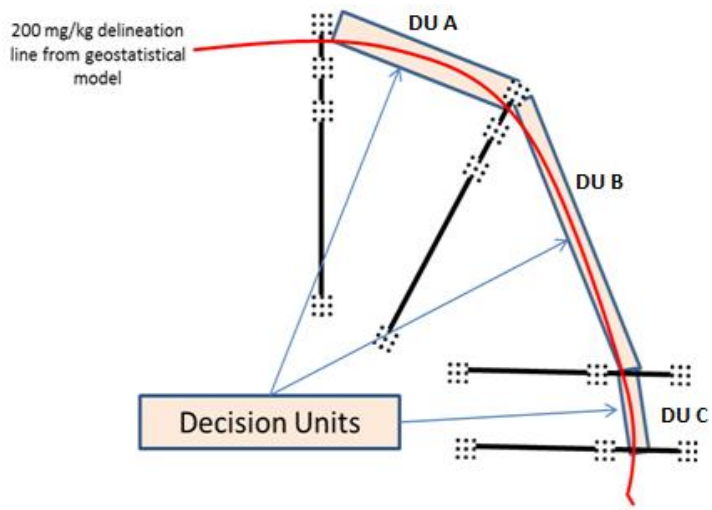
Section 3: DU Stage (Surface boundary confirmation incremental sampling)

The following strategy will significantly reduce the sample collection and XRF workloads by avoiding taking incremental sample replicates on every boundary DU, yet will ensure that false negative decision errors are avoided. The target frequency for triplicate samples in border DUs is 20% (3 DUs at a minimum). The strategy outlined below should ensure that those DUs needing replication in order to limit decision uncertainty will be preferentially selected into those 20%.

<u>Introductory Note</u>: The first reading of the decision-making and work flow process described below may seem complicated, however it is actually straight-forward in implementation.

- The benefit of the following decision-making strategy is the time and labor saved by reducing the number of field samples requiring collection in potentially difficult soil or vegetation conditions, while maintaining a measurably high degree of decision confidence.
- The following mathematical strategy is possible for the following reasons:
    - Highly accurate quantitation of each DU's Pb concentration is not required, since the data need only demonstrate at high confidence that border DUs meet the boundary condition of 200 ppm or less.
    - Therefore, decision uncertainty can be managed through mathematical/statistical mechanisms, which can be performed with just the typing of a few numbers into an Excel calculator, which is much faster and easier than field sample collection and analysis.

<u>Item 1. DU placement:</u> When modeling of the SU data is judged to have produced a sufficiently confident estimate of the 200 ppm contour line, band-shaped DUs (about 10 ft. wide) will be used to confirm the border sections of the surgical cleanup area



- A border confirmation DU may be placed over the 200 ppm contour line bridging transects (as in the figure to the right), or may be positioned with the DU's inner edge on the contour line.
    - The choice of DU position will rest with professional judgment based on the level of confidence in the modeled 200 ppm contour line.
- Border confirmation DUs will have areas ranging between 1000 and 6000 square feet.
- Since a maximum of 16 transects are anticipated, a maximum of 15 border DUs are anticipated.
    - The field QC goal for DU data is to have triplicate replication in at least 20% (1/5th) of the boundary confirmation DUs.
    - Therefore, a minimum of 3 border DUs need triplicate incremental samples (ISs), although it is likely there will be more.
- Border DUs will be sampled with 30 increments per IS.
- Pb concentrations in the subsurface soil this far from the LSA center are anticipated to be consistently well below 200 ppm (as demonstrated the SU data).
    - If this holds true, boundary confirmation DUs will sample only the 0-6" surface soil interval.
    - If this does not hold true, border DUs may require sampling of both the surface (0-6") and subsurface (6-24") intervals.

<u>Item 2. DU sample processing:</u> All final DU decisions are based on the Pb content in the <100-mesh particle fraction. Samples must be sufficiently disaggregated to produce a sufficiently representative <100-mech sample.

- If soil conditions are such that disaggregation is difficult, and if it is found that DU "step-outs" are frequently required, the following procedure can be used to save time and labor:
    - Sieve several DU samples to <10-mesh initially and analyze
    - Re-sieve the samples to <100-mesh and analyze
    - Compare the results for the <10-mesh and <100-mesh particle fractions
        - If the concentration difference between the two fractions is insignificant, or if the concentration of the <10-mesh fraction is greater than that of the <100-mesh fraction, the 10-mesh fraction can be used as an intermediate value until the final DU footprint is achieved

<u>Item 3. DU representativeness QC strategy:</u> This strategy will allow reduction of the sampling workload by using a single DU-IS sample to conservatively estimate the DU concentration for first testing of a border DU. In this way, 95% statistical decision confidence can be maintained without the need for field triplicates for every border DU. The following describes how this QC strategy will operate:

- The initial 2 border DUs will have triplicate 30-point ISs, and for each the following test will be applied:
  - If all 3 IS results are <200 ppm, and the 1-sided 95% t-UCL for those 3 results is <200 ppm, that border DU is acceptable.
  - If any of the 3 IS results are >200 ppm, or the UCL is >200 ppm, that border DU is unacceptable. That DU's footprint will be moved outward and the triplicate sampling process repeated.
- The first 2 acceptable DUs count toward the minimum of 3 replicated DUs for the project.
- Once 2 acceptable border DUs are established, the variability data from these 2 DUs will be used to establish a QC Criterion for each future DU (DU-X). The DU-specific QC Criterion will determine the acceptability of each DU for representing the 200 ppm border for that section of the boundary. The QC Criterion is calculated using the following steps:
  - From the first 2 acceptable DUs, the RSD for each set of triplicates will be calculated, and those 2 RSDs averaged (using the relative variance as the averaging intermediate). In other parts of the QAPP, this value is called a "consensus %RSD" to avoid confusion over what an "average" %RSD is.
    - The Excel formula for the average RSD is =sqrt(sumsq(value1,value2)/2)
- This average ("consensus") RSD will be used to calculate a DU-specific SD that will be used to predict a UCL for any DU having only a single IS collected from it.
  - Letting DU-X IS = DU-X's single IS result, the following is the Excel equation that will be used to calculate the predicted UCL (which will serve as the DU-specific QC Criterion):

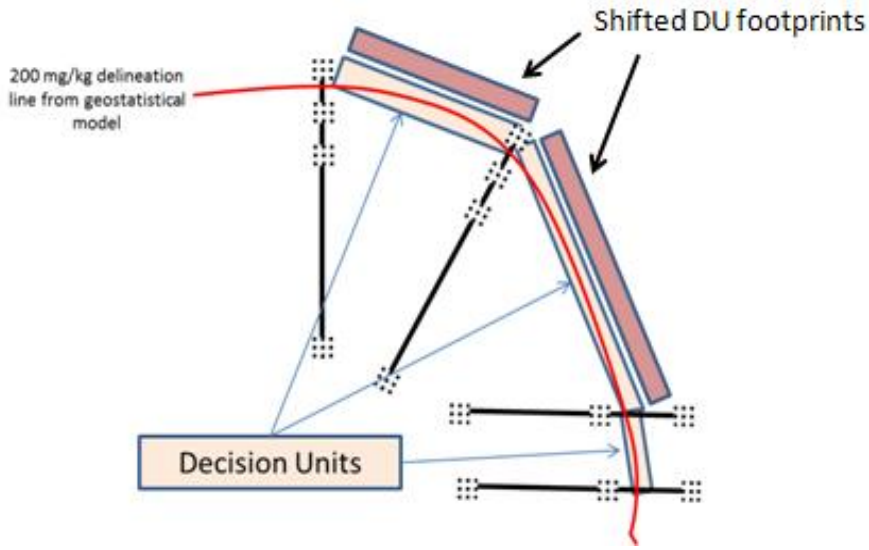
    DU-X QC Criterion = DU-X IS + (TINV(0.1,2)*(DU-X IS*ave RSD)/sqrt(6))

    [Note: The square root of 6 is used because the RSD value was derived from 2 sets of DU-IS triplicates. Although the group of 6 are not truly independent in the context of the sqrt(n) term, it is expected that the 2 DUs will have nearly the same concentration, and the violation of independence will have minimal effect for the intended use of the predicted UCL as a QC acceptance criterion.]

  - Using the QC Criterion is a mechanism to account for within-DU data variability while reducing the sampling workload by using a single DU-IS sample to conservatively estimate the DU concentration.
- An Excel calculator has been set up to assist with all these calculations ("Border DU Criterion calculator"), see the "Calculation of Criterion Value's RSD for Predicting DU UCLs" figure at end of Section 5.

Item 4. A DU with only a single IS result is considered acceptable if its DU QC Criterion value is 200 ppm or less; any DU with an IS result >200 ppm is automatically judged unacceptable.

Item 5. Unacceptable DUs will have a step-out DU placed and sampled, as shown in the figure:



Item 6. If an un-replicated DU has an IS result well below 200 ppm, but the predicted UCL/QC Criterion value is only slightly >200 ppm, 2 additional DU replicates can be collected to see if the actual 95% UCL is less than the predicted. If the actual UCL on the mean is <200 ppm, then that DU is acceptable.

- Extra sampling of a DU may be favored over shifting the DU footprint if difficult field conditions (such as dense shrubby undergrowth and trees) are present in the step-out locations.

Item 7. To meet the overall DU QC frequency stated in Worksheet #12, a total of 3 DUs must be replicated.

- The 3rd DU to be replicated would ideally be chosen from a border segment that has relatively higher uncertainty in the geostatistical modeling.
- If sufficient modeling uncertainty exists, additional DUs should be replicated.
- Confirm that RSDs from the 3rd (or more) replicated DUs are similar to the RSDs from the first 2 border DUs.
    - If the new RSDs are higher than those from the first 2 DUs, recalculate the average RSD and use it to recalculate predicted UCLs for previous un-replicated DUs.
    - If previously acceptable DUs are now unacceptable, either use a step-out DU, or collect 2 additional field replicates and calculate the actual UCL on the DU mean.
    - Use the new RSD for calculating the QC Criterion for future un-replicated DUs.

Item 8. At the end of the DU process, at a minimum there will be a cleanup footprint defined by the 200 ppm boundary as proven by the ring of DU border segments that cover the 0-6" depth.

Section 4: Subsurface delineation

- From indications provided by the 2015 Pb data, it is anticipated that the area of >200 ppm contamination in the 0-6" interval will overlay and extend well beyond that in the 6-24" interval.
- Contamination in the 6-24" interval may be sufficiently delineated by the SUs collected thus far. If not, additional subsurface SUs may be required to complete geostatistical modeling of the 200 ppm boundary in the 6-24" layer.

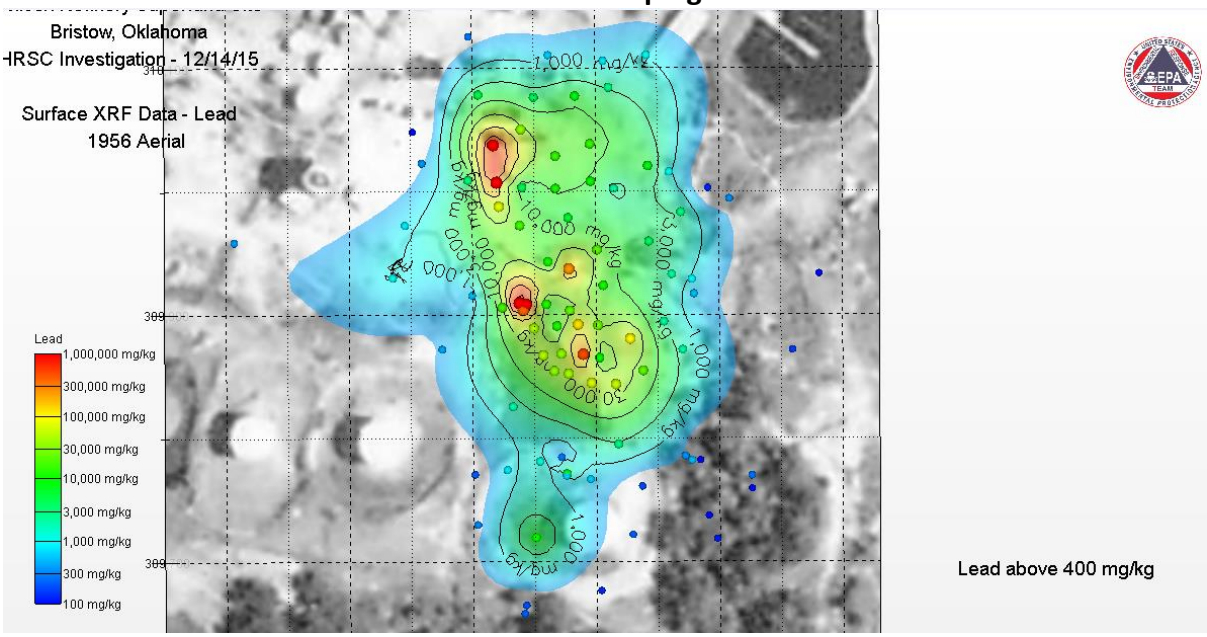
Section 5: LSA wrap-up to produce materials for use by the RPM

- Flag boundaries
- Take sufficient GPS readings and distance measurements to produce accurate maps
- Use GIS or other spatial modeling to generate estimation of the volume of soil with Pb concentrations >200 ppm for the surface and subsurface intervals.
- Where applicable, mathematically combine the 0-6" and 6-24" interval data to produce an exposure point concentration for the 0-24" interval.

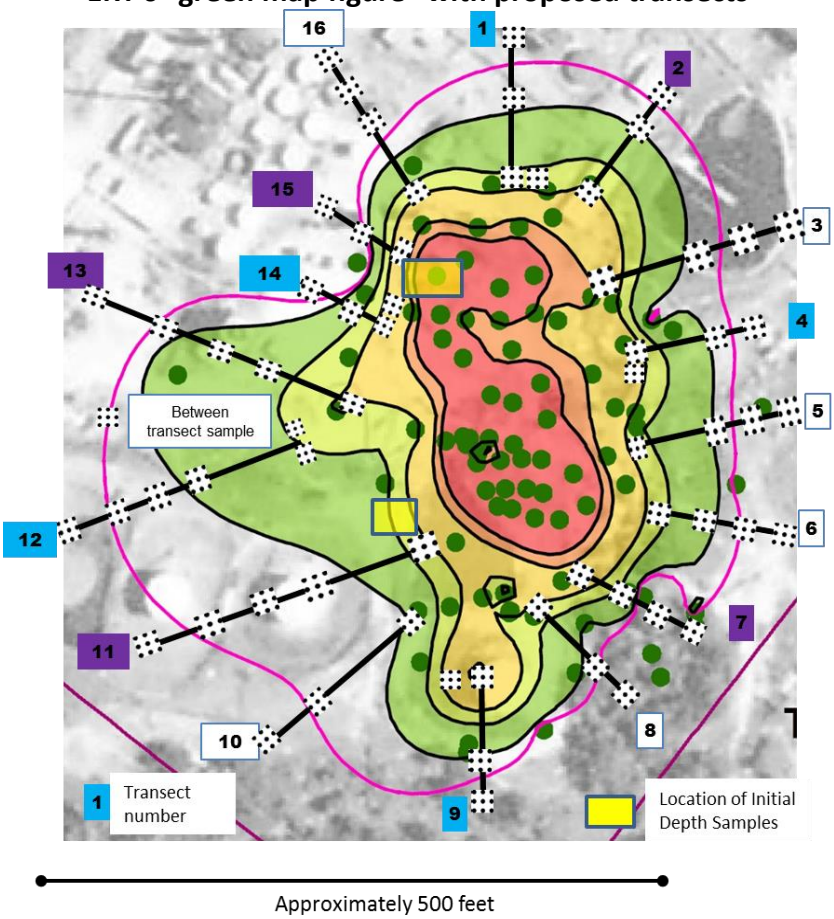
Calculation of Criterion Value's RSD for Predicting DU UCLs

Calculation of Criterion Value's RSD			Criterion Value calculation & record-keeping for each singlet DU-IS			
						DU Co
Enter the following values for DUs A & B:	DU A bag conc	DU B bag conc	Enter the following value for single DUs:	DU ID	DU-IS initial result	Criterion Value	
DU-X-IS-Rep1	150	130		DU C	175	**195.8**	lat
DU-X-IS-Rep2	175	145					long
DU-X-IS-Rep3	180	160		DU D			
DU X's mean conc =	168.3	145.0					
DU X's SD =	16.1	15.0		DU E			
DU X's mean RSD =	0.095	0.103					
DU X's mean %RSD =	9.5%	10.3%		DU F			
DU X's 95% t-UCL =	195.4	170.3					
				DU G			
relative variance for DU X =	0.0091	0.0107					
averaged relative variance for DUs A & B =	0.0099						
average RSD for DUs A & B =	**0.100**						

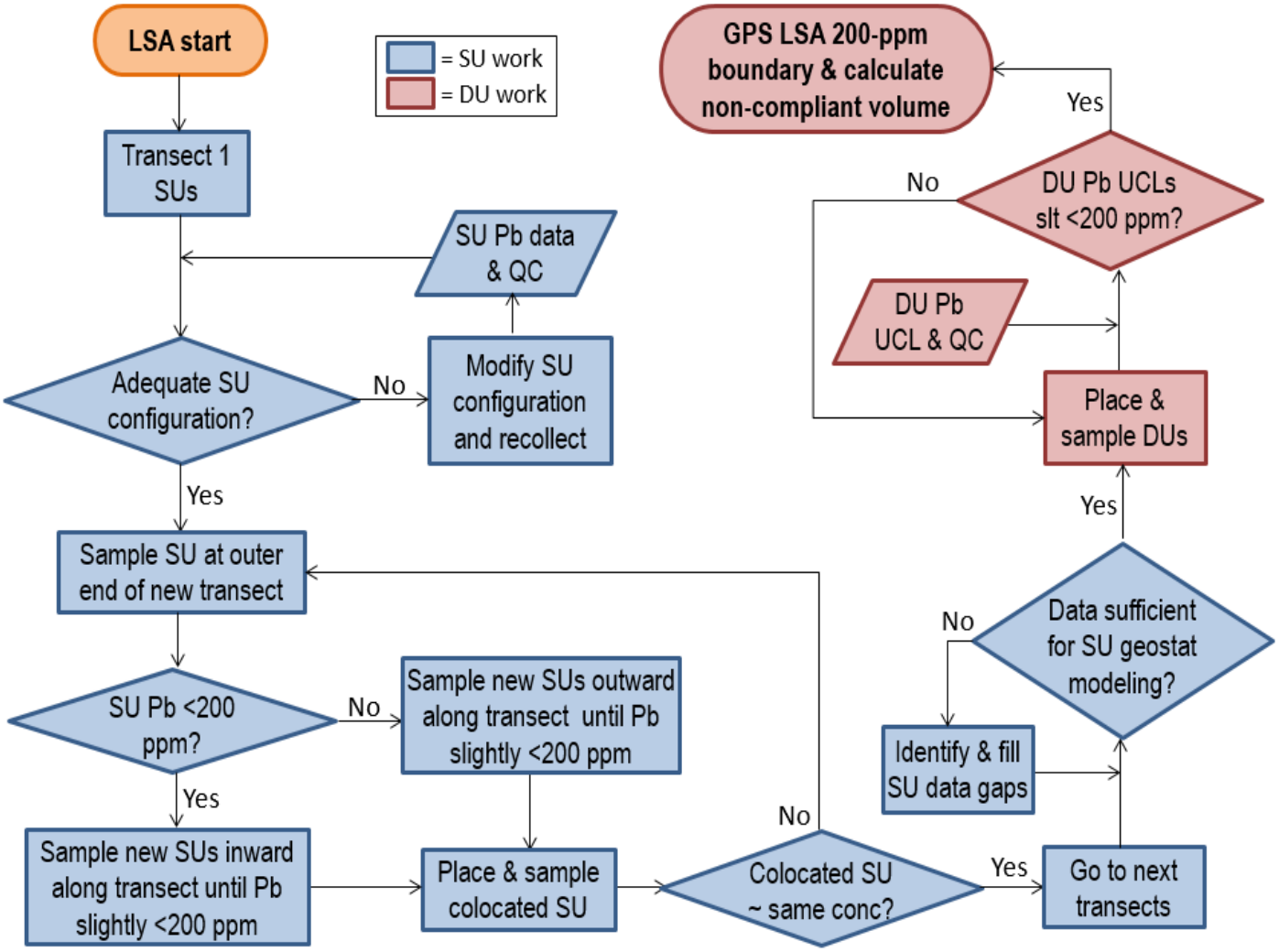
ERT's "blue map figure"



ERT's "green map figure" with proposed transects



Graphical summary of LSA field work plan



Attachment B – EBA Field Work Flow Plan

Meet the night before to tentatively assign next day's field tasks

Anticipated work crews:

- obstacle clearing
- sample collection
- sample processing/XRF analysis
- geostatistical modeling/field communications

Preliminary Stage

- Flag location of highest hit in ERT's kriged map of 2015 XRF results (see end of this work flow)
- Inspect the 2 buildings and flag potential sources areas (PSAs) such as
    - Piping and valves,
    - Doorways
    - Outflows
    - Low-lying areas where spills could accumulate and infiltrate into the ground
    - Stained soil/distressed vegetation

Section 1: Investigation outside the buildings

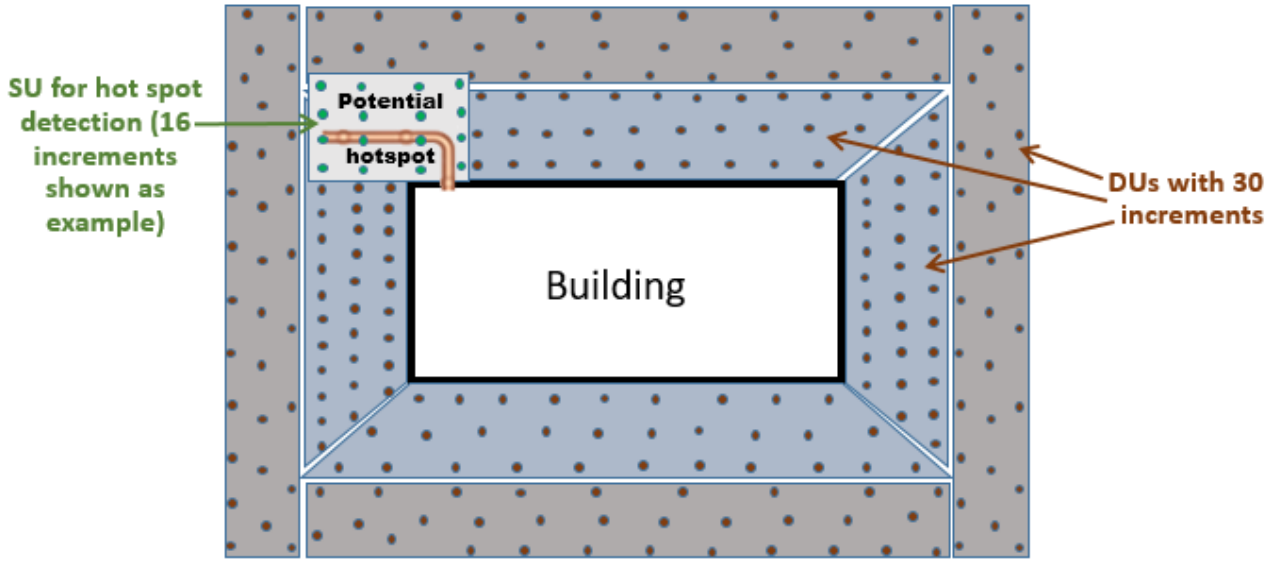
Item 1. Collect one 9 to 16-point SU (using the default 3x3 over 2x2 sq.ft. configuration or the SU configuration optimized in the LSA work) at all flagged locations at both the 0-6" and 6-24" depth intervals.

- There should be at least 2 SUs on each side of the structures. If there are no PSAs on a side, place the SUs randomly.
- Process samples from both depth intervals by sieving through 10-mesh sieve; place the <2-mm particle size in a read bag and XRF while using the RTeX form to run statistics on multiple readings over the read bag
- Using the 1-sided 95% t-UCL from the RTeX form, identify any SU sample having a conservatively estimated mean Pb concentration >200 ppm. Such an SU is considered to be a "hot spot."
    - To evaluate the potential for hot spots, return to any >200 ppm location and collect additional SU samples (at both depths) near the original location and along the same side of the building
        - Place the additional SU samples such that their borders touch the borders of the first SU, and there is continual spatial coverage.
        - If all bordering SUs are <200 ppm, and if the SU configuration being used is larger than 4 sq.ft., cover the original SU (the high concentration area) with up to four 4-sq.ft. SUs to determine the actual size and location of the hot spot.
- *In situ* readings with hand-held XRF may also assist in this effort. See also the discussion in Attachment E (Sample Labeling and Identification), under "EBA SUs".
    - Ensure there a sufficiently dense pattern of *in situ* XRF readings to have confidence that the area is correctly identified
    - When initially taking readings in a particular SU, take at least 3 15-sec *in situ* readings in a single "spot" or "location" by moving the XRF slightly between readings. This is to control for particle effects that could cause non-representative individual readings.
        - After a pattern of *in situ* results has been established, SUs or locations that appear to show little variability (i.e., insignificant particle effects) do not need frequent replicate readings.
        - Replicate in situ readings can be reserved for verifying unusual or unexpected readings.
    - *In situ* field results are not entered into an RTeX form. The readings are used only as qualitative results to understand contaminant patterns within an SU or chase contamination that appears to be migrating.

        - Detailed suggestions for how to record the results of *in situ* XRF readings in the field logbook and the XRF logbook appear in Attachment E, under "EBA SUs."
    - If the *in situ* results suggest that a concentration gradient away from a structure may be present, SU transects can be placed transects to characterize a possible trend prior to placing DUs.

Item 2. <u>Placing DUs:</u> If all SU samples on a particular side of the building are <200 ppm in both depth intervals

- Place a 10-ft wide DU along that side of the building
- Collect 30 increments (3x10 or other configuration as indicated by SUs carved from the DUs) from both depth intervals (see figure below)
- Predicted UCLs may be employed (as described in the LSA Field Work Flow), however the variability term may be different from the variability determined for the LSA. If predicted UCLs are employed in the EBA, an EBA-specific variability term should be determined.
    - Collect triplicate ISs from the first 2 DUs to calculate their 95% UCLs, and to derive a consensus %RSD to use to predict UCL from single DU field samples for subsequent EBA DUs
    - The third EBA DU should have 3 replicate field samples as well to compare the actual against the predicted UCL using the consensus %RSD; modify the consensus %RSD using the third DU's %RSD if necessary.
    - This strategy is the same as that used in the LSA strategy (Attachment A, Section 3, Item 3)
- If DUs next to a structure have actual or predicted UCLs >200 ppm, add additional step-out DUs to determine the >200 ppm boundary around the structure
- See figure below



Item 3. <u>DU sample processing:</u> All final DU decisions are based on the Pb content in the <100-mesh particle fraction. Samples must be sufficiently disaggregated to produce a sufficiently representative <100-mech sample.

- If soil conditions are such that disaggregation is difficult, and if it is found that DU "step-outs" are frequently required, the following procedure can be used to save time and labor:
    - Sieve several DU samples to <10-mesh initially and analyze
    - Re-sieve the samples to <100-mesh and analyze
    - Compare the results for the <10-mesh and <100-mesh particle fractions
        - If the concentration difference between the two fractions is insignificant, or if the concentration of the <10-mesh fraction is greater than that of the <100-mesh fraction, the 10-mesh fraction can be used as an intermediate value until the final DU footprint is achieved

Item 4. Flag boundaries and take spatial measurements that will allow estimation of the volume of soil with Pb concentrations >200 ppm for possible removal.

- If unexpectedly high concentrations of Pb are found in the EBA, collect enough data to perform geostatistical modeling.
- Collect sufficient data at both depths to allow for risk assessment for each depth interval and in the combined (0-24" interval).

Section 2: Investigation inside the buildings

Item 1. Sample the dirt floor contained within the east building

- Place 1 or more DUs inside the building as circumstances indicate
- Sample from both depth intervals if possible
- Collect a single IS (30 increments) from each DU/depth interval
- Sieve and analyze the initial IS samples
    - If the east building DU samples are >200 ppm, designate the area for cleanup and additional ISs replicate samples are not required.
    - If the east building DU samples are <200 ppm, collect 2 additional replicate samples and calculate the 95% UCL for each DU/depth interval.

Item 2. Inspect the inside of the west building for soil or similar loose material that can be gathered into a read bag

- Collect and XRF those samples to determine whether inside construction materials might be contaminated with Pb.

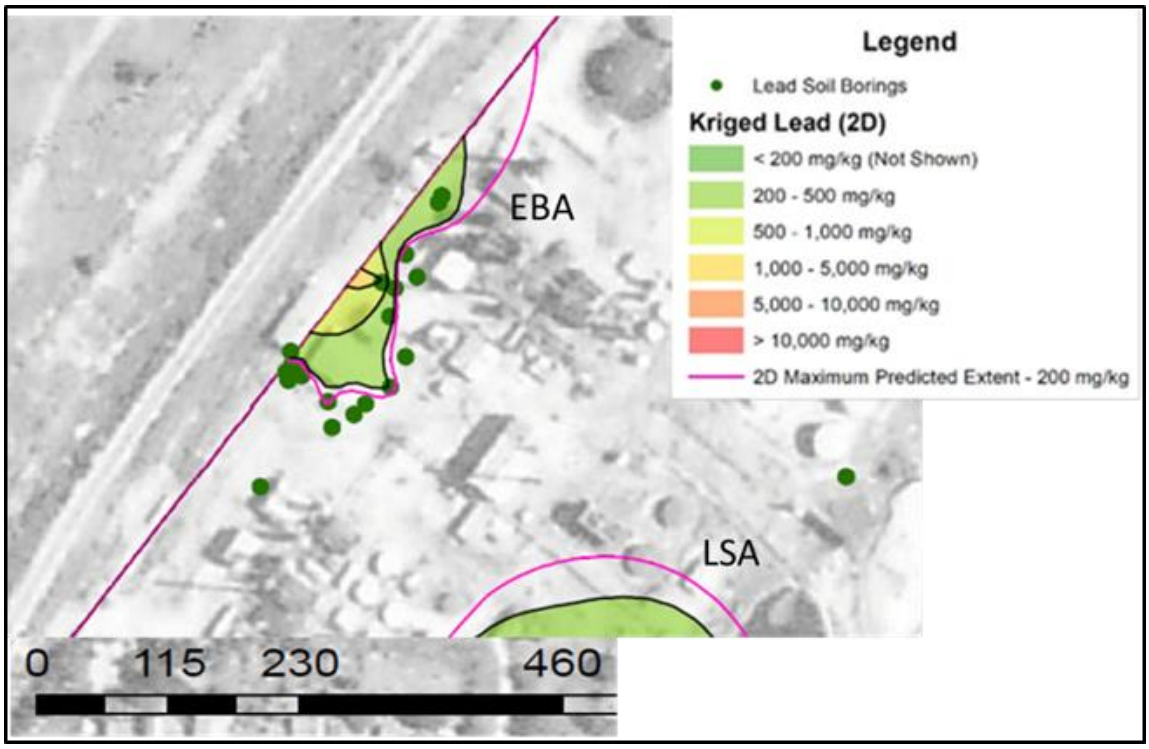
Item 3. If desired by the RPM, an attempt may be made to use the Niton XRF in handheld mode to test materials in place (such as concrete and wood).

- Loose material may offer interference for the XRF, and the XRF results may not be reliable: this is a coarse screening only.
    - Consider that the XRF is calibrated for a soil-type matrix, and may not perform equivalently for a material with a completely different matrix
    - Check the spectra for misshapen peaks: peak shape different from those observed for a soil matrix indicate that any numerical readings are completely unreliable
- If peak shape appears acceptable, use multiple *in situ* shots over some area of a single material
    - Determine and record the area over which the shots were made
    - Calculate the average concentration for that area.

Section 3: EBA field wrap-up to produce materials for use by the RPM

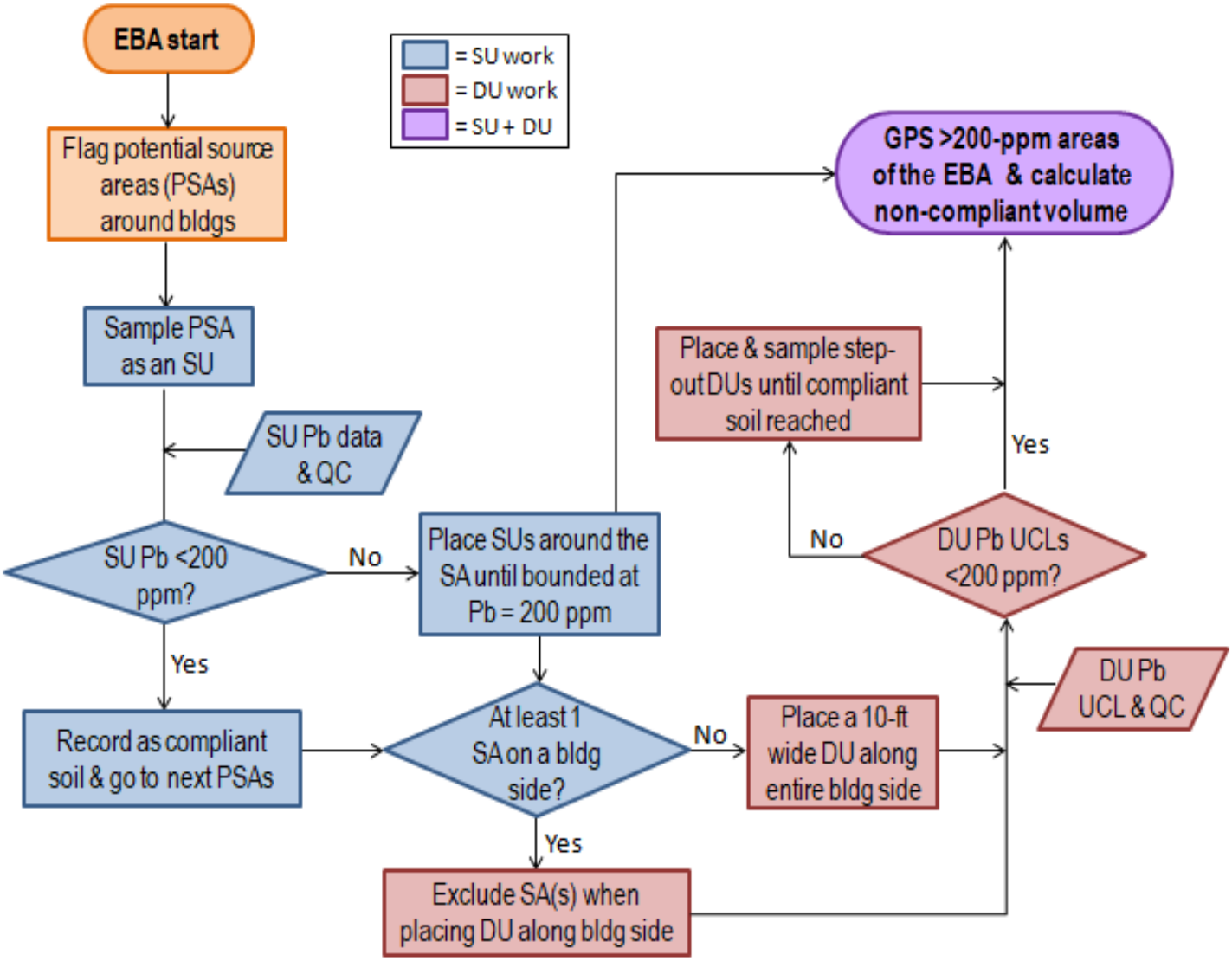
- Flag boundaries
- Take sufficient GPS readings and distance measurements to produce accurate maps
- Use GIS or other spatial modeling to generate an estimate of the volume of soil with Pb concentrations >200 ppm for the surface and subsurface intervals.
- Where applicable, mathematically combine the 0-6" and 6-24" interval data to produce an exposure point concentration for the 0-24" interval.

ERT's kriged EBA map



(section continues below)

Graphical summary of EBA work plan



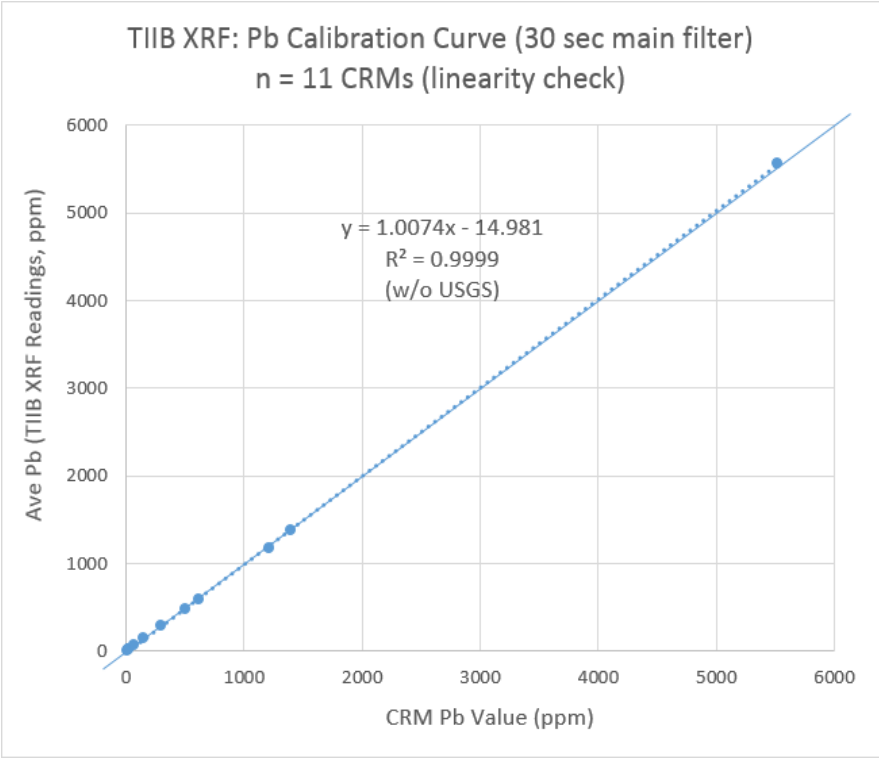
Attachment C: TIIB Niton XL3t XRF (S/N 92959) Operation Performance Measures

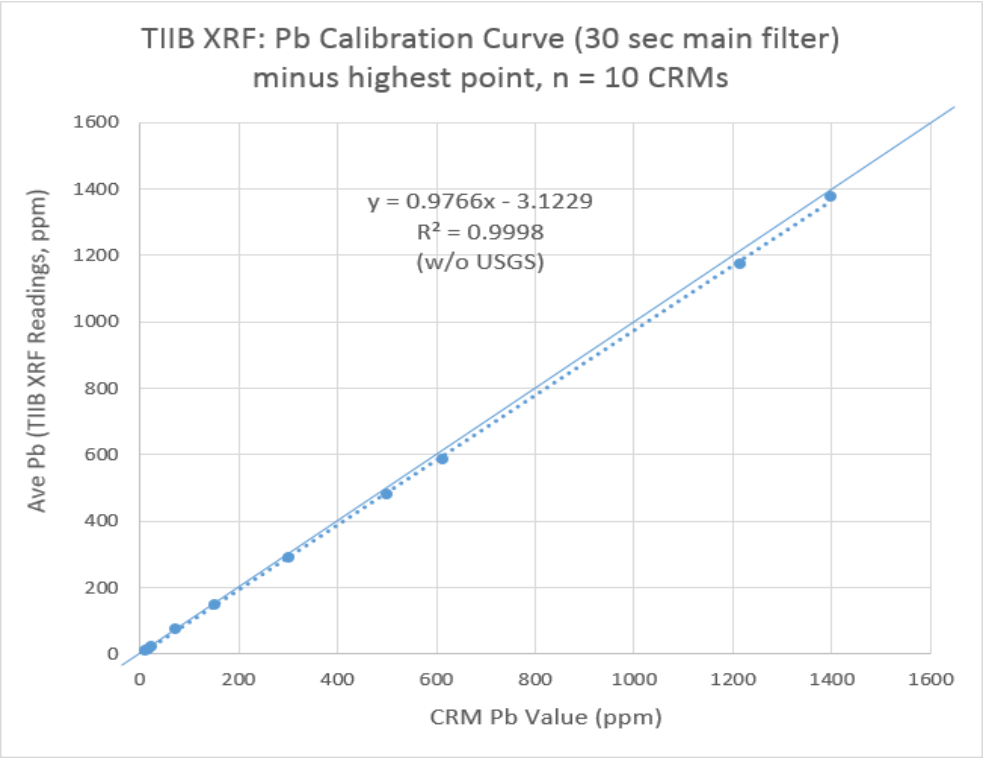
Calibration Status and Linearity Determination for Pb (current as of May 2017)

Linear to at least 5600 ppm Pb (see linearity check graph below left, which contains the extreme high data point)

Calibration curve parameters are determined from second curve (which lacks the extreme high data point that could bias regression parameters):

- Slope = 0.977; Y-intercept = -3.1 ppm; R^2 = 0.9998





Niton instrument limit of detection (LOD) for Pb:

- 5.5 ppm (determined as 3 x signal/noise ratio, on a “clean” CRM with 11 ppm Pb concentration, and a 30-sec read time)
- 6.8 ppm (determined as 3 x signal/noise ratio, on a CRM with 24 ppm Pb concentration, and a 30-sec read time)

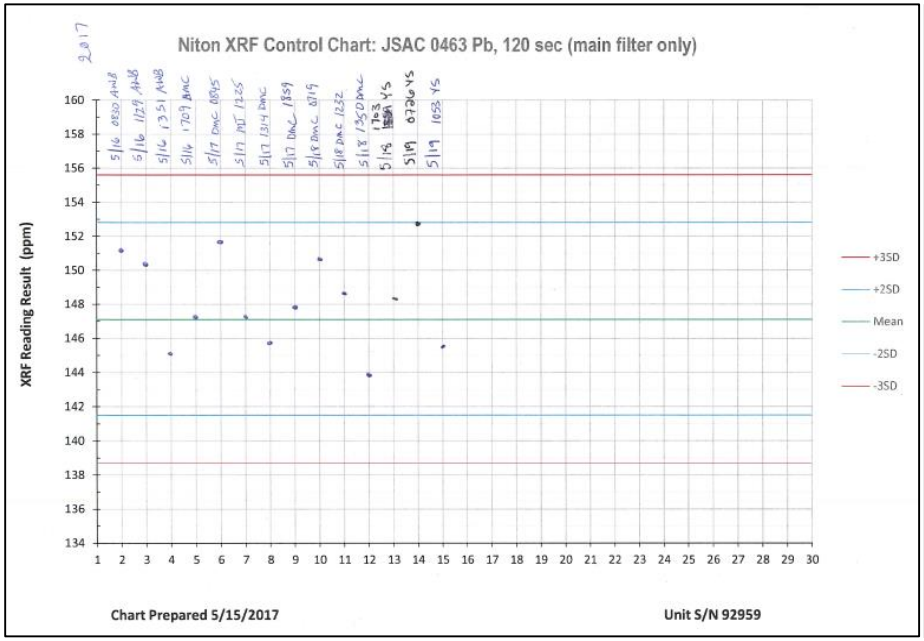
Niton instrument Quantitation Limit (QL) for Pb:

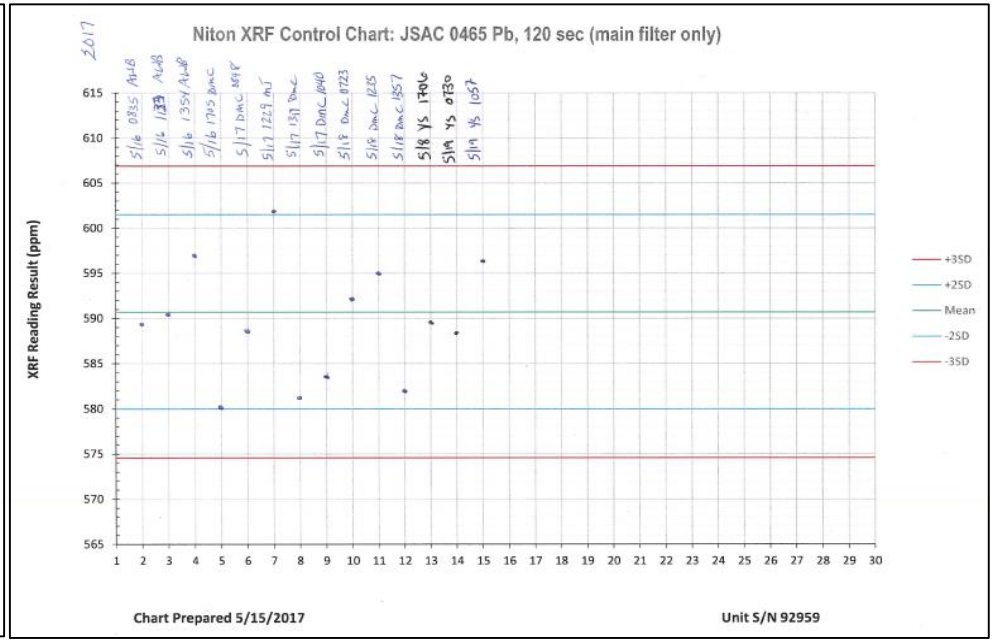
- 10 ppm (determined as the concentration at which the analytical %RSD = ~10 % in a “clean” matrix with a 30-sec read time)

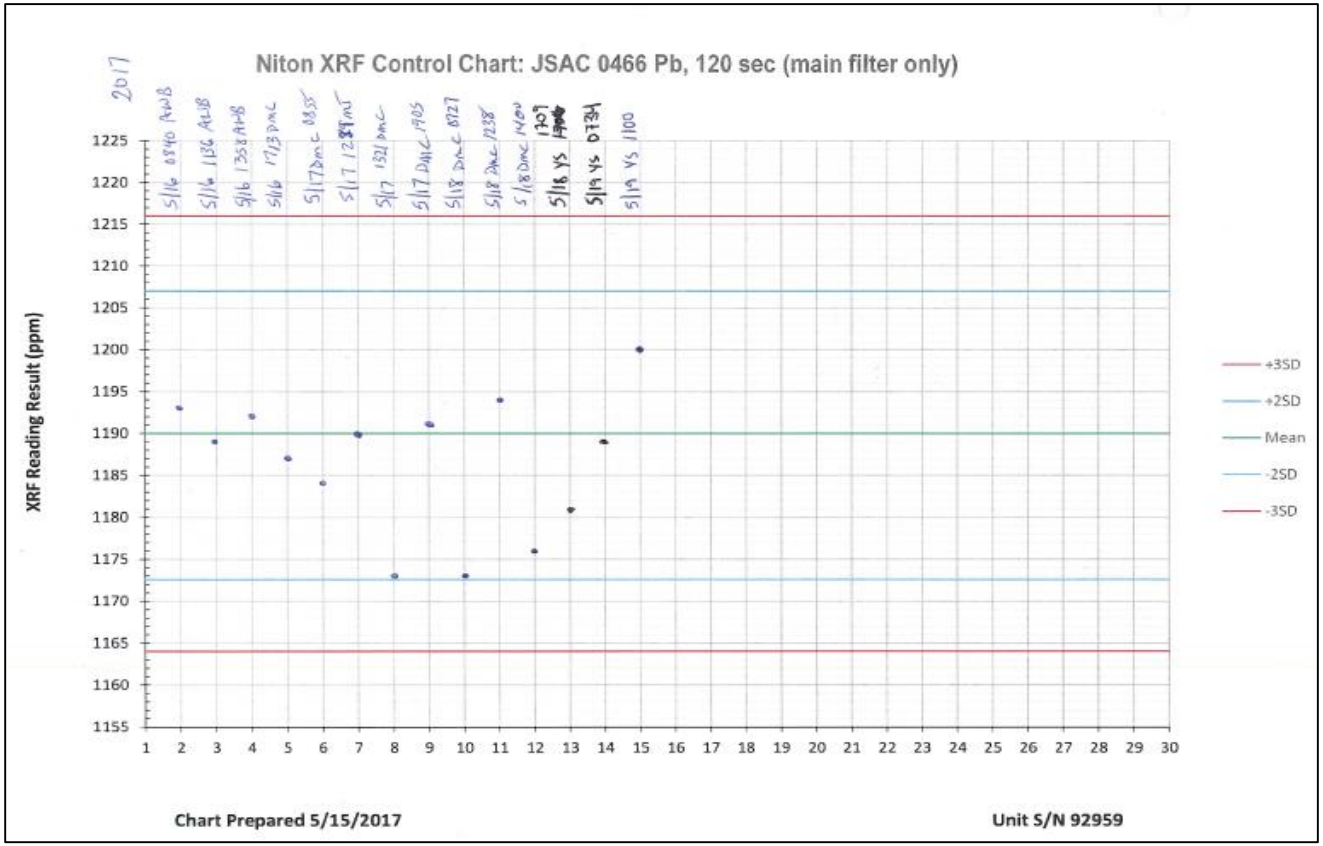
Niton instrument analytical precision:

- 8.8% RSD (on CRM with 11 ppm Pb and a 30-sec read time)
- 1.1% RSD (on CRM with 300 ppm Pb and a 30-sec read time)

Recent Niton control charts for 3 concentrations levels for Pb are shown below







Niton LCS performance/control chart summaries (May 2017):

- JSAC 0463 (Low-level Pb) mean: 147 ppm (cert: 151.6 ppm = 97%); ±2 SD range: 142-153 ppm (±4.1%)
- JSAC 0465 (Mid-level Pb) mean: 591 ppm (cert: 612.4 ppm = 96%); ±2 SD range: 580-602 ppm (±1.9%)
- JSAC 0466 (High-level Pb) mean: 1190 ppm (cert: 1214 ppm = 98%); ±2 SD range: 1173-1207 ppm (±1.4%)

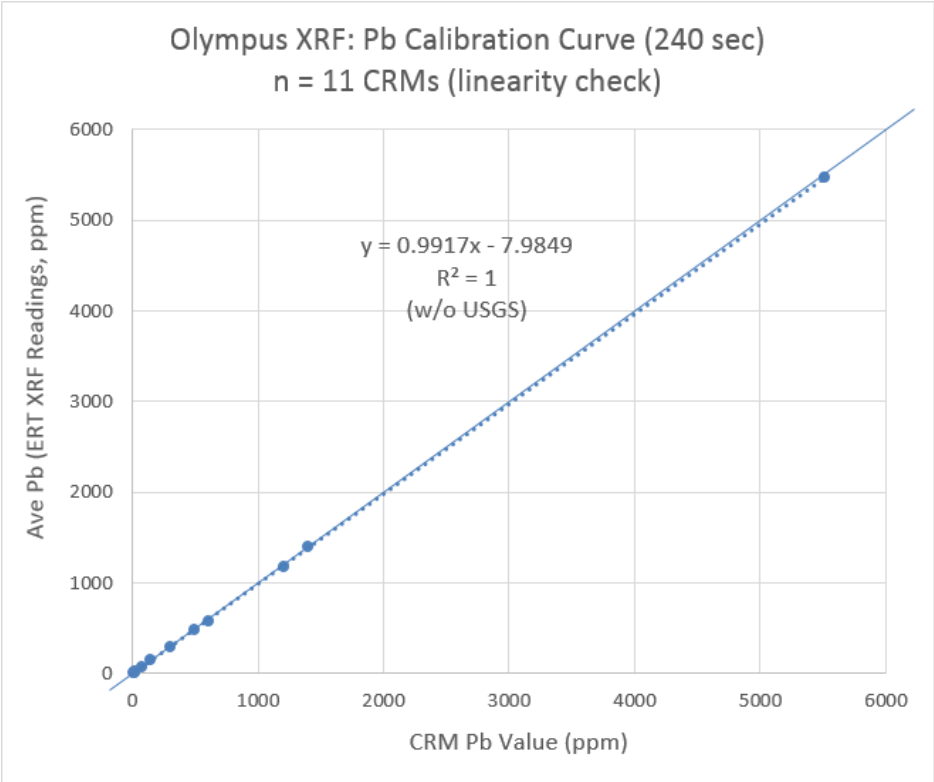
Attachment D: ERT Olympus X-5000 XRF (S/N 202309) Operation Performance Measures

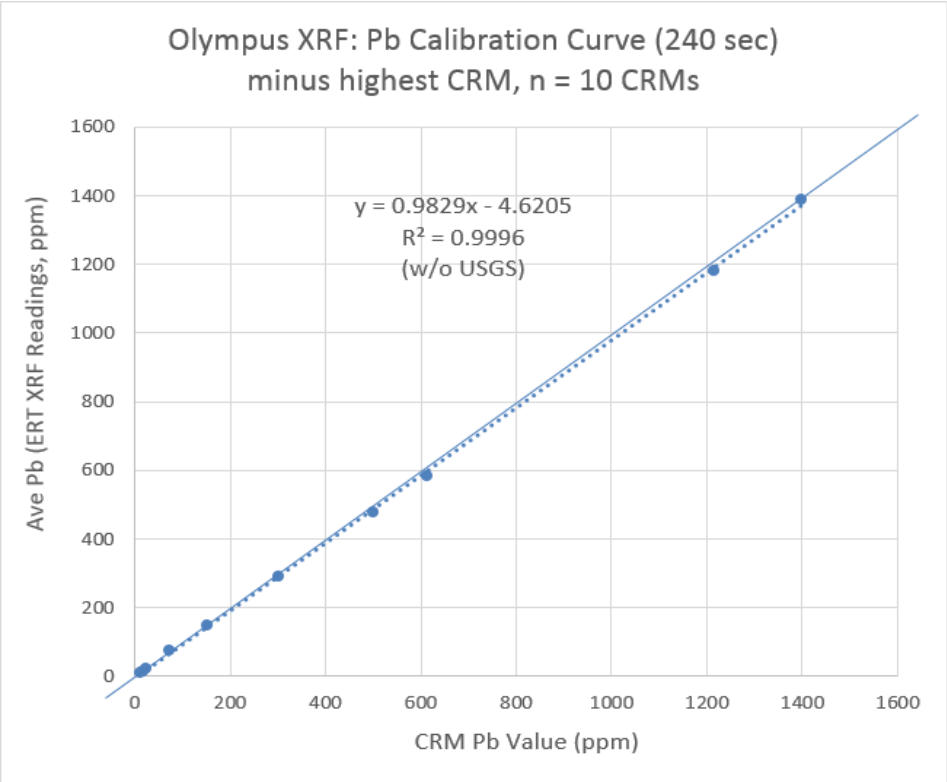
Calibration Status and Linearity Determination for Pb (current as of May 2017)

Linear to at least 5600 ppm Pb (see linearity check graph below left, which contains the extreme high data point)

Calibration curve parameters are determined from second curve (which lacks the extreme high data point that could bias regression parameters):

- Slope = 0.983; Y-intercept = -4.6 ppm; R^2 = 0.9996





Olympus instrument limit of detection (LOD) for Pb:

- 3.3 ppm (determined as 3 x signal/noise ratio, on a CRM with 11 ppm Pb concentration, and a 240-sec read time)
- 4.2 ppm (determined as 3 x signal/noise ratio, on a CRM with 24 ppm Pb concentration, and a 240-sec read time)

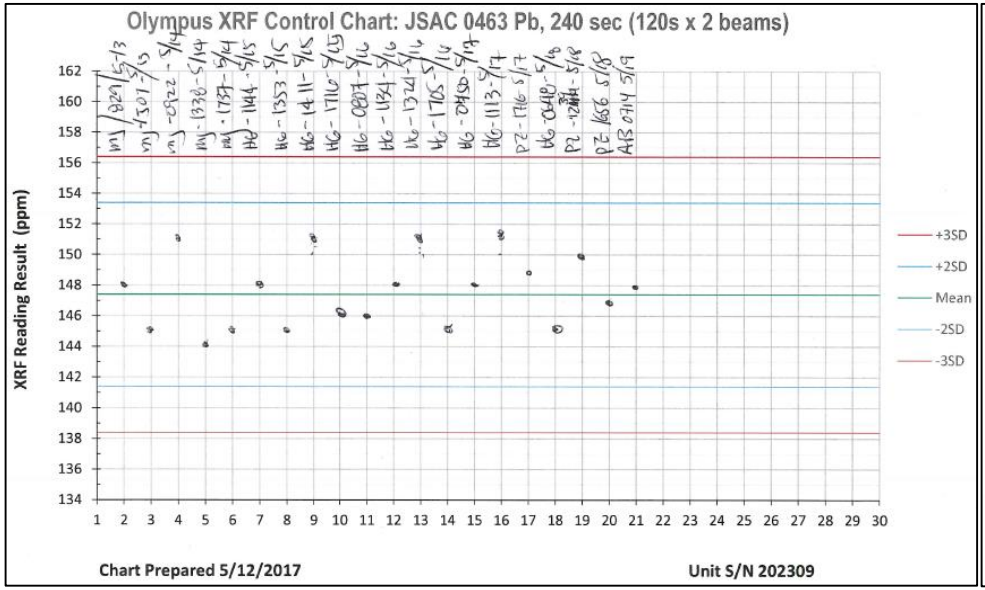
Olympus instrument Quantitation Limit (QL) for Pb:

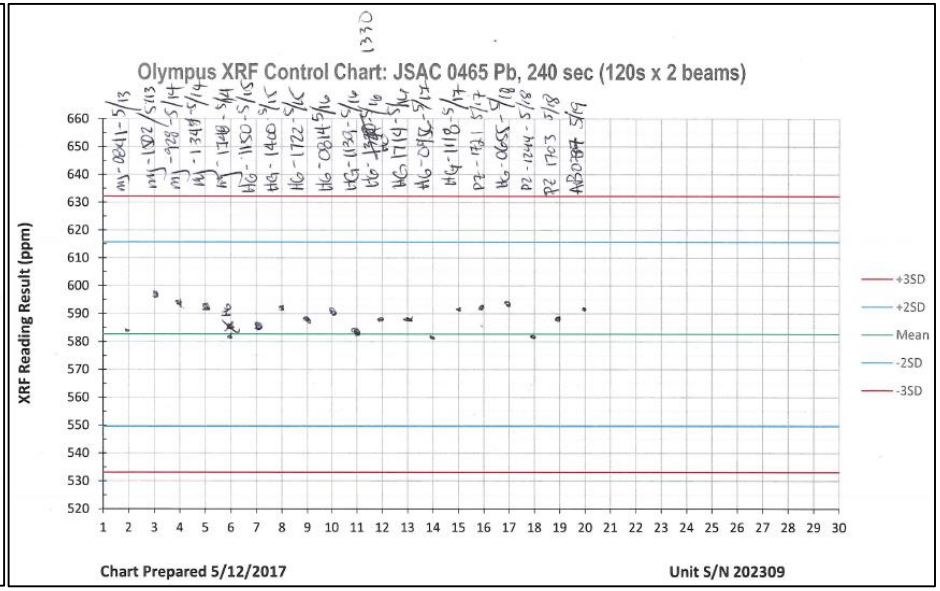
- 14 ppm (determined as the concentration at which the analytical %RSD = ~10 % in a "clean" matrix with a 240-sec read time)

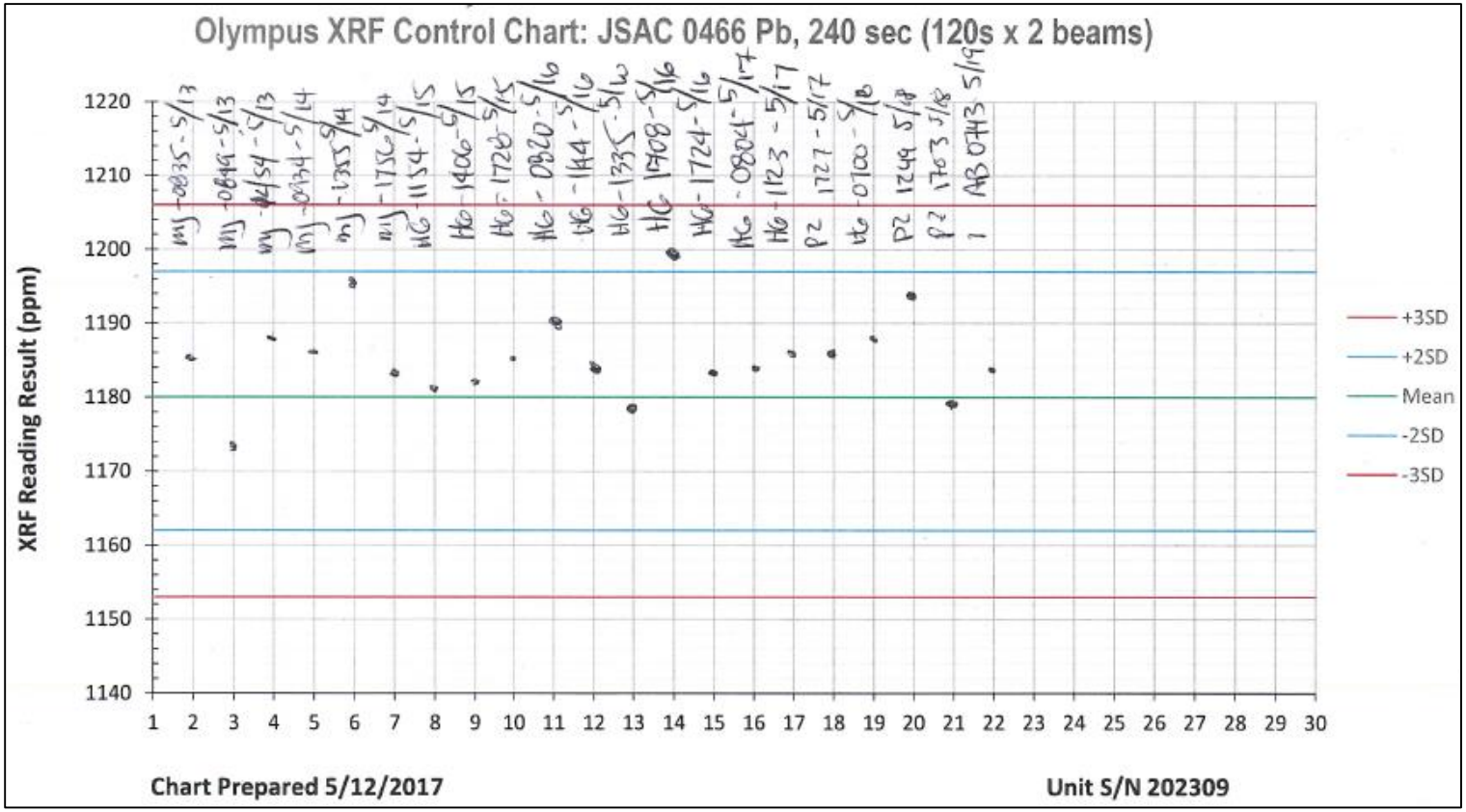
Olympus instrument analytical precision:

- 11.6% RSD (on CRM with 11 ppm Pb and a 240-sec read time)
- 1.5% RSD (on CRM with 300 ppm Pb and a 240-sec read time)

Recent Olympus control charts for 3 concentrations levels for Pb are shown below







<u>Olympus LCS performance/control chart summaries (May 2017):</u>

- JSAC 0463 (Low-level Pb) mean: 147 ppm (cert: 151.6 ppm = 97%); ±2 SD range: 141-153 ppm (±4.1%)
- JSAC 0465 (Mid-level Pb) mean: 583 ppm (cert: 612.4 ppm = 95%); ±2 SD range: 550-615 ppm (±5.7%)
- JSAC 0466 (High-level Pb) mean: 1180 ppm (cert: 1214 ppm = 97%); ±2 SD range: 1160-1197 ppm (±1.6%)

Attachment E: Sample Labeling and Identification

In the sample logbooks for LSA and EBA,

- Record the GPS reading for the center of each SU (including each member of a couplet, which are placed so that there is 1-2 ft. between their adjacent edges), and
- Record the SU configuration as the area and number of increments.
- DUs are GPS at their corners. Record the number of increments per field sample, as well as the number of replicate field samples within a DU.

Proposed Sample Labeling Schema for LSA

LSA SUs

Test SUs for optimizing configuration (all have couplets):

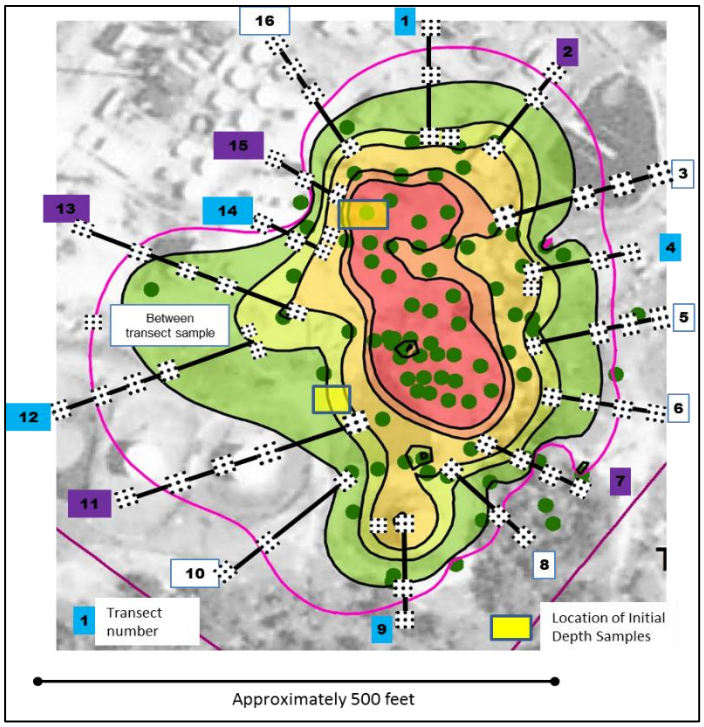
- LSA-Test1-SUXY where X = 1, 2, 3… for numerical order of collection; and Y = A or B for the couplet member for testing the default configuration (2x2 sq.ft/9 inc)
    - Example: LSA-Test1-SU1A and LSA-Test1-SU1B
- LSA-Test2-SUXY as above, but for testing the second configuration (3x3 sq.ft/12 inc), if needed
- LSA-Test3-SUXY as above, but for testing the third configuration (4x4 sq.ft/16 inc), if needed

Delineation SUs along transects (some have couplets):

- For transect SU samples without a couplet: LSA-SUTW,X where T = "transect", W = transect number (the transect numbering may follow the labeling given in the figure below or the numerical order of sampling as work progresses in the field); X = 1, 2, 3… for numerical order of collection along that transect
    - Example, for the first and second SU samples collected along transect #16: LSA-SUT16,1 and LSA-SU16,2
- For transect SU samples with a couplet: LSA-SUTW,XY as above, except that Y = A or B for the couplet member
    - Above SU example but with the second transect location having a couplet: LSA-SUT16,2A and LSA-SUT16,2B

Fill-in SUs between transects (some may have couplets):

- For fill-in SU samples without a couplet: LSA-SUFW-W,X where F = "fill-in", W-W = the 2 transects between which the SU is located; X = 1, 2, 3… for numerical order of collection between those transects
- For fill-in SU samples with a couplet: LSA-SUFW-W,XCY as above, except that Y = A or B for the couplet member
    - Example of the first fill-in SU couplet between transects 8 and 9: LSA-SUF8-9,1A and LSA-SUF8-9,1B



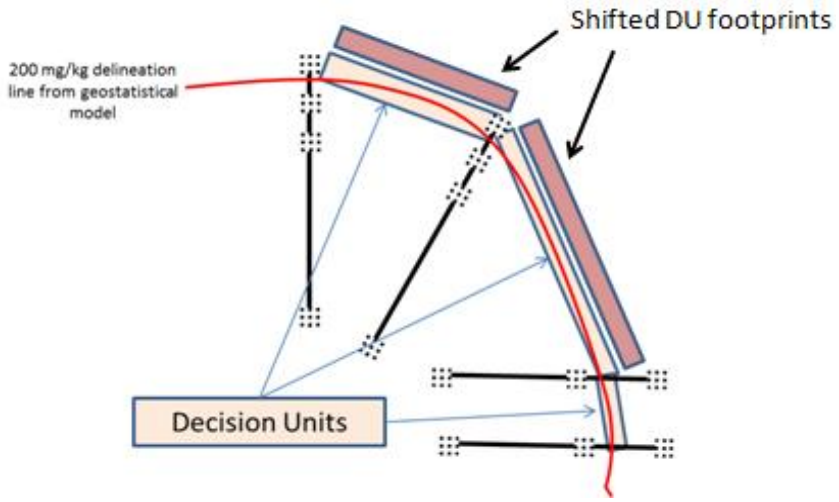
LSA DUs

In the sample logbook for LSA,

- Record the GPS readings for the corners of the DU, and
- Record the DU area and number of increments.

Boundary confirmation DUs:

- For initial placement and sampling of a border segment DU having replicate field samples: LSA-DUTW-W,1RY where T = "transect"; W-W = the 2 transects that the border DU bridges; 1 = the first DU between those 2 transects; R = "replicate"; and Y = A, B or C for the triplicate member
    - Example, an LSA DU that bridges transects 14 and 15, with 3 replicates, would have these sample IDs:
        - LSA-DUT14-15,1RA, LSA-DUT14-15,1RB, and LSA-DUT14-15,1RC
- For initial placement and sampling of a DU NOT having replicate field samples: LSA-DUTW-W,1 as above except no R or Y designations
- For placement and sampling of a shifted or step-out DU having replicate field samples: LSA-DUTW-W,2RY where T = "transect"; W-W = the 2 transects that the border DU bridges; 2 = the first step-out DU between those 2 transects; R = "replicate"; and Y = A, B or C for the triplicate member
- For placement and sampling of a step-out DU NOT having replicate field samples: LSA-DUTW-W,2 as above except no R or Y designations
    - Example continuing the previous example: if LSA-DU14-15 needed to be stepped out because the first bridging DU was >200 ppm, and if it had no replicates, the DU would have this sample ID: LSA-DU14-15,2



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(EBA is below)

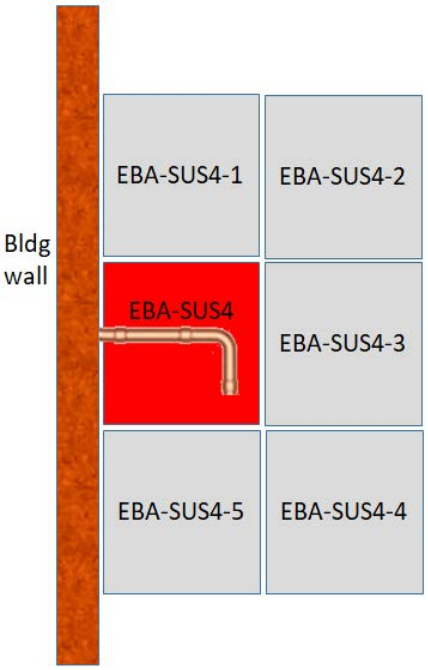
EBA SUs

Proposed Sample Labeling Schema for EBA

- For SUs that search for sources or hot spots around the structures: EBA-SUSX where the S after SU = "source"; X = the numerical order of sampling the flagged potential source area (PSA) locations
    - Example of the fourth PSA sampled in the EBA: EBA-SUS4

- For SUs that characterize a detected hot spot found by a EBA-SUSX sample: EBA-SUSX-Y as above, with the Y = the numerical order of collecting additional SUs around SUSX
    - Example of the fourth PSA SU sampled in the EBA, which was >200 ppm and needed to be delineated by surrounding with SUs (as shown in the figure): EBA-SUS4-1, EBA-SUS4-2, EBA-SUS4-3, EBA-SUS4-4, and EBA-SUS4-5

- Hot spot delineation that is guided by *in situ* XRF readings will use the following:
    - XRF operator: The operator will enter the SU identifier (ex: EBA-SUS4) into the instrument. It is not necessary for the XRF operator to add an additional identifier to the individual readings within the same SU. The instrument reading number will be the identifier that links the instrument data download to the XRF logbook record.
    - Field logbook: The recorder for the field crew will make a sketch of the SU and its environs in the field logbook, including GPS coordinates.
        - Reading results will be recorded into the sketch in the field logbook, along with the order number of the location being tested (such as Loc #1, #2, etc.)
        - Replicate shots in the same location to control for particle effects will be designated with A, B, C, etc. If only a single reading is taken in a location within the SU, designate this with an S after the Loc#.
            - SUs or locations that appear to show little variability do not need frequent replicate readings in the same location.



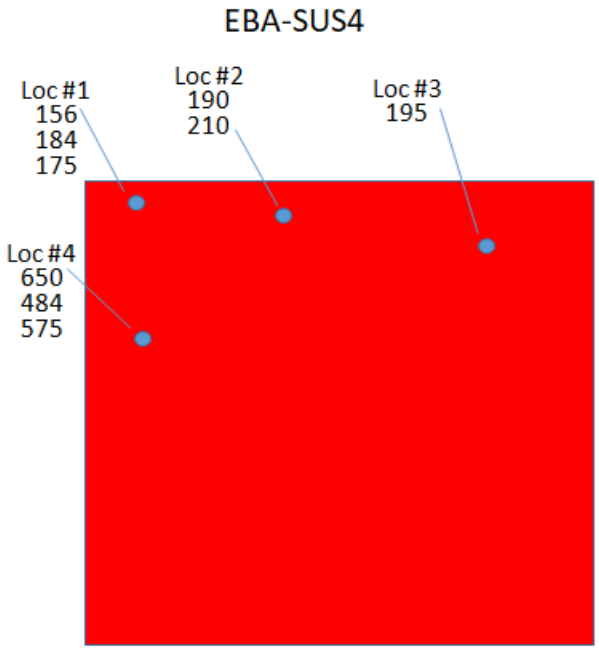
    - XRF logbook: The recorder will enter the SU identifier (e.g., EBA-SUS4), the Loc #, and the replicate letter, plus the instrument reading number, the clock time the reading was taken, the acquisition time of the reading (e.g., 15 sec), the Pb result & instrument error (as 1 SD).
    - See the figure below for an example of field and XRF logbook entries for an SU
    - *In situ* field results are not entered into an RTeX form because they are used qualitatively to understand contaminant patterns within an SU, or to chase contamination that appears to have migrated.

- For transect SUs in the EBA (if it is discovered they are needed): EBA-SUTW,X where T = "transect", W = transect number in order of sampling, and X = numerical order of SUs collected along that transect

In XRF Logbook

SU ID	Rdg#(Inst)	Time	AcqTime	Rdg ID	Pb (err)
EBA-SUS4	358	1430	15 sec	Loc#1A	156 (4.3)
	359	1430	15 sec	Loc#1B	184 (4.7)
	360	1431	15 sec	Loc#1C	175 (4.6)
	361	1431	15 sec	Loc#2A	190 (4.3)
	362	1431	15 sec	Loc#2B	210 (4.4)
	363	1432	15 sec	Loc#3S	195 (4.4)
	364	1432	15 sec	Loc#4A	650 (6.7)
	365	1433	15 sec	Loc#4B	484 (5.5)
	366	1433	15 sec	Loc#4C	575 (6.0)

In Field Logbook



EBA DUs

- For DUs around the structures: EBA-DUX where X = numerical order of DUs being collected.
- Triplicate DUs have A, B or C attached.
- The first five DUs sampled in the EBA are expected to have these sample IDs (Refer to Attachment B, Section :
    - EBA-DU1A, EBA-DU1B, and EBA-DU1C
    - EBA-DU2A, EBA-DU2B, and EBA-DU2C
    - EBA-DU3A, EBA-DU3B, and EBA-DU3C
    - EBA-DU4
    - EBA-DU5

Wilcox ISM Procedure 1.3- ISM Sample Processing

This Procedure contains thirteen sections:

1.0 Purpose
2.0 Application
3.0 References
4.0 Associated Procedures
5.0 Equipment
6.0 Decontamination
7.0 Logging a Sample into the Laboratory
8.0 Weighing Samples
9.0 Drying and Disaggregation
10.0 Sieving
11.0 Bagging
12.0 Reprocessing Samples
13.0 Tools and Forms

1.0 Purpose

The purpose of this Procedure is to provide information for how to process Incremental Sampling Methodology (ISM) samples using Gy-correct techniques in order to obtain a representative sample from a decision unit (DU).

2.0 Application

This Procedure applies to the preparation of ISM samples collected in the field for laboratory analysis. This includes logging the sample in the lab, weighing samples, drying and disaggregation, quality control (QC), sieving, and bagging. This procedure assumes that the samples will be sieved for analysis of fine particle fractions for exposure assessment using XRF or similar analysis. These sample processing procedures may be modified for use in other analytical methods.

One tool and three forms are included with this Procedure as Excel spreadsheets.

3.0 References

U.S. Department of Agriculture, Natural Resources Conservation Service 2014. Soil Survey Field and Laboratory Methods Manual. Soil Survey Investigations Report No. 51, Version 2.0. R. Burt and Soil Survey Staff (ed.).

U.S. Environmental Protection Agency. (2016). Recommendations for Sieving Soil and Dust Samples at Lead Sites for Assessment of Incidental Ingestion. OLEM Directive 9200.1-128. July. https://semspub.epa.gov/work/HQ/100000133.pdf

U.S. Environmental Protection Agency. (2003). Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples. Office of Research & Development. EPA/600/R-03/027. November. https://clu-in.org/download/char/epa_subsampling_guidance.pdf

4.0 Associated Procedures

- ISM Procedure 01: Overview of ISM Sample Collection and Handling *(under development)*
- ISM Procedure 01.1: Laying out the evenly-spaced triplicate grids for a DU
- ISM Procedure 01.2: Incremental sample collection using a CMIST ("pogo-sampler")
- ISM Procedure 01.4: Archiving samples after analysis *(under development)*
- ISM Procedure 01.5: Determining Increment Spacing to Ensure Hot Spot Inclusion in Incremental Samples *(under development)*
- ISM Procedure 01.6: Incremental Sample Collection with Soil Probes
- ISM Procedure 01.7: Non-disposable Equipment Decontamination
- XRF Procedure 01.4: Subsampling and Analysis for Comparability Assessment
- XRF Procedure 02.1.3: Using the XRF Bag Checker and Calculator Tool

5.0 Equipment

- Nitrile gloves
- Permanent marker
- Calibrated balance with sensitivity of 0.01 kg and a capacity of at least 3 kilograms
- Heavy-duty plastic bags (exact type of bulk bag used in field, used to tare balance)
- Small "sandwich" thin-walled plastic bags ("certified interference free" XRF "small read bag") available from retail and grocery stores
- Large thin-walled (1.2 mil) polypropylene plastic bags ("certified interference free" XRF "large read bag") For the Wilcox site, the bags were obtained from Paper-Mart, Inc.
- Heavy duty aluminum foil or butcher paper
- Large, shallow drying pans (cookie sheets work well)
- Laboratory hood
- Rolling Pin and/or rubber mallet
- Sieves: brass or plastic No. 10-mesh and No. 100 mesh standard US sieve, lid, and bottom collection pans.
- Sieve cleaning brushes
- Mechanized sieve shaker
- Personal Protective Equipment (e.g., lab coats, eye protection, respiratory protection), as directed by the lab's Health and Safety plan.

6.0 Decontamination

All non-disposable equipment that comes in contact with the soil sample will be decontaminated. Decontamination procedures will be followed in accordance with Wilcox Sample Collection Procedure 1.7 Non-disposable Equipment Decontamination**.**

7.0 Logging a Sample into the Laboratory

All samples collected in the field will be logged into a master sample table (paper or electronic, as most convenient) prior to sample processing. The list will be cross-checked with the field

logbook and other records to ensure all samples remain accounted for. The table will be similar to the table illustrated in Figure 1 below. If a paper log is used, it will be scanned to pdf as a permanent record. An example form is provided in the Excel file *Procedure 1-3 ISM Sample Prep Tools and Forms.xlsx*

Sample ID	Log-In Date	Process Date	XRF Analysis Date	XRF mean (Pb, ppm)	XRF mean (As, ppm)	Subsample Date (if applicable)	XRF Date for Subsample	Date to ICP	Date to Bioacc test
XXXX-XX-XXXX	xx/xx/xx	xx/xx/xx	xx/xx/xx			xx/xx/xx	xx/xx/xx	xx/xx/xx	xx/xx/xx

Figure 1: Master sample table example

8.0 Weighing Samples

Samples and sample fractions will be weighed and recorded on the appropriate forms at these points in the process and with these tares:

- Before opening the bag as received from the field (tare using a clean bag of the exact kind bagging the sample). This weight represents the undried, initial sample weight and can be used to evaluate the moisture content.
- After sample drying (subtract the weight of pan and aluminum foil). This sample weight is used for quality control as a baseline to compare against the sum of the sieved fractions.
- After sieving, each particle size fraction produced by sieving, after placement in read or storage plastic bags (use exact kind of bag for tare).

8.1 Procedure for Weighing Samples

1. Weigh the sample as received from the field before opening the bag.
    a. Tare using a clean bag of the exact kind used to bag the field sample.
    b. All sample weights should be recorded in a sample and fraction masses data entry table (Figure 2). The information in this table will be transferred into an Excel spreadsheet for automated calculation of sample and fraction masses and other parameters.

This table records sample and fraction masses for later entry into a calculation spreadsheet.

No.	Sample ID	Log-In Date	Original sample bag (g)	Original bag tare (g)	Dried sample + pan (g)	Pan tare (g)	Dried oversize fraction (g)	Oversize bag tare (g)	Dried mid-sized fraction (g)	Mid-sized fraction bag tare (g)	Dried fine fraction (g)	Fines bag tare (g)	Tech initials / Notes
1													
2													
3													
4													

Figure 2: Sample and fraction masses data entry table

2. After satisfactory dryness is achieved, the pan, foil and soil are weighed and that weight recorded, along with the elapsed drying time, etc. After the sample has been transferred into the sieves, weigh the now empty pan and foil as a unit and record as “pan tare.”
3. After sieving is complete, sieve fractions will be gathered into plastic bags. The process of establishing the 200-ppm Pb boundary will use soil samples sieved to 10-

mesh (<2 mm particle size) to expedite sample processing. Once located, confirmation of the 200-ppm boundary will use the <100-mesh (<150 µm) soil particle size fraction, which is expected to be the most relevant particle size for risk evaluation.

9.0 Drying and Disaggregation

9.1 Initial Disaggregation

Initial disaggregation of the sample and removal of large stones or non-soil materials will be done after weighing the undried bulk soil, but before drying of the sample. This initial disaggregation will facilitate XRF analysis of the undried bulk soil to establish a baseline bulk Hg concentration.

Disaggregation involves breaking apart agglomerations of soil that are simply stuck to each other, but does not reduce the size of small pebbles or other hard particles. This is performed by crushing soil clumps with gloved fingers, a hand-operated mortar and pestle, a coffee grinder, rolling pin, or a rubber mallet. Disaggregation helps ensure that soil agglomerations formed during drying are not removed from analysis of the final target particle size by sieving.

9.2 Drying

If the soil feels or looks moist, there may be sufficient moisture to impede disaggregation and sieving of the sample. In that case, the soil will be air-dried overnight in shallow pans lined with foil.

1. Determine if soil requires drying by assessing the initial texture and moisture content of the samples. Soils with moisture content less than 15 - 20 percent by weight generally do not cause interference with XRF analysis, although this can depend on the soil's properties.
    a. Before drying, large rocks and debris (> 1/4 inch) will have already been removed, and an initial disaggregation already performed. At this point, perform additional disaggregation by hand (using powder-free exam gloves) as much as possible.
    b. Disaggregation of clayey soils is much easier when the soil is slightly damp.
    c. If the inside of the sample bag is wet and a significant amount of soil is sticking to it (>1-2 grams), it must also be dried.
    d. Do not wipe the inside of the bag (this will remove fines that belong in the sample).
    e. Keep a wet bag completely open and allow it to air dry (prop it open with a small lab funnel, etc., if necessary). If necessary (due to the amount of moisture or to speed up processing) circulate the air in the bag with very gentle airflow from an indirect or small, weak fan, etc. Airflow must not be strong enough to mobilize small particles inside the bag as they dry. Add dried soil particles from the bag to the bulk sample.
2. Line a pan with aluminum foil. Spread soil evenly over the foil. Note the color of the un-dried soil. Record the sample ID on the foil using a permanent marker, or use another method to ID the sample pan.

3. Place the soil pan in the area designated for air-drying. The location should provide good air circulation and protect the sample from loss of contaminants and cross contamination.
    a. The length of time required for drying soil is a function of the soil composition (% clay and organics), density, initial moisture content, and the ambient temperature and humidity.
    b. Inspect the soil periodically. Continue disaggregation by hand, and stir soil around with a blunt tool that will not tear the foil.
    c. To determine if soil is dry enough: Check to ensure the color has changed throughout the sample, check moisture below surface layers, make sure soil breaks / crumbles easily.

9.3 Disaggregation after drying

During disaggregation, continue to remove any obvious stones larger than 2 mm, twigs, etc. and place in an “Oversized material” bag

1. Hand-disaggregation: This can be the fastest and easiest way to disaggregate small amounts of soft, semi-cohesive materials such as sandy and loamy soils. However, human fingers quickly tire with the continuous pressing and rolling motions required by hand disaggregation. Repetitive motion injury is also a concern.
2. Hands must be gloved (powder-free) whenever handling soil.
3. Hand disaggregation can be accomplished by massaging through the plastic bag containing the soil.
4. If there is a large amount of soil being processed in the bag, empty the bag contents into a pan for inspection to make sure no agglomerates were missed.
5. Rolling pin: This option works well for soils able to be disaggregated by hand, but will be less tiring. Some soils may be rolled while still the original plastic bag; others can be rolled in a new bag. Either way, samples will need to be emptied into a pan for inspection to make sure disaggregation was complete.
    a. If rolled in a pan, make sure the pan is very shallow or is wide enough to accommodate the length of the rolling pin, so that the handles are unobstructed.
    b. If larger stones, sticks, or anything sharp is present, remove them from the bag so they cannot interfere with the rolling pin or punch a hole in the bag. (Anything larger than 2 mm will eventually be removed anyway.) The plastic bag can be lined with butcher paper to protect against sharps punching through the bag.
        - This technique might not be effective for hard clay agglomerates which could skitter away from the pressure.
        - If a rolling pin is used on soil that is outside of an enclosed bag, care must be used to avoid “popping” particles out of the sample. Lay sheets of butchers’ paper above and below the soil layer to be rolled. Fold, tuck and/or tape the edges, so the material is completely enclosed and contained.
6. Rubber mallet: Used to break up hard clods and small groups of particles while soil is in a heavy plastic bag or another enclosure, such as the butchers’ paper described above. Remove all excess air from the bag prior to disaggregation, and strike the bag repeatedly in a pattern that contacts all area of the bag, turning the bag over occasionally. Use the minimal amount of force necessary to disaggregate particles so

the bag does not perforate. The grinding action of particle-to-particle contact will break up small clods effectively.

9.4 Disaggregation quality control

The first five samples to be disaggregated should have the completeness of the disaggregation procedure(s) verified. This is discussed under Section 10 - Sieving. If disaggregation is 95% or more complete after the first round of disaggregation and sieving for all five samples, this QC check can be discontinued. However, it may be performed at any time at the discretion of the operator based on observations of sample matrix characteristics.

A notation for how many extra rounds of “disag/siev” are used for any particular sample should be made in the “Notes” section of the mass recording sheet mentioned in Figure 2.

A calculator has been developed to assist with the calculations for multiple rounds of “disag/siev”. Record the information on a log sheet such as the one provided in the attached Excel file (*Procedure 1-3 ISM Sample Prep Tools and Forms.xlsx*).

10.0 Sieving

Sieving is used to obtain the desired particle size that will undergo analysis. A sieve of a given mesh size allows particles to pass through if at least two of the three dimensions that are smaller than the mesh size. The desired particle size for an investigation is based on exposure risks, site conditions, contaminant of concern, etc. and should be determined prior to sample collection. Refer to the QAPP for site-specific sieving goals.

The process of establishing the 200-ppm Pb boundary will use soil samples sieved to 10-mesh (<2 mm particle size) to expedite sample processing. Once located, confirmation of the 200-ppm boundary will use the <100-mesh (<150 µm) soil particle size fraction. (Refer to http://www.sigmaaldrich.com/chemistry/stockroom-reagents/learning-center/technical-library/particle-size-conversion.html for more information about sieve sizes.) If multiple fractions will be sieved, stack the sieves by fitting the smallest sieve onto the bottom collection pan.

1. Fit the desired mesh sieve (10- or 100-mesh) on top of the bottom collection pan. Then fit the lid onto the top of the desired mesh sieve.
    a. A 10-mesh sieve has a nominal 2-mm opening. Particles larger than 2 mm do not meet the definition of “soil” for chemical testing purposes. (USDA NRCS Soil Survey Field and Laboratory Methods Manual Soil Survey Investigations, page 75) So material retained by the 10-mesh sieve should not be included in samples intended for chemical analysis. This material is saved in a bag designated for “oversized” materials.
    b. The 100-mesh sieve is used to isolate the target soil particle size which is relevant to exposure pathways. For the Wilcox Site, both the 10- and 100-mesh sieves will be used.
2. If shaking the sieve stack is done by hand, it is easiest to judge completeness of the sieving by periodically removing the bottom pan and pouring the contents into the plastic bag in which the sample will be analyzed by XRF. (Do this over clean foil or butcher paper to catch any escaping particles, such as those falling through the bottom sieve while the collection pan is off the stack. Return such particles to the sample.) When no more appreciable amounts of small particles come through with additional shaking, the sieving is done.

3. A sieve shaker is much more efficient and much less labor-intensive than hand-shaking and is recommended for any study with more than a few samples. A tall shaker may be able to accommodate two stacks at a time. Sieving generally requires less than ten minutes. The time used for sieving should be recorded on a form or log book. An example is provided in the attached Excel file (*Procedure 1-3 ISM Sample Prep Tools and Forms.xlsx*).
4. Over clean butcher paper or aluminum foil, empty sieves into their appropriate labeled plastic bags: the >10-mesh fraction goes into a storage bag, the other sieved fractions go into small "XRF read bags." Use the exact kind of bag for tare.
5. Weigh and record the total mass of material retained on the sieve(s).
6. Weigh and record the total mass of material that passed through the 100- mesh sieve into the bottom pan.

10.1 Sieving disaggregation quality control

Until ease of disaggregation for these soils is known, check to ensure that disaggregation was complete. This is done by examining the material retained on the fine fraction screen (>10- or >100-mesh) soil material for soil clods remaining after the first sieving round. Record the information on a log sheet such as the one provided in the attached Excel file (*Procedure 1-3 ISM Sample Prep Tools and Forms.xlsx*)

For the first five samples processed, automatically perform a second round of disaggregation and sieving as QC no matter what is observed.

1. If the newly recovered fine material (i.e., <10- or <100- mesh soil fraction) is 5% or less of the fine soil mass produced in the first sieving, disaggregation and sieving are considered complete.
2. Add whatever new fines are recovered to the XRF read-bag, re-weigh and record the final weight. If the newly recovered fines are >5% of the fines produced in the first sieving, disaggregation was incomplete in the first round.
3. If the newly recovered fines are <10% of the initial mass, add the new material from the second round into the XRF read bag, and put more effort into thorough disaggregation for subsequent samples. A third round of disaggregation and sieving on this sample is not needed.
4. If improved disaggregation completeness for subsequent samples is demonstrated (i.e., <5% new fines are produced in the second round of disaggregation and sieving) on five samples in a row, the QC (i.e., second) round of disaggregation and sieving can be discontinued for subsequent samples.
5. However, the completeness of disaggregation should still be assessed after the first disaggregation and sieving round for EVERY sample by examining the >10- or >100-mesh material for remaining clods. Perform a second round of disaggregation and sieving if incompletely disaggregated material is present.

If the newly recovered fines are >10% of the initial fines mass, add the fines recovered from the second round to the XRF read-bag, then perform a third round of disaggregation and sieving.

1. Verify that the fines recovered from the third round are <5% of the original mass of fines. Make concerted efforts to improve disaggregation.

2. Repeat disaggregation QC checks until five samples in a row produce <5% new fines after a second round of disaggregation and sieving, as discussed above.

A calculator tool (QC Check on Disaggregation Completeness) has been developed to assist with determining the need for multiple rounds of disaggregation and sieving. See Excel File Procedure 1-3 ISM Sample Prep Tools and Forms.xlsx for the calculator tool.

QC Check on Disaggregation Completeness Tool

No.	Sample ID	Mass of fines recovered from 1st sieving (g)	5% of initial fines mass (g)	10% of initial fines mass (g)	Mass of fines recovered from 2nd sieving (g)	Another round needed? (Yes or No)	If yes, just re-enter the sample ID on another line. Note if a sample is redone based in observation.
1			0	0			
2							
3							

Figure 3: Disaggregation Completeness tool

If extra rounds of disaggregation and sieving are used for any particular sample, make a notation in the "Notes" section of the mass recording sheet (Figure 2).

11.0 Bagging

The oversized fraction (>10-mesh and other non-soil material) goes into separate labeled storage bags.

- Labeling will be done by hand using a permanent marker. Adhesive sample labels will change the weight of the bag. If adhesive labels are desired, they can be added after weighing is completed.
- All information on the original sample bag should be duplicated on the 2 storage bags, except that the processors' initials should go on these 2 bags rather than the collection team initials.

The <10 and<100-mesh fractions go into the approved and tested XRF read bags.

- Labeling of the read bags must not interfere with taking XRF readings over the bag. Label these bags at, or near, the top of the bag. Do not write on more than the top one-quarter (1/4th) of the bag length from the bag opening.
- Take care not to dent or create crinkles in the read bags.

All sample fraction bags should be stored together in the original bag (or a similarly labeled replacement bag).

12.0 Reprocessing Samples

Some samples may require reprocessing if disaggregation and sieving did not meet project or QC requirements. Reprocessed samples should be clearly identified on the sample bag label and the specific activities related to re-processing (additional drying, disaggregation, sieving) should be noted in the forms and log books.

13.0 Tools and Forms

This Procedure includes four Tools and Forms as worksheets in an Excel file (*ISM Sample Prep Procedure Tools.xls*):

- Disaggregation Completeness tool (*Disaggregation QC tool*)

- Example Master Sample Table (*Master Sample Table*)
- Example Sample and Fraction Masses data entry table (*Sample Fraction Table*)
- Sieve and drying time log (Sieve and Drying Log)

Wilcox ISM Procedure 01.4.0- Subsampling and Analysis for Comparability Assessment

This Procedure contains seven sections:

1.0 Purpose
2.0 Application
3.0 References
4.0 Associated Procedures
5.0 Equipment
6.0 Decontamination
7.0 Procedure

1.0 Purpose
This procedure provides the instructions to be used for subsampling bags of prepared soil for paired Inductively Coupled Plasma (ICP) analysis, and for other analyses performed by others. The process of selecting bags to subsample, creating the subsample, and analyzing the subsample with the XRF is covered.

2.0 Application
This procedure is part of a series of XRF procedures developed by the USEPA HQ Office of Superfund Remediation and Technology Innovation (OSRTI) Technology Innovation and Information Branch (TIIB). It is written for comparability with traditional lab analyses specifically for the Wilcox site (Pb by ICP), but the process can also be applied to preparing any small subsample that is required for analysis for comparisons to be performed by others. This is a subordinate XRF procedure, which provides operational details for procedures discussed in XRF Procedure 01.0. These procedures contain appendices that provide explanations of concepts and activities to round out an operator's understanding of the "why" behind the procedure.

3.0 References

None

4.0 Associated procedures
- ISM Procedure 1.3: ISM Sample Processing
- XRF Procedure 01: General XRF Operation and Maintenance (*under development*)
- XRF procedure 01.1: Operation of the TIIB Niton XL3t GOLDD+ Ultra (*under development*)
- XRF procedure 01.3: Taking XRF Readings on Soil in Plastic Bags
- XRF Procedure 02: XRF Quality Control and Data Validation
- XRF procedure 02.1: The Instrument Evaluation Period
- XRF procedure 02.1.1: Assessing Instrument Precision and Bias
- XRF Procedure 02.1.2: Creating and Using XRF Control Charts
- XRF Procedure 02.1.3: Using the XRF Bag Checker and Calculator Tool

- XRF Procedure 02.1.4: Converting a Spreadsheet into a Readable PDF File *(under development*)
- XRF Procedure 02.2.2: Establishing Comparability between Paired XRF and ICP Data Sets (*under development*)

5.0 Equipment

- XRF instrument (Niton XL3t GOLDD+ Ultra, or equivalent), power cords and data transfer cables
- Laptop or desk computer with Excel software installed
- Balance with sensitivity of 0.01 gram
- XRF read bag (interference free)
- Lab logbook
- Heat sealer
- Permanent marker

6.0 Decontamination

Sample analysis is conducted on samples contained in a plastic bag and generally there should be no need for decontamination of the XRF in a laboratory setting. However, in some instances bags will leak or dust may accumulate on the instrument or stand and will require removal with a laboratory wipe or puff of air.

7.0 Procedure

7.1 Introduction

Data comparability is based on the concept of “equivalence.” In the context of the Wilcox Site, the most relevant issue is comparability between the results for the target metal, Pb by XRF and traditional laboratory techniques (ICP) that are preceded by a partial digestion procedure. Briefly, XRF has the ability to measure all of these target metals present in the soil matrix interrogated by the XRF’s X-ray beam. In contrast, analysis by traditional laboratory methods often uses a digestion procedure that extracts the more soluble metals out of the soil into a liquid that can be injected into the instrument for quantitation.

If both the XRF and the destructive method analyze the exact same soil mass, XRF and the other data would be directly comparable if all of the Pb atoms present in that soil mass were completely solubilized. However, the solubilization procedures (per SW-846 Method 3050B for ICP) that will be used for laboratory analysis of metals in this study may not fully solubilize metal atoms that are tightly held in mineral matrices. Therefore, the degree of comparability between paired XRF and ICP data depends on what fraction of metals in an analytical sample are solubilized by the digestion procedure. Since that depends on how tightly metals are bound in mineral particles, comparability depends to some degree on what form metals were in when released, and how long they have been present in the soil undergoing weathering and mineral remodeling.

The degree of comparability between XRF and ICP data is usually assessed using regression analysis. The slope of the regression is a measure of the comparability between the two data sets, which is another way of saying that the slope (which is nearly always less than 1.0 for contaminated soils) represents the fraction of total metals solubilized averaged over all the individual sample pairs in the data set. For example, a slope of 0.92 reflects an average of 92% solubilization in that group of samples, as long as precision in the regression data set (which is measured by the R^2) is high.

A complication for comparability analysis on real soils is the high degree of within-sample heterogeneity evinced by high variability (imprecision) in replicate soil analyses from the same sample using the exact same analysis procedures. For a comparability analysis to be reliable, within-sample variability (can also be referred to as “subsampling error”) must be low.

7.2 Perform the Subsampling

Selected samples will be subsampled to produce analytical subsamples for ICP analysis. The target mass is 2 grams, because this is a minimum amount of soil needed for proper interaction with the X-ray beam and an accurate XRF analysis. This procedure assumes that one subsample is required but can be adapted if more are required for project specific applications.

A sample bag having a targeted Pb concentration will be subsampled in the following manner (see also the photos at the end of this section):

1. Thoroughly mix the sample bag by rotating in a vertical plane.
2. Carefully open the sample bag.
3. Tare an empty XRF read bag containing a narrow tube that had been created with a heat sealer (Figure 1) and allow it to remain on the balance.
4. Reach into the sample bag with a small scoop and dip the scoop repeatedly into the soil surface 4 to 5 times, adding a tiny amount of soil to the scoop with each dip.
5. When a small amount (about 0.25 g) of soil has been accumulated on the scoop, carefully deposit the scooped soil into the narrow tube in the bag.
6. Using the scoop, move the soil in the sample bag around to expose a new surface, and repeat the subsampling procedure to add soil incrementally to the bag on the balance. Monitor the progress on the balance up to ~2 grams (Figure 2).
7. When the target mass is reached, close up the sample bag. Record the mass of Subsample A in the lab logbook to as many digits as available from the balance.
8. Express excess air from the tube of the read bag, and heat seal across the top of the tube to ensure soil will not escape from the tube into the rest of the bag. Allow sufficient space in the tube to mix the subsample.
9. Use a permanent marker to write the exact subsample mass on the empty part of the bag, or on prepared labels that are affixed to the bag after weighing.

Figure 1. “Subsample tube” prepared in an interference-free sandwich “read” bag using a heat sealer.

Figure 2. Packing of soil in the tube of the read bag to make a sufficiently thick “pillow” for accurate XRF analysis.

7.3 Analyzing the Subsample

Analyze the subsample in the same manner as bagged samples (refer to XRF Procedure 01.3) and using the XRF-RTeX worksheet corresponding to the parent sample. The XRF subsample results for each of the target analytes are entered into special data boxes adjacent analyte data boxes for the parent sample.

1. Tap the read bag tube to pack the soil into the bottom of the tube to create as thick a “pillow” as possible. Fold the bag if necessary to maintain the “pillow.” A weight can be placed on top of the bag to maintain the folded configuration.
2. Use the XRF’s camera (if available) to make sure the tube’s soil layer is squarely on the XRF detector. Ensure that the XRF is shooting through only a single plastic layer!
3. Take 2 readings on each side, moving the tube slightly between each of the 2 readings to get independent readings, and enter into the XRF-RTeX form. Evaluate whether more readings are needed to achieve a tight confidence interval (ideally +/- 15% of the tube’s mean).

4. If readings seem to fluctuate excessively, consider whether the “pillow” is consistently as thick as possible. Pillows that are too thin when a reading is take may allow inconsistent interaction of the X-rays with the soil matrix.
5. Take readings for all subsamples (Subsamples A and B in this example).
6. Compare the concentrations of the subsamples to the parent bag concentration to ensure they all in the same concentration bin.
7. Submit the XRF-analyzed subsample for the intended alternate analytical method (e.g., ICP). The technician will cut the bag to pour out the subsample for extraction or digestion. If static charge causes significant amounts of small particles to be retained in the tube, flushing of the tube with the extraction fluid may be needed to retrieve them.

Wilcox Procedure 1.6- Incremental Sample Collection with Soil Probes

This Procedure contains eight sections:

1.0 Purpose
2.0 Application
3.0 References
4.0 Associated Procedures
5.0 Equipment
6.0 Decontamination
7.0 Collecting a Soil Sample
8.0 Tools and Forms

1.0 Purpose

The purpose of this Procedure is to provide information for how to collect Incremental Composite Samples (ICS) samples from depths up to 2 feet using a small diameter soil sampling probe to obtain a representative sample from a sampling unit (SU) or decision unit (DU).

2.0 Application

This Procedure applies to the collection of ICS soil samples for real-time XRF analysis. The procedure allows for samples to be collected from discrete intervals (e.g., 0 to 6 inches, 6 to 12 inches, 12 to 18 inches and 18 to 24 inches) or as a composite across the entire probe length (2 feet). This procedure assumes that the samples will be sieved for analysis of fine particle fractions for exposure assessment using XRF or similar analysis. The sample collection procedures may be modified for use in other analytical methods.

3.0 References

U.S. Environmental Protection Agency. (2016a). Expedited Site Assessment Tools for Underground Storage Tank Sites: A Guide for Regulators. EPA 510-B-16-004. https://www.epa.gov/ust/expedited-site-assessment-tools-underground-storage-tank-sites-guide-regulators

U.S. Environmental Protection Agency. (2016b). Recommendations for Sieving Soil and Dust Samples at Lead Sites for Assessment of Incidental Ingestion. OLEM Directive 9200.1-128. July. https://semspub.epa.gov/work/HQ/100000133.pdf

4.0 Associated Procedures

- Procedure 01: Overview of ISM Sample Collection and Handling *(under development)*
- Procedure 01.1: Laying out the evenly-spaced triplicate grids for a DU *(under development)*
- Procedure 01.2: Incremental sample collection using a CMIST ("pogo-sampler")
- Procedure 01.4: Archiving samples after analysis *(under development)*

- Procedure 01.5: Determining Increment Spacing to Ensure Hot Spot Inclusion in Incremental Samples *(under development)*
- Procedure 1.7: Non-disposable Equipment Decontamination

5.0 Equipment

- Sample location map
- Logbook
- Permanent marker
- Camera
- Personal Protective Equipment (e.g., lab coats, eye protection, respiratory protection), as directed by the lab's Health and Safety Plan.
- Chain of Custody records and custody seals
- Field data sheets
- Survey equipment or global positioning system (GPS) to locate sampling points
- Tape measure
- Survey stakes or flags
- One-gallon heavy duty zip close plastic bags
- Large stainless steel bowl or plastic 5-gallon bucket
- Cooler(s) or bin for transporting samples
- Small stainless steel spatulas, spoons or Teflon rods for removing sample from probe
- Tally counter (optional)
- Decontamination supplies/equipment
- Thin wall tube sampler
- Extra tips for sampler
- Soil core catchers
- Wrenches for disassembly of sampler
- T-handle
- Drive hammer (slide hammer, fence post driver, electric or pneumatic)
- Foot jack for removal of sampler

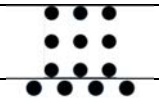
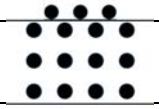
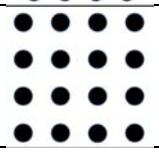
6.0 Decontamination

All non-disposable equipment that comes in contact with the soil sample will be decontaminated. Decontamination procedures will be followed in accordance with Wilcox Sample Collection Procedure 1.7 Non-disposable Equipment Decontamination.

7.0 Collecting a Soil Sample

Samples collected using ICS methodology contain multiple increments collected over a pre-defined area at a pre-defined depth. The procedures below describe how to locate a sample, collect the sample, and prepare the sample for transport to the analytical team.

SUs include multiple increments collected over a relatively small area to reduce the effects of small scale heterogeneity of soil contamination. Example SU sizes are shown in the table below.

Number of increments	Sample Area Dimensions	Arrangement
9	2 foot by 2 foot	
12	2 foot by 3 foot	
16	3 foot by 3 foot	

The sampling equipment consists of pre-cleaned sample collection device such as a corer (or probe), core tips, and a driving device (slide hammer, fence post driver or powered hammer drill). For shallow samples (6 inches) the T-handle can be used to push the sampler. Examples of sampling equipment are shown in the figures below from *EPA Expedited Site Assessment Tools for Underground Storage Tank Sites, A Guide for Regulators, October 2016, EPA 510-B-16-004.*

a) Manual hammer

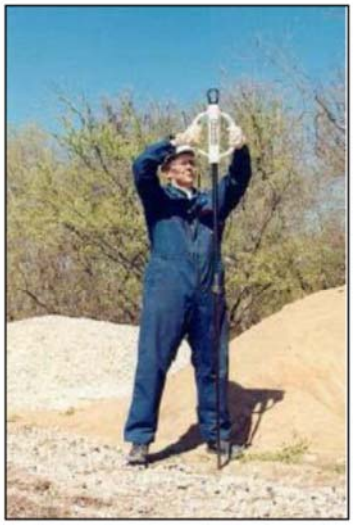


Image courtesy of and reprinted with permission of Geoprobe Systems®.

b) Hand-held mechanical hammer

Reprinted from http://www.terraprobeenvironmental.com/specialty-sampling.htm with permission of Terra Probe Environmental, Inc.

For the Wilcox site, sampling will be performed with a small diameter, thin-walled, hand driven sampling probe capable of collecting a sample at a maximum depth of 2 feet. The dimensions of the core barrel define the volume and depth interval of sample collection. For the Wilcox site, a one-inch diameter by 24-inch long sampler with a replaceable tip (shown below) will be used to collect the required sample volume for ICS samples.

Image from AMS, Inc. catalog, part number 425.52

The approximate maximum soil mass for various sample support is shown in the table below.

Sample interval	SU with 9 increments	SU with 12 increments	SU with 16 increments	DU with 30 increments
0 to 6 inches	0.85 kg	1.1 kg	1.5 kg	2.8 kg
6 to 24 inches	2.5 kg	3.4 kg	4.5 kg	8.5 kg*

Assumptions: ID of corer is 7/8 inch (2.2cm); soil density = 1.6 g/cc; full volume of sample from all increments is collected.
*DU sample mass will be reduced as described in section 7.2 u below.

7.1 Locating the Sample Points

The coordinates of an SU or boundaries of a DU must be precisely located in order to accurately represent the concentration of the area sampled. If DQOs state that a high level of precision is required for defining areas of contamination, each SU should be located at its center with a survey-quality GPS and the boundaries of each DU should be mapped with survey quality GPS. A high precision survey might be required if the area is to be re-occupied for additional sampling or excavation. High precision sample locations may be required if sample data will be used in GIS or mapping applications. In many cases the location of SUs and DUs can be approximated based on the distance and direction from permanent cultural features such as USGS or other surveyor benchmarks, permanent monitoring wells, fire hydrants, building corners, or other permanent cultural features.

At the Wilcox Oil site, a combination of pre-defined sample locations and field-defined sample locations will be used as described in the QAPP. For SUs at the Lead Sweetening Area, the two high concentration samples and innermost sampling points of each traverse will be predefined and located in the field using GPS. The orientation of each traverse is predefined and will be marked in the field using GPS. Samples along each traverse will be selected based on field decisions and located from the innermost sample point using a tape measure and surveyed with GPS after all samples have been collected. Opportunistic samples (between traverse lines, and other locations selected by the field team) will be flagged and surveyed after the samples have been collected.

For DUs at the Lead Sweetening Area, the edges of the DU will be surveyed to provide a high precision identification of the 200 mg/kg boundary and facilitate accurate re-occupation of the area for excavation. The location of incremental sample points within the DUs will not be recorded.

No predefined sample locations have been identified for the Ethyl Blending Area. All samples will be based on visual observations in the field, and results of XRF analysis of adjacent samples. For SUs at the Ethyl Blending Area, sample locations will be marked with flags bearing the sample ID. Locations will be measured from the nearest building corner and recorded in the field book. For DUs at the Ethyl Blending Area, the edges of each DU will be measured from

building corners and marked with flags. All SU locations and DU boundaries will be surveyed with GPS after all samples have been collected.

7.2 Collecting the Sample

Sample protocols for SUs and DUs are similar but vary slightly due to the area over which the sample is collected.

Sampling SUs

Once the sampling point has been located, multiple increments of soil will be collected from a pre-defined area around the point, and over pre-defined depth. This procedure can be applied to collecting the 0 to 6-inch sample, or the 6 to 24-inch sample.

1. Don appropriate PPE.
2. Inspect the ground surface around the sample points and record the conditions. Note any evidence of waste (crystals or discoloration). If necessary, adjust the location to avoid large rocks and debris. Remove any vegetation and debris that will interfere with sample collection.
3. Mark the edges of the sample area with rope or twine, or use tape measure to ensure the sample is collected over the correct area. The location of the sample points within the SU is not critical but should be evenly spaced.
4. Assemble the sample probe. If the 24-inch sample probe is to be used, mark the 6-inch, 18-inch, and 24-inch points on the sample probe for reference. Attach the drive mechanism or T-handle to the top of the sample probe. If the R4 surface sampler will be used, follow the instructions provided by R4 for preparing the sampler for use.
5. Collect the samples as described below using a tally counter or other technique to ensure the correct number of increments are collected.
6. Place the sampler at the first increment location and drive the sampler to 6 inches.
7. Remove the sampler by gently pulling up. Place the 0 to 6-inch sample into a large container (stainless steel bowl or 5-gallon plastic bucket).
8. Collect the remaining increments for the 0 to 6-inch sample in a similar manner and place all increments into the large container.

If deeper samples are required (up to 24 inches), continue sampling using the following procedure.

9. Place the 24-inch soil probe sampler into the same hole used for 0 to 6-inch sample and drive the sampler to the desired depth (24 inches). The probe should recover 18 inches of soil.
10. Remove the sampler by gently twisting and pulling straight up. Be careful to avoid bending or vibrating the probe, as this will loosen the sample in the probe and it may fall out. Bending may damage or break the probe. It may be necessary to gently rock the probe from side to side to reduce friction and ease retrieval. If the probe is wedged tightly, use a probe retrieval jack to remove the sampler.
11. Note the volume of soil in the sampler. If the sampler is less than 75% full (approximately 13 inches of soil) try to recollect the sample. If recovery is still less than

75%, note this in the field book with an explanation of what interval was most likely collected.

12. Extrude the sample into a large container (stainless steel bowl or 5-gallon plastic bucket) using a push rod, spatula, or other device, being careful not to lose sample volume. Make sure the soil in the probe tip is removed.
13. If samples from specific depth ranges are to be collected (i.e. 6 to 12 inches, 12 to 18 inches, 18 to 24 inches), carefully extrude or scrape each interval into separate bowls or buckets marked with depth ranges.
14. Collect the remaining increments in a similar manner and place all increments for the sampled depth range into the large container.
15. Fill all holes with excess soil or native soils, if required. Reseed if required.

<u>Sampling DUs</u>

1. Don appropriate PPE.
2. Mark the perimeter of the DU with flags, stakes or other tools.
3. Inspect the ground surface around the sample points and record the conditions. Note any evidence of waste (crystals or discoloration).
4. Mark the 30 incremental sample locations within the DU using flags or other markers. Avoid debris, obstacles and rocks. For efficiency, this step may be omitted if the DU is small and relatively square or sampling points can be regularly spaced visually.
5. Follow steps 4 through 12 above.
6. Since the sample mass for DUs can be excessive (greater than 8 kg), collect only a representative portion of the entire core length (approximately 1/3). This can be done by collecting only the exposed part of the soil in the probe and scooping approximately half of the material from the probe tip. The figure below shows a soil probe with the exposed part of the soil core removed.

Image from Ontario Ministry of Agriculture, Food and Rural Affairs website

7. If samples from specific depth ranges are to be collected (i.e. 6 to 12 inches, 12 to 18 inches, 18 to 24 inches), carefully scrape each interval into separate bowls or buckets marked with depth ranges.
8. Collect the remaining increments in a similar manner and place all increments for the sampled depth range into the large container.
9. Fill all holes with excess soil or native soils, if required. Reseed if required.

Sample Collection Considerations

Refer to the table below for additional sampling considerations

Issue	Possible cause	Possible resolution
Sample falls out of probe	Sandy, dry or non-cohesive soil	Install a plastic soil core catcher in the sampler tip: Collect multiple samples from smaller intervals in the same hole. Drive sample deeper into cohesive soils and discard the lower depths intervals. Use a different sampler or sample tip that will retain the sample better.
Sample probe cannot be advanced to total depth	Obstruction/debris, tight soils, dense clay	Check sample tip for damage or obstruction. Clean or replace tip and retry sample. Collect multiple samples from smaller intervals in the same hole.
Sample probe cannot be removed from hole	Differential pressure on exterior of probe; probe wedged between rocks	Gently rotate probe with T-handle and rock probe in a circular motion to loosen soil. Leave probe in hole until all other increments are collected and loosen soil around probe with shovel or another sampler.
Deep samples (6 to 24 inches) contain more than 18 inches of sample	Material from the top 6 inches of the hole is falling in.	Discard the top of the sample (anything greater than 18 inches) Use the 24-inch sampler from 0 to 24 inches and discard the top 6 inches of sample. Protect the upper part of the hole from falling in using a short section of PVC pipe as casing.

7.3 Bagging the Sample

After all sample increments have been collected remove any vegetation and large rocks or debris. Place the composite increments into a plastic bag labeled with the sample ID and sample depth. Place the bag in the cooler.

8.0 Tools and Forms

This Procedure includes one form:

- Field Sample Form

Wilcox Procedure 1.7- Non-disposable Equipment Decontamination

This Procedure contains six sections:

1.0 Purpose
2.0 Application
3.0 Associated Procedures
4.0 Equipment
5.0 Decontamination Summary
6.0 Decontamination Procedure

1.0 Purpose
The purpose of this Procedure is to provide field personnel with a description of the methods used for preventing cross-contamination between sampling unit (SU) and decision unit (DU) incremental composite samples by properly decontaminating any non-disposable equipment that comes into contact with potentially contaminated soil.

2.0 Application
This Procedure applies to the collection of ICS soil samples for real-time XRF analysis. This procedure should be used by field personnel responsible for the decontamination of field equipment and sampling tools.

3.0 Associated Procedures
- Procedure 01: Overview of ISM Sample Collection and Handling *(under development)*
- Procedure 01.1: Laying out the evenly-spaced triplicate grids for a DU *(under development)*
- Procedure 01.2: Incremental sample collection using a CMIST ("pogo-sampler")
- Procedure 01.4: Archiving samples after analysis *(under development)*
- Procedure 01.5: Determining Increment Spacing to Ensure Hot Spot Inclusion in Incremental Samples *(under development)*
- Procedure 01.6: Incremental Sample Collection with Soil Probes

4.0 Equipment
- Nitrile gloves and other PPE
- 5-gallon buckets
- Polyethylene sheeting
- Scrub brushes (dedicated wet and dry)
- Approved decontamination water (i.e. distilled, deionized, potable)
- Detergent (Alconox)
- Aluminum foil

5.0 Decontamination Summary

Removing or neutralizing contaminants from equipment minimizes sample cross-contamination and reduces the likelihood of transfer of contaminants to clean areas. This procedure should be followed after all of the sampling of an individual SU or DU has been completed and the field personnel are ready to begin sampling a new SU or DU. There is no need to decontaminate

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Wilcox XRF Procedure 1.3- Taking XRF Readings on Soil in Plastic Bags

This Procedure contains twelve sections:

1.0 Purpose
2.0 Application
3.0 References
4.0 Associated Procedures
5.0 Equipment
6.0 Decontamination
7.0 XRF Quality Control (QC)
8.0 Using the XRF Logbook
9.0 Using the XRF-RTeX Form
10.0 Sample Inspection
11.0 XRF Readings on Full Bagged Samples and Data Recording
12.0 Tools and Forms

1.0 Purpose

The purpose of this Procedure is to provide information for how to take measurements of metal concentrations in soils using a handheld XRF. This Procedure is part of a series of XRF Procedures developed by the USEPA HQ Office of Superfund Remediation and Technology Innovation (OSRTI) Technology Innovation and Information Branch (TIIB) to support the use of XRF as a real-time data collection tool.

2.0 Application

This Procedure provides the procedure to be used for taking XRF readings on soil samples while the soil is contained within a plastic bag. This Procedure assumes the sample has been processed in accordance with *Sample Collection Procedure 1.3 Incremental Composite Sample Processing*. The measurement procedure described in this Procedure requires multiple XRF readings of the same sample and results in a sample concentration and the statistical support for the confidence of that value. The method can be used for any metal that can be detected with the XRF.

For some projects a subsample of the bagged sample will be collected after the full bagged sample measurements are made. These samples may be sent to another laboratory for comparative analysis or analysis of different parameters. Subsample analysis procedures are provided in *XRF Procedure 1.4 Subsampling and Analysis for Comparability Assessment*.

This Procedure is specifically developed for the Niton XL3t GOLDD+ Ultra when used with the sample stand and attached to a laptop computer. Other models of handheld XRF tools will operate in a similar manner, but some modifications to this Procedure may be required.

3.0 References

Thermo Fisher Scientific, 2010. Niton Analyzers, XL3 Analyzer User's Guide. Version 7.0.1 Revision C, November.

4.0 Associated Procedures

This Procedure is subordinate to *XRF Procedure 01: General XRF Operation and Maintenance* which provides operational details for operating and maintaining and XRF analyzer for soil sample analysis.

- ISM Procedure 01.3: Incremental Composite Sample Processing
- XRF Procedure 01: General XRF Operation and Maintenance (*under devlopment*)
- XRF Procedure 01.1: Operation of the TIIB Niton XL3t GOLDD+ Ultra (*under devlopment*)
- XRF Procedure 01.4: Subsampling and Analysis for Comparability Assessment
- XRF Procedure 02: XRF Quality Control and Data Validation
- XRF Procedure 02.1: The Instrument Evaluation Period
- XRF Procedure 02.1.1: Assessing Instrument Precision and Bias
- XRF Procedure 02.1.2: Creating and Using XRF Control Charts
- XRF Procedure 02.1.3: Using the XRF Bag Checker and Calculator Tool
- XRF Procedure 02.1.4: Converting a Spreadsheet into a Readable PDF File

5.0 Equipment

- XRF instrument (Niton XL3t GOLDD+ Ultra, or equivalent), power cords and data transfer cables
- XRF instrument sample stand
- Laptop or desk computer with XRF instrument-specific data collection and management software installed
- QC Check materials
    - Laboratory control samples (LCS) in sample cups
    - Silica blank
- LCS control charts
- XRF Logbook

6.0 Decontamination

Sample analysis is conducted on samples contained in a plastic bag and generally there should be no need for decontamination in a laboratory setting. However, in some instances bags will leak or dust may accumulate on the instrument or stand and will require removal with a laboratory wipe or puff of air.

7.0 XRF Quality Control (QC)

This section outlines the quality control check schedule for the XRF equipment. Refer to the QAPP for a site specific QC check schedule if work periods are different than the normal working day. This schedule assumes instrument start-up around 7:30 – 8 am and end-of-day shut-down at 4:30 – 5:30 pm.

Quality control is essential to ensure readings are useable for decision making. *XRF Procedure 02: XRF Quality Control and Data Validation,* and the subordinate Procedures provide requirements for assuring the instrument is operating properly. The steps below summarize the quality control measures required for proper XRF operation.

7.1 Morning instrument start-up:

1. System check (performed by the instrument/software) or energy calibration
2. 99.995% silica blank (verify non detects (NDs) for target analytes) for first day of operation at a new location or as needed
3. Other CRM cups for which data is being collected

7.2 Mid-morning:

1. All LCSs (plot target analytes on LCS control charts) if a large number of samples are run

7.3 Mid-day (just before mid-day break)

If the instrument will be in continuous use the entire day, at mid-day perform the following before continuing to another batch of samples:

1. All LCSs (plot target analytes on LCS control charts)
2. Instrument duplicate (a sample from the previous day)
3. Other CRM cups for which data is being collected

If the instrument will be idle more than 20 minutes during lunch, run all LCSs, then shut-down the instrument before leaving for lunch. Restart after lunch break and run:

1. System check or energy calibration
2. All LCSs (plot target analytes on LCS control charts)
3. Other CRM cups for which data is being collected

7.4 Mid-afternoon:

1. All LCSs (plot target analytes on LCS control charts) if a large number of samples are run

7.5 End-of-day shut-down:

1. All LCSs (plot target analytes on LCS control charts)
2. 99.995% silica blank
3. Other CRM cups for which data is being collected (as time permits)

Note that all reported data must be bounded by in-control LCSs (see *XRF Procedure 02.1.2 Creating and Using XRF Control Charts* for specific QC requirements). Unexpected results from QC checks should be double-checked and investigated if the results are inconsistent with previous results and patterns. Trouble-shooting suggestions are provided in Procedure 02.1.2.

8.0 Using the XRF Logbook

Each XRF instrument will have a dedicated logbook (usually a bound composition book) for that instrument and project. The book will be clearly labeled on the front with the instrument model, name and serial number, project name (if a rental instrument is used for one specific project), start date of the log book, and contact information for the instrument owner. The purpose of the log book is to maintain a record of all instrument activities and unexpected conditions. The log book entries should be detailed enough to reconstruct the sequence of all instrument activities throughout the day. The instrument logbook is a critical part of XRF data validation. Use the logbook to communicate information that the XRF data validator will need to understand any problems with the data.

A logbook is dedicated to a single instrument. When the XRF instrument is owned (as opposed to rented), the logbook can be used for more than one project as long as there is capacity in the log book. Project-specific portions of a logbook should be scanned to provide the records that are kept with the project documentation files. The logbook itself (and any completed logbooks) should remain in the possession of the XRF's custodian as part of the maintenance documentation tied to that instrument.

When the XRF is being used a new logbook page is started at the beginning of each day or when a new operator takes over. Record the date, the operator's name, and any other relevant information. Record times for instrument start-up and shut-down. Any changes to the information in the log book shall be noted by a single strikeout line, and initialed by the person making them, along with date and time.

All XRF readings for LCSs, blanks, instrument duplicates and samples shall be legibly recorded in the logbook using permanent ink. At a minimum, logged data under a sample ID will include the following:

- Instrument reading # (automatically generated by the instrument for each measurement),
- Time of the reading (may be approximate, or only the first and last times for a particular sample can be recorded), and
- The reading value for each target analyte. Recording the instrument-reported error along with each reading is optional, but there should be consistency among the operators working on the same project. If a sample is non-detect, report the value as ND <LOD, where LOD is the level of detection reported by the instrument.

Allow blank lines between different samples in case additional readings or notes need to be added to that sample later.

Remember that another person may need to reconstruct what was being done. Record any unusual events, problems, trouble-shooting, or reasons for deviations from procedures. The entries in this logbook are vital for reconciling incorrect sample IDs or other types of conflicts for sample ID and meta-data entered via the instrument's menus and recorded in the XRF's raw data files and/or in the XRF-RTeX[1] form.

Periodically the pages of the logbook will be scanned into a pdf file to be shared with team members as needed and for archives.

9.0 Using the XRF-RTeX Form

The XRF-RTeX Form is an Excel spreadsheet used to record data, and evaluate and run statistics in real-time on XRF data collected from samples. The general set-up of the spreadsheet is shown in Figure 1 below for a project with two analytes.

The format for a sheet template is specific to the project data needs and must be set up before the sheet is used. A generic sheet has eight vertically stacked data entry blocks. Blocks are easily duplicated for customization of the data sheets. The worksheet can be modified to accommodate more analytes. In Figure 1 below the sheet is set up for analysis of lead and arsenic. To enable rapid data entry, color-coding can be used to distinguish different analytes from the same reading.

9.1 Basic Data Entry

Each tab in the Excel workbook represents a unique sample. The top part of each page provides general project, operator, and sample information and a summary of the calculated mean and other statistical information for each analyte. For each reading, the time, reading number, instrument measurement time duration, result, and instrument error for each analyte is

[1] RTeX - an XRF Real-Time Excel spreadsheet form used to record instrument readings and evaluate statistical attributes of XRF data from samples in real-time. Developed by OSRTI TIIB, and adaptable to the needs and analytes of specific projects.

recorded by the operator. Repetitive entries can be made to populate automatically to save time. Sheets for new samples in the same project can be made by duplicating the current worksheet and deleting the unique information. The spreadsheet automatically calculates the mean and standard deviation, as well as relative percent standard deviation, upper and lower confidence limits, and sampling and instrument error.

Project:	Colorado Smelter, Community sampling; DMA					
Property ID:	**FY1504**					
	<60-mesh particle fraction read					
Operator:	D. Crumbling					
Date:	18-May-2015					
As mean	**As UCL**	**As %RSD**	**Pb me**	**Pb UCL**	**Pb %RSD**	
14.0	17.3	24.8	45.0	49.1	9.7	

This sheet records XRF concentration results for DU bag

Read Bag lot = PO262010

DU or Bag ID: $1504-FY-1218-01 **Element: As**

Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrumt Result (ppm)	Instrumt Error (as 1 Std Dev)	Note?
Sample or Location ID =						
Replicate reading 1	1323	239	30	11.57	2.35	
2	1328	240	30	11.96	2.31	
3	1331	241	30	15.10	2.34	
4	1336	242	30	19.61	2.36	
5 (optional)	1340	243	30	11.68	2.46	
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	14.0		
			SD	3.47	**Tl %RSD**	24.8
			n =	5		
		ProUCL distribution =				
	2-sided	Smple 95% t-LCL =		9.7		
	2-sided	Smple 95% t-UCL =		18.3		
	1-sided	Smple 95% t-LCL =		10.7		
	1-sided	Smple 95% t-UCL =		17.3		
	1-sided Smple 95% Chebyshev LCL =			7.2		
	1-sided Smple 95% Chebyshev UCL =			20.7		
subsampling error =		18.15	instrument error =		16.91	as %RSD

DU or Bag ID: $1504-FY-1218-01 **Element: Pb**

Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrumt Result (ppm)	Instrumt Error (as 1 Std Dev)	Note?
Sample or Location ID =						
Replicate reading 1	1323	239	30	45.4	2.96	
2	1328	240	30	44.5	2.89	
3	1331	241	30	46.3	2.89	
4	1336	242	30	38.3	2.82	
5 (optional)	1340	243	30	50.4	3.11	
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	45.0		
			SD	4.35	**Tl %RSD**	9.68
			n =	5		
		ProUCL distribution =				
	2-sided	Bag 95% t-LCL =		39.6		
	2-sided	Bag 95% t-UCL =		50.4		
	1-sided	Bag 95% t-LCL =		40.8		
	1-sided	Bag 95% t-UCL =		49.1		
	1-sided Bag 95% Chebyshev LCL =			36.5		
	1-sided Bag 95% Chebyshev UCL =			53.5		
subsampling error =		7.15	instrument error =		6.53	as %RSD

Figure 1: General XRF-RTeX form

Pb mean	Pb UCL	Pb %RSD
186.3	190.9	2.1

Original Analysis/Bag ID: LSA-DUT1-2,1RA **Element: Pb**

Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
Replicate reading 1	0934	14	240	185.0	2.0	
2	0941	15	240	183.0	2.0	
3	0946	16	240	185.0	3.0	
4	0953	17	240	192.0	3.0	
5 (optional)						
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	186.3	LOD =	7.65
			SD	3.95	**Ttl %RSD**	2.1
			n =	4		
		ProUCL distribution =				
-2SD Lower bag limit		Mean - 2 SD =		178.4		
+2 SD Upper bag limit		Mean + 2 SD =		194.1		
	1-sided	Bag 95% t-LCL =		181.6		
	1-sided	Bag 95% t-UCL =		190.9		
	1-sided Bag 95% Chebyshev LCL =			178		
	1-sided Bag 95% Chebyshev UCL =			195		
subsampling error =		1.62	instrument error =		1.37	as %RSD

Duplicate Bag Analysis **Run by:** H. Gerard **Run date:** 5/16/2017

Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
For duplicate sample analysis (repeat analysis of same bag)						
Replicate reading 1	1020	23	240	191.00	3.00	
2	1025	24	240	192.00	3.00	
3	1031	25	240	188.00	3.00	
4	1038	26	240	189.00	3.00	
5 (optional)						

Figure 2: XRF-RTeX form specific to the Wilcox Site

9.2 Comparability Data

If analysis of subsamples for data comparability purposes is planned, calculation blocks of a sheet can be set up to accommodate XRF analysis of those subsamples, as shown below in Figure 3. The sheet can be adapted to accommodate many subsamples from a single bag. Subsample columns should be set up next to the primary sample columns on every sheet. When the initial analysis is performed, subsample columns can be “hidden” (Cells/Format/Visibility/Hide and Unhide) to reduce entry errors and scrolling the page. If a particular sample is later selected for subsampling and comparability analysis, the subsample columns can be “unhidden” for use.

If limits on the concentration difference between the subsample and the primary sample bag are required, these limits can be programmed into the statistical calculation lines for a calculation block below the primary data blocks.

DU or Bag ID: S1504-FY-0206-02 **Element: Pb**

Replicate Bag Readings	Date & Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
Sample or Location ID =						
Replicate reading 1	1422	254	30	367.7	6.8	
2	1424	255	30	337.2	6.5	
3	1427	256	30	346.4	6.7	
4	1430	257	30	350.5	6.7	
5 (optional)	1432	258	30	351.0	6.8	
6 (optional)	1435	259	30	344.7	6.9	
7 (optional)	1437	260	30	350.1	6.7	
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	349.7		
			SD	9.30	**Ttl %RSD**	2.66
			n =	7		
	ProUCL distribution =					
-2SD Lower bag limit		Mean - 2 SD =		331.1		
+2 SD Upper bag limit		Mean + 2 SD =		368.3		
	1-sided	Bag 95% t-LCL =		342.8		
	1-sided	Bag 95% t-UCL =		356.5		
	-10% limit	Mean - 10% =		314.7		
	+10% limit	Mean + 10% =		384.6		
subsampling error =		1.83	instrument error =		1.92	as %RSD

XRF on Comparability Subsamples

Operator: DMC **Run date: 2Jun15** **on TIIB XRF**

Subsample #1 Replicate Readings	Date & Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
Intended Lab Analysis:		ICP	MH0AL7			
Replicate reading 1	1354	385	30	369.0	6.7	
2	1357	386	30	339.2	6.4	
3	1401	387	30	357.4	6.6	
4	1403	388	30	340.3	6.4	
5 (optional)						
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	351.5		
			SD	14.35	**Ttl %RSD**	4.1
			n =	4		
	ProUCL distribution =					
	2-sided	Bag 95% t-LCL =		329		
	2-sided	Bag 95% t-UCL =		374		
	1-sided	Bag 95% t-LCL =		335		
	1-sided	Bag 95% t-UCL =		368		
1-sided Bag 95% Chebyshev LCL =				320		
1-sided Bag 95% Chebyshev UCL =				383		
subsampling error =		3.64	instrument error =		1.86	as %RSD

Figure 3: Data entry and calculations for a subsample sent for comparability analysis (the block on the right)

9.3 Sample Duplicates

Space for entering a duplicate analysis of a sample bag is provided immediately below the original data entry block in the RTeX form, as shown in Figure 4. The duplicate analysis block automatically performs a Student's t-test to assess whether the original and duplicate analyses are statistically equivalent. The outcomes of the t-test (the p-value and conclusion at the 95% confidence level) are automatically reported (contrast the lower portions of Figures 4 and 5).

Bag ID:				Element:	Pb	
Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
Replicate reading 1	0936	423	120	26.02	3.74	
2	0940	424	120	19.50	3.68	
3	0942	425	120	22.35	3.67	
4	0945	426	120	28.60	3.68	
5 (optional)						
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	24.1	LOD =	11.08
			SD	4.01	Ttl %RSD	16.6
			n =	4		
		ProUCL distribution =				
-2SD Lower bag limit		Mean - 2 SD =		16.1		
+2 SD Upper bag limit		Mean + 2 SD =		32.1		
	1-sided	Bag 95% t-LCL =		19.4		
	1-sided	Bag 95% t-UCL =		28.8		
	-10% limit	Mean - 10% =		21.7		
	+10% limit	Mean + 10% =		26.5		
subsampling error =		6.45	instrument error =		15.31	as %RSD

Duplicate Bag Analysis			By:	DMC	Run date:	7/16/2017
Replicate Bag Readings	Date & Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
For duplicate sample analysis (repeat analysis of same bag)						
Replicate reading 1	1300	589	120	20.42	3.69	
2	1303	590	120	29.29	3.78	
3	1306	591	120	23.69	3.70	
4	1309	592	120	24.60	3.71	
5 (optional)						
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	24.5	LOD =	11.16
Hypothesis Test for			SD	3.66	Ttl %RSD	15.0
Duplicate Agreement			n =	4		
T-test p-value =		ProUCL distribution =				
0.8926	2-sided	Sample 95% t-LCL =		18.7		
Dups DO agree	2-sided	Sample 95% t-UCL =		30.3		

Bag ID:				Element:	Pb	
Replicate Bag Readings	Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
Replicate reading 1	0936	423	120	26.02	3.74	
2	0940	424	120	19.50	3.68	
3	0942	425	120	22.35	3.67	
4	0945	426	120	28.60	3.68	
5 (optional)						
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	24.1	LOD =	11.08
			SD	4.01	Ttl %RSD	16.6
			n =	4		
		ProUCL distribution =				
-2SD Lower bag limit		Mean - 2 SD =		16.1		
+2 SD Upper bag limit		Mean + 2 SD =		32.1		
	1-sided	Bag 95% t-LCL =		19.4		
	1-sided	Bag 95% t-UCL =		28.8		
	-10% limit	Mean - 10% =		21.7		
	+10% limit	Mean + 10% =		26.5		
subsampling error =		6.45	instrument error =		15.31	as %RSD

Duplicate Bag Analysis			By:	DMC	Run date:	7/16/2017
Replicate Bag Readings	Date & Time	Reading No.	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
For duplicate sample analysis (repeat analysis of same bag)						
Replicate reading 1	1300	589	120	20.42	3.69	
2	1303	590	120	19.29	3.78	
3	1306	591	120	13.69	3.70	
4	1309	592	120	14.60	3.71	
5 (optional)						
6 (optional)						
7 (optional)						
8 (optional)						
9 (optional)						
10 (optional)						
			Mean	17.0	LOD =	11.16
Hypothesis Test for			SD	3.35	Ttl %RSD	19.7
Duplicate Agreement			n =	4		
T-test p-value =		ProUCL distribution =				
0.0355	2-sided	Sample 95% t-LCL =		11.7		
Dups do NOT agree	2-sided	Sample 95% t-UCL =		22.3		

Figure 5: T-test result when sample duplicates do not agree

9.4 Simplifying Data Retrieval and XRF-RTeX Forms

Because samples are seldom processed or analyzed in a set order, a system is needed that allows the XRF-RTeX entry for a particular sample to be easily retrieved for data validation or other purposes. A workable organization for small projects is to make sample IDs stand out clearly in the XRF logbook, so scanning for a particular sample is easy and fast.

- A new XRF-RTeX file should be used each day by saving a new copy of the XRF-RTeX template customized for this project. Include the date in the file name.
- Each unique sample should have its own worksheet in the file. Name each sheet with the sample ID.
- A sheet name tag can be color-coded if that sample is selected for subsampling for comparability analyses.
- Each target analyte (when there is more than one) has its own color-coded column of calculation block(s) in the sample's sheet.
- If desired, completed XRF-RTeX files can be duplicated and then individual sheets rearranged to group sample results in ways that make data analysis or data archiving/retrieval more efficient.

A searchable electronic master table of samples can be vital for projects involving many samples. The master sample table should record field sample and subsample progress through laboratory log-in, sample processing, XRF analysis, etc. (see example below). Dates for each completed step should be entered, allowing rapid location of records in the XRF logbook and in the XRF-RTeX forms. An example of a master sample table is shown in Figure 3.

Sample ID	Log-In Date	Process Date	XRF Analysis Date	XRF mean (Pb)	XRF mean (As)	Subsample Date (if applicable)	XRF Date for Subsample	Date to ICP	Date to Bioacc test
XXXX-XX-XXXX	xx/xx/xx	xx/xx/xx	xx/xx/xx			xx/xx/xx	xx/xx/xx	xx/xx/xx	xx/xx/xx

Figure 6: Example Master Sample Table

Discussion of how the XRF-RTeX form is used to guide the number of XRF readings taken during sample analysis is covered under Section 11.0, XRF Readings on Full Bagged Samples and Data Recording.

10.0 Sample Inspection

Inspect each bag before analysis to confirm the following:

1. The sample is in the correct type of plastic bag, which must be a bag from a lot number that had been previously verified as acceptable for taking XRF readings (refer to *XRF Procedure 02.1.3 Using the XRF Bag Checker and Calculator Tool*). If the sample is double-bagged, remove the outer bag for analysis.
2. There are no crinkles or dimples in the bag walls that could interfere with the measurement.
3. The appearance of the soil particles should be identical on both sides of the bag. If the sides appear different in color, texture or particle size, perform the following to evenly distribute soil particles in the bag:
    a. First, check that the bag is sealed properly. If it appears the bag may leak, use transparent tape to seal the bag's seams and corners as necessary.
    b. Do not place the transparent tape in ways that could obstruct XRF readings.
    c. Suspend the bag by 2 corners and rotate the bag in the air through 360 degrees of rotation 5 times so that the soil tumbles through the full length of the bag. This will mix and redistribute segregated soil particles.
4. Re-inspect the bag, and repeat rotation until the soil appears similar on both sides of the bag.

11.0 XRF Readings on Full Bagged Samples and Data Recording

The operation of the XRF analyzer is addressed in *XRF Procedure 01.1: Operation of the TIIB Niton XL3t GOLDD Ultra,* or the instrument specific operations manual. Operation of the XRF instrument will require input of sample specific information in the Data Entry Screen prior to taking measurements. This information may include sample ID, operator, sample container (bag or cup), sample type (QC or sample), sample particle size, and other information. Once a

reading has started, this information cannot be changed. Any corrections must be noted in the log book.

The following procedure applies to an XRF fixed into a bench stand. Perform instrument start-up and the designated quality control (QC) checks given in the schedule above.

1. If all QC checks are successful, lay the bag flat on the sample stand over the XRF window. Close the cover on the bench stand.
    a. Make sure any taped areas of the sample bag are not in the area to be scanned by the XRF.
    b. Use the camera to check that no gaps are present in the portion of the sample to be scanned.
2. Enter the sample ID and other relevant meta-data into the laboratory logbook
3. Take two readings on the first side of the bag (moving the sample between the two readings). Record each target element result (along with the associated instrument error) in the XRF's logbook when the result is displayed.
4. Carefully, flip the bag over.
5. Take two additional readings on the second side of the bag (moving the sample between the two readings). Again, record the required information into the XRF logbook. If not done already, enter the four readings and their errors into the day's XRF-RTeX form spreadsheet file.
6. If high variability is observed, take additional readings until the results seem to stabilize (remixing of the bag may be required).
7. When the current readings have been entered into the XRF-RTeX, check whether the statistical confidence goals for the sample have been met:
    a. If the mean is lower than the decision limit for the metal being examined, compare the 95% upper confidence limit (95% UCL) on the mean to the decision threshold/action level. If the UCL is also below the decision threshold, then no further analysis of the bag is necessary.
    b. If the mean is greater than the decision limit, compare the 95% lower confidence limit (95% LCL) of the mean to the decision threshold. If the LCL is also above the decision threshold, then no further analysis of the bag is necessary.

    If further analysis is necessary, continue making additional measurements in pairs (one on each side of the bag) until one of the following occurs:

    a. The mean and UCL are both below the decision limit, or the mean and LCL are both above the decision limit.
    b. Ten measurements have been made, and the mean and UCL (or LCL) are still on opposite sides of the decision limit, but the RSD for the ten measurements is below 10%.
    c. Ten measurements have been made, and the mean and UCL (or LCL) are still on opposite sides of the decision limit, and the RSD for the ten measurements is above 10%. There are several options for subsequent actions:
        - The bag can be remixed and reanalyzed as if it were a new sample (using another sample calculation block on the XRF-RTeX sheet). If the second batch of readings resolves the problem, record in the logbook and in the XRF-RTeX that the first set of ten readings should not be used.

- If a pattern is emerging where remixing sample bags is not able to reduce data variability (as measured by the RSD) or able to resolve decision uncertainty [as indicated by the relative positions of the mean and UCL (or LCL) with respect to the decision threshold], the problem may be that the true sample concentration is too close to the decision threshold, or that analyte-specific particle effects may be too strong for bag remixing to resolve the problem. Consult with the project's quality assurance manager or decision-maker to decide whether additional actions are required.
- Use the logbook to record what actions were taken to address the problem, or to flag samples for special consideration during XRF data validation.

12.0 Tools and Forms

This Procedure includes one Form as an Excel file:

- RealTime Excel Data Formatting Tool (*Template XRF-RTeX.xlsx*)

Wilcox XRF Procedure 02.1- The Instrument Evaluation Period

This Procedure contains nine sections and four attachments:

1.0 Purpose
2.0 References
3.0 Associated procedures
4.0 Equipment
5.0 Decontamination
6.0 The Measurement Principle of X-ray Fluorescence
7.0 Glossary and Acronyms
8.0 Instrument Evaluation Period
9.0 Tools and Forms
Appendix A - Glossary and Acronyms
Appendix B - Considerations for Choosing a Measurement Time
Appendix C - Considerations for Selecting the Proper Filter
Appendix D - Considerations on the Number of CRMs and/or LCSs Required for Control Charts

1.0 Purpose
The purpose of this procedure is to aid in the evaluation of the performance of an XRF that is new to the operator, whether newly purchased, or received as a rental. Evaluating a new instrument is vital to establish a baseline record of the instrument's accuracy, precision, and electronic stability to ensure the instrument will provide reliable data. By following the practices in this procedure, the operator will be able to detect developing problems before XRF data quality on project samples can be compromised. This procedure also allows the operator to become familiar with the operation of a specific instrument and understand the characteristics of readings made any that particular instrument. The operator cannot assume that rental instruments are checked by the rental company before they are sent out. The operator is responsible for making sure the instrument performs adequately for the intended purpose.

2.0 Application
This procedure is written to support the generation of XRF data suitable for definitive use in decision making, with full scientific and legal defensibility. Using XRF data for less rigorous purposes may not require all of the activities discussed in this procedure.

This procedure is applicable to all newly purchased, borrowed, or rental XRF analyzers used to make concentration measurements on soil samples. Although XRF analyzers are available to assess metal concentrations in consumer products, lead paint, alloys, and other materials, those applications require a different model or calibration of an XRF analyzer, which is not interchangeable with analyzers used for analysis of metals in soils. This procedure incorporates the operational and data characteristics for the Niton XL3t GOLDD Ultra but the approach is applicable to any XRF instrument set up to measure the concentrations of metals in soil with the

XRF. The procedure is required as part of a comprehensive baseline instrument evaluation and is part of a group of quality control procedures that apply to all XRF analysis.

Subordinate procedures for assessing bias, checking plastic bags for interference, and creating control charts are summarized here to provide the user with a high level process for implementing all the actions required to evaluate an XRF instrument.

3.0 References

None

4.0 Associated procedures

- ISM Procedure 1.3: ISM Sample Processing
- XRF procedure 01: General XRF Operation and Maintenance *(under development)*
- XRF procedure 01.1: Operation of the TIIB Niton XL3t GOLDD+ Ultra *(under development)*
- XRF procedure 01.3: Taking XRF Readings on Soil in Plastic Bags
- XRF procedure 01.4: Subsampling and Analysis for Comparability Assessment
- XRF procedure 02: XRF Quality Control and Data Validation
- XRF procedure 02.1.1: Assessing Instrument Precision and Bias
- XRF procedure 02.1.2: Creating and Using XRF Control Charts
- XRF procedure 02.1.3: Using the XRF Bag Checker and Calculator Tool
- XRF procedure 02.1.4: Converting a Spreadsheet into a Readable PDF File

5.0 Equipment

- XRF instrument power cords and data transfer cables
- XRF Instrument Manual
- Laptop or desk computer with Excel software installed
- QC Check materials
    - Laboratory control samples (LCS) in sample cups
    - Silica blank
- XRF Logbook
- Plastic sample bag expected to be used for XRF analysis

6.0 Decontamination

The QC check materials (Certified Reference Materials (CRMs)) are contained in a plastic sample cup covered with a thin plastic film. This film must remain clean and undamaged by keeping prepared cups in a protective holder whenever not being analyzed. If necessary, the film can be gently wiped clean with a soft tissue. Generally there should be no need for decontamination of the XRF in a laboratory setting. However, in some instances the sample cup or bag may leak or dust may accumulate on the instrument or stand and will require removal with a laboratory wipe or puff of air. XRF cups containing clean sand or silica blanks are analyzed periodically to establish baseline responses for a clean XRF. Elevated blank readings are a possible indication of contamination of the XRF window.

7.0 The Measurement Principle of X-ray Fluorescence:

The following sections and appendices contain technical terms and acronyms unique to the XRF analysis. Key terms and abbreviations are explained in *Appendix A – Glossary and Acronyms.*

An XRF Instrument works by sending out a burst of X-rays from the X-ray source (an electronic generator tube in newer instrumentation; potentially a radioactive source in older units) contained inside the instrument; then using a detector to measure the energies of X-rays sent back to the instrument from atoms in the sample which had absorbed energy from the out-going X-rays, then re-emitted that energy as X-rays at lower energy. The process of an atom absorbing, then re-emitting, energy of any kind is called fluorescence.

Each element emits a unique X-ray energy signature that is used by the instrument to identity the element. The detector counts how many X-rays of specific energies are re-emitted from the sample. The number of X-rays of a specific energy re-emitted for an element in the sample is used to quantify the number of atoms (concentration) of the element in the sample that were excited to fluoresce by the incoming X-rays.

Some XRF analyzers are equipped with excitation filters that optimize the analyzers' sensitivity for various elements. Typically there is a "main" filter that is used for most elements, and "high" and "low" filters for heavier and lighter elements. The operator should determine the optimal use of filters based on the project needs and recommendations by the manufacturer provided in the instrument manual.

8.0 The Instrument Evaluation Period

8.1 Introduction

An instrument that is new to the operator (whether it is a rental, on loan from another region or agency, or purchased new or refurbished instrument) must go through an evaluation period before it is used to report data for unknown samples. The evaluation period allows time for the operator(s) 1) to learn how to operate the instrument, and 2), assess the baseline performance of the instrument.

8.1.1 Knowing how to operate the instrument

There are several manufacturers and brands of XRFs, with multiple models within each brand, much like the make and model of a car. It is expected that different XRF models will have different operational buttons and menu screens, different detector standardization procedures, and different software capabilities for an operator to modify input or output parameters. A wide range of models are available for rental or for purchase as second-hand equipment. Over the past 15 years, XRF instruments have undergone upgrades and significant design changes in response to electronic advancements including chip miniaturization, increased memory, display screen improvements, and other technology that have allowed XRFs to become increasingly self-contained and less dependent on connection to a separate computer.

Many improvements in hand-held XRF technology have been made, such as

- X-ray generation has progressed from the early radioisotope-containing instruments (X-rays are always on) to the current miniature X-ray tube systems (X-rays are off when not measuring a sample);

- Recent advances in detector design that increase detection sensitivity (lowering detection limits for elements like arsenic and cadmium); and
- Improvements in battery technology that allow for more powerful X-ray tubes that can increase the list of elements reportable by hand-held XRF instruments.

Knowing how to operate one XRF model does not mean it will be obvious how to operate another model, especially if it is a different brand. It is always wise to read the manual for an instrument, although some manuals may be short on the details an operator needs to optimize the XRF's operation. Time might be required to resolve some questions by trial-and-error or calls to customer support.

How to mount an XRF to a stand and connect it to a computer may not be obvious when the operator is faced with a handful of nearly identical-looking wires and plugs. Loading XRF software onto a computer can be a problem if the operator does not have administrator privileges, or if the computer has been upgraded to a new operating system and a new driver for the XRF software is not readily available. It is suggested to allocate a full day to getting a new XRF instrument up and running.

Instrument setup and evaluation is particularly important for rentals. Because of cost or scheduling limitations, the operator may get an XRF brand or model different from what was requested. Even if the operator has experience with the brand and model of instrument received, previous users may have altered input/output options to settings that are unfamiliar. The operator should allow time to examine and adjust instrument settings to those required for the sample analysis planned for their particular project.

8.1.2 Assess the baseline performance of the instrument

This is critical for rental units because the operator does not know the conditions the instrument previously encountered. For example, it is possible that the electronics had been stressed by past operation in very humid, very cold, very hot, or very dusty conditions or perhaps an instrument had been subjected to physical shock so that the X-ray source or detector is slightly out of alignment.

Ideally, the rental company rechecks the performance of an instrument before renting it out again, but a renter seldom has reassurance of that. Possibly wear and tear have been building up, but only start degrading performance partway through the current project. The evaluation period is intended to allow the operator to assess whether the instrument (rental, borrowed, newly purchased, or one that has not been used for some time) is operating within acceptable QC control limits prior to collection of data on unknown samples.

At the very least, when the instrument arrives the operator must verify

- The instrument is electronically stable (*XRF Procedure 2.1.1 Assessing Instrument Precision and Bias*);
- The calibration and precision for the project's target analytes are reasonable for the intended project application(*XRF Procedure 2.1.1 Assessing Instrument Precision and Bias*) ;

- The extent of the instrument's linear range (how high and low the instrument can accurately measure) for the project's target analytes (*XRF Procedure 2.1.1 Assessing Instrument Precision and Bias*), and
- Data comparability between XRFs if more than one instrument is used in the same project. The operator(s) cannot assume that different XRFs will give equivalent results. To use data from multiple XRFs interchangeably, the operator must first establish comparability between the various instruments. This is easily done without the need for extra data collection by comparing the calibration check results of the different XRFs. Ideally the calibration checks will have used the same set of CRMs, but that is not absolutely necessary.

8.2 Purchase of a New XRF Instrument

A new XRF should include a dedicated performance evaluation period that provides data to establish its baseline performance. Routine QC will then monitor performance over the instrument's lifetime.

If a systematic deviation from baseline performance becomes evident as the instrument ages, factory maintenance and/or recalibration is warranted. If the instrument suffered a fall or exposure to extreme conditions that could damage performance, the change in QC performance will indicate a problem requiring corrective action before a project begins. It is a good practice to check an instrument's performance immediately after a borrower returns it.

By following the practices in this procedure, the operator will be able to detect developing problems before XRF data quality on project samples can be compromised. QC documentation is vital to validate XRF sample data for use in rapid project decision-making. It also provides the evidence that proves the scientific defensibility of XRF results if legal proceedings ever call the data into question.

8.2.1 Activities Performed During the Instrument Evaluation Period

1. Set up and start the XRF according to the manufacturer's instructions for that model. Allow time for installing software, understanding the input and output screens, and customizing output files, such as the order of analytes. Customizing output files is particularly important if more than one XRF will be used on a single project. Setting up identical input and output files on each instrument will save time and reduce clerical errors later when data are processed.
2. Choose the amount of time (variously called read time, acquisition time, or measurement time) the XRF will use to make a measurement using each filter (if a newer instrument is being used that has filters). A discussion of measurement time is provided in *Appendix B: Considerations for Choosing a Measurement Time.*) During a baseline evaluation, it is useful to gather data on all the analytes the instrument can report, using all available filters (*Appendix C: Considerations for Selecting the Proper Filter*.) During the actual project, the operator need not run all filters if the instrument allows for unnecessary filters to be turned off, which can reduce the read time without sacrificing XRF precision and detection limits for the target analytes.
3. Select other settings for operating the XRF. These may include customization of data entry screens, such as entering a sample identification, sample type, operator and sample

container type. Some XRF software may offer the option of creating customized drop-down menus for frequently used sample IDs, such as reference material cups, saving data entry time and encouraging standardization of entry IDs.

4. Make a concentration measurement of the blank reference sample(s), which is usually either plain clean sand or pure (99.995%) silica contained in a sample cup. Collect concentration data for all elements reported by the XRF.
   a) If excessive concentrations of target analytes are found in the blank, the problem could be with the blank or the XRF. (Note that some element concentrations will naturally be higher in a sand blank than in pure silica blank.) The following troubleshooting actions should be taken.
      i) Check the membrane on the blank cup for dust or soil particles. Gently wipe the membrane with a clean lab wipe.
      ii) Inspect the cup membrane for leaks, creases, dimples or other damage.
      iii) Check the XRF window membrane for dust or soil particles. Blow on the membrane to dislodge the particles. (The operator should protect against blown particles getting in the eyes.)
      iv) Consider whether the detection ability of the XRF instrument is so good (i.e., low enough) to occasionally detect the true low concentration of the blank (especially a sand blank).
5. Collect 25 to 30 concentration measurements of target analytes from each of the five (or more) certified reference materials (CRMs). Note that many elements will be measured and recorded by the XRF, but the operator should ensure that the filter settings allow all target analytes to be collected. These measurements must be independent and generated over a period of seven or more working days. The usual schedule for collecting this data is reading the CRMs four times over an eight- to nine-hour period for a total of 28 (7 x 4) replicate readings per CRM. This time must be planned into any rental schedule.
6. For the 25 to 30 replicate readings on CRMs over seven or more days, note the following considerations:
   a) The working days need not be consecutive.
   b) The objective of collecting data over an extended period is to capture the true variability of the instrument response.
   c) During those seven-plus days, the operator should
      i) Become comfortable with operating the instrument,
      ii) Learn its capabilities, selection menus, and available options for customizing input screens for entering sample information,
      iii) Learn how to download data out of the instrument and into spreadsheets for statistical analysis, and
      iv) Try to automate some of the more time-consuming, repetitive tasks to the extent allowed by the XRF's software, for example creating "pick lists" to streamline the sample entry screen.
7. The CRM data collected during the evaluation period will be downloaded from the XRF instrument into a spreadsheet for analysis.
   a) A version of the spreadsheet should be archived and contain as much information as the XRF instrument can provide.
   b) Spectral data from the XRF should be preserved in whatever format provided by the instrument manufacturer. The original raw data spreadsheet should be protected so that unauthorized or accidental changes cannot occur.

c) A copy of the original spreadsheet must be maintained in spreadsheet form until the project is closed, and/or it is not anticipated that anyone will need to go back and perform calculations on the data.
d) Spreadsheets can also be converted to a more permanent or publicly accessible format, such as a PDF file. *Procedure 02.1.4: Converting a Spreadsheet File into a Readable PDF File* (under development) provides instructions for this task.

8. The CRM data sets will be used for the following tasks as summarized below:
   a) Determine the calibration curve of the instrument (*Procedure 02.1.1: Assessing Instrument Precision and Bias)*;
   b) Serve as the data sets from which the project's laboratory control sample (LCS) CRMs (at least 3) will be selected (*Procedure 02.1.2: Creating and Using XRF Control Charts*);
   c) Allow operators to become familiar with using the instrument and its software;
   d) Determine battery life;
   e) Assist with checking for plastic bag interference (*Procedure 2.1.3 Assessing Interference from Plastic Sample Bags*); and
   f) Serve as the basis for establishing comparability between multiple XRFs for the same project.
9. Follow *Procedure 02.1.1: Assessing Instrument Precision and Bias* to determine if the baseline detection limits, bias and precision of the instrument are acceptable. If they are acceptable the CRMs may be selected for use as control charts.
10. The CRMs that will have control charts prepared for the target analytes are called laboratory control samples (LCSs). The LCS control charts will be used during deployment to monitor XRF performance and validate the sample data. The choice of CRMs to use as LCSs should be made based on the types of decisions to be made on the XRF data. Selection of CRMs for control charts is described *in Appendix D - Considerations for the Number of CRMs and/or LCSs Required for Control Charts* and the method for preparing control charts for the target analyte(s) is described in *Procedure 02.1.2: Creating and Using XRF Control Charts*. These charts will be used during project deployment to monitor XRF performance. At a minimum, three LCSs need to be selected from the group of CRMs that were previously run to assess the calibration of the XRF instrument. The reasons for three LCSs are:
    a) Enables selection of a low, a medium, and a high concentration LCS.
    b) If one of the three LCS cups is damaged during the course of the project, the operator can continue collecting data on unknown samples using the two remaining LCSs until the damaged one is repaired or replaced.
    c) If the project starts by using only two LCSs and one is damaged, only one LCS would be available during deployment. One LCS is insufficient to ensure data of known quality for definitive use since it cannot provide the information needed to verify that the XRF's calibration is holding steady over a range of concentrations. The XRF's calibration performance (initially determined during the Evaluation period) is verified by showing that the calibration's slope is not changing over the course of the project. This cannot be done with only one LCS.
11. If soil samples will be analyzed by XRF in plastic bags during deployment, check the plastic bags for interference using *Procedure 2.1.3 Assessing Interference from Plastic Sample Bags.*
12. If an instrument shows calibration or precision problems, return it to the rental company for replacement or, if the instrument is not a rental, return it to the manufacturer for service.

13. If a CRM cup that came with the rented XRF shows membrane or other problems, return it to the rental company for replacement.
14. Organizations running many XRF projects should consider obtaining their own set of CRMs with concentrations that match the needs of their projects. There are many benefits to this that can outweigh the cost.
15. If the project will be using the XRF on battery power during deployment (as opposed to having the XRF continually plugged in), run the instrument on battery power while collecting the initial batch of CRM data. Leave the instrument on to gage the battery life. This allows the operator to know how many batteries are required to get through an entire day, or allows arranging for batteries to be switched out and recharged.

9.0 Tools and Forms

This procedure includes two tools as worksheets in an Excel file (*XRF procedure 2.1 Instrument Evaluation Period Tools.xlsx*)

- Calibration Assessment Tool (under development)
- Statistical Analysis using ProUCL when Non-detects are Present (under development)

Appendix A - Glossary and Acronyms

Action Level (AL): Denotes the value of a quantity that will cause the decision maker to choose one of the alternative actions. The action level may be a project specific concentration guideline level, background level, release criteria, regulatory decision limit, etc.

Certificates of Analysis (CoAs): A written description of the reference material including its source, preparation and homogenization procedures, measurements of residual heterogeneity, the various analytical methods used to determine elemental concentrations, statistical analyses to derive certified concentrations and their uncertainty.

Certified Reference Materials (CRMs): Commercially prepared soils certified to have known concentrations for various elements or compounds. The known values are expressed as a mean and range of variability in a certificate of analysis (CoA). NIST is a well-known supplier of CRMs, and the term “standard reference material” (SRM) is trademarked by NIST to refer solely to their CRMs.

Control chart: In this procedure’s context, a control chart is a graphical representation of the acceptable limits for concentration results from a CRM of known concentration. The purpose of a control chart is to monitor the performance of an XRF instrument before and after batches of field samples are analyzed. Control limits on a concentration axis (the y-axis) display the range of acceptable results. When an LCS is measured, the result is plotted to show where it falls in relation to the acceptable control limits. Results that fall outside of the limits are termed out-of-control and indicate there is an analytical problem that needs to be resolved before sample results can be finalized and reported.

Detection Limit (DL): A generic term used to denote the lowest concentration the instrument can reliably identify as present, although there is likely to be considerable uncertainty about the actual concentration. A variety of detection limit terms exist depending on what specific statistical strategy is used to determine how low a concentration an instrument can detect. The term “Limit of Detection” is typically used for XRF instrumentation.

keV: A unit of energy for electromagnetic radiation (i.e. photons) such as X-rays, expressed in thousands of electron-volts (k is the symbol for 1000, and eV stands for electron-volts).

Laboratory Control Sample (LCSs): In the XRF context, LCSs are certified reference materials (CRMs) which are selected to be used as on-going checks on instrument performance while the instrument is being operated. LCS measurements are plotted immediately on a control chart to verify that the instrument was performing normally during field sample analysis.

Limit of Detection (LOD): When an XRF instrument cannot detect enough atoms of a particular element during its measurement time to determine that the element is truly present, the conclusion is that the element is not detected above the LOD. For XRF instrumentation, an LOD is generally determined from the signal to noise (S/N) ratio in the

counting statistics (see below). Along with the report of <LOD, an XRF is able to assign a measurement-specific numerical value to the LOD. For example, an arsenic result might be reported as <LOD, and the LOD given as 12 ppm. That means that the amount of arsenic present is less than 12 ppm, which is as low as the XRF can reliably detect arsenic in that particular measurement on that particular sample. An XRF determines a sample-specific numerical LOD value for each measurement it reports as non-detect (< LOD). Samples with matrix-interference at a specific keV can often be identified because their LODs are higher than LODs from samples without matrix interferences.

NIST: National Institute of Standards and Technology; a U.S. government associated provider of SRMs.

Quality Control (QC): Specific technical checks that allow a determination of whether the associated batch of products or services meets the specifications defined for that product or service. Analyzing samples of known composition (e.g., blanks and laboratory control samples (LCSs)) is an important QC check on instrument performance. If an XRF performs well (i.e., gives results close to expected) on QC samples, then the assumption of equally good performance on unknown samples of a similar matrix may be justified.

XRF Concentration Calibration: In analytical chemistry, calibration is the process of assigning concentration values to the magnitude of an instrument's response. In the case of an XRF, calibration equates the number of X-rays of specific energy returning to the instrument with the amount of element present in the sample. Calibration of XRF instruments is done in the factory and tailored to the type of matrix the XRF will be analyzing (soils, alloys, mining ores, paint, plastic, toys, etc.). For example, an XRF calibrated to measure lead (Pb) in paint will not provide accurate Pb results if it is used to measure Pb soil samples.

XRF Energy Calibration (also called "Standardization"): The process of setting the detector to correctly identify the energies of in-coming X-rays. For example, if an x-ray with an energy of 5.00 keV hits the detector, the detector should recognize the energy as 5.00 keV, and not 5.55 or 6.00 keV. Correct identification of energy levels of X-rays re-emitted to the instrument after interaction with the sample is the mechanism for identifying the elements in the sample. Some XRFs perform detector standardization when the instrument analyzes a metal alloy of defined composition. Standardization is done when the instrument is started up and periodically during operation. Some newer instruments perform standardization internally and a piece of alloy is not needed.

XRF sample batch: the group of samples bounded by LCS results. A sample batch must be bounded by in-control LCS results before the sample results for that batch can be reported. An LCS that is out-of-control at the start of a batch means that the batch cannot be analyzed until the performance problem has been resolved. An LCS that is out-of-control at the end of a batch means that the batch cannot be reported until the problem is resolved, and the samples rerun.

XRF Counting Statistics: Each reported XRF measurement result is actually the average of hundreds to thousands of short count intervals performed continually during the XRF's specified measurement time (which can be set for 15, 30, 60, 120, etc. seconds) for an analytical measurement. During each short counting interval, the XRF counts the number of X-rays of specific energies re-emitted by sample atoms (refer to Glossary entry for "The Measurement Principle of X-ray Fluorescence"). The instrument compiles all the individual counts for the short intervals into a data set on which the XRF performs on-going statistical calculations. At the end of the XRF measurement time for the analytical measurement (e.g. 30 sec.), the XRF finalizes and reports the mean and standard deviation for all the short count intervals in the full data set. The standard deviation of the counting statistics represents the noise (or imprecision) in the instrument's measurements. If the XRF is functioning correctly, the amount of noise is influenced by

- matrix characteristics of the sample,
- how much of a particular analyte is present, and
- the measurement time.

The LOD is calculated by the instrument as two to three times the standard deviation of the counting variability. This approach to sample specific determination of the LOD accounts for certain properties of XRF analysis:

- The longer the measurement time for the analysis of a particular sample, the lower the standard deviation of the counting statistics, and the lower the LOD.
    - For example: a sample that is non-detect at a 30-second measurement time might give a detected result at a 60-second measurement time
- The "cleaner" the sample matrix, the lower the standard deviation and the lower the LOD.
    - For example, a sample with large amounts of non-target elements or matrix components that interact with X-rays will have more variability in the counting statistics than a sample having lower amounts of those materials. Target analytes will have higher LODs in samples containing very high amounts of other elements.
    - The LODs achievable on sand or silica blank material are lower than the LODs for most real, complex soil samples.

Appendix B - Considerations for Filter Selection

The TIIB-owned XRF instrument (Thermo Scientific Niton XL3t GOLDD Ultra) and many other XRF analyzers are equipped with excitation filters that optimize the analyzers' sensitivity for various elements. For the Niton XL3t, the "Main Range" filter provides optimum sensitivity for the elements manganese (Mn) through bismuth (Bi), which includes As, Pb, Hg and Se. The "Low Range" filter is used to optimize the sensitivity for the elements from titanium (Ti) through chromium (Cr). Note that the main range filter can be used to analyze Ti, V and Cr, but the sensitivity is not as good as when using the low filter. The "High Range" filter optimizes for analytes such as Sb, Sn, Cd and Ag. The "Light Range" filter is available only with He-purged and GOLDD technology analyzers, and is typically used in light element analysis, such as S and P. The amount of time that the analyzer spends in each filter position is user definable. Please note that the analyzer will continue alternating excitation filters until the user selectable maximum analysis time is reached or the operator terminates the measurement.

Filters that are run do not have to be run for the same time period (although that is the easiest strategy to implement). When altering filter options, consider the following:

a) Make sure that the instrument algorithms calculating target analyte concentrations do not require readings from more than one filter to complete their calculations. A technical person at the manufacturer can address this possibility.
b) Be aware that analytes from filters that are not run will not be recorded in the raw data files.
c) Analytes from filters run for shorter measurement time will have higher (i.e., not as good) detection limits than from longer run times, and the data will not be as precise. The trade-off between time saved vs. reduced performance must be balanced against the data quality needed to support its intended use.

If there is a possibility that data for non-target analytes may be helpful at some time in the future, keep their filter(s) on. The data will then always be accessible in the XRF's raw data files (which must be maintained as part of the project's permanent record).

Appendix C - Considerations for Choosing a Measurement Time

The general rule is that quadrupling the measurement time for an analyte will lower the detection limit by one-half, or conversely, cutting measurement time by 4 will double the detection limit.

> For example: If a particular XRF has a detection limit of 30 parts per million (ppm) for a particular analyte when the measurement time is 15 seconds, the detection limit will be reduced to 15 ppm (30/2) if the measurement time is increased to 60 seconds (15 x 4).

The first time that a particular instrument is started up, the operator should analyze all available CRMs, collecting at least one measurement for each blank and CRM. The results are compared to the certified values using procedures outlined in *Procedure 2.1.1 Assessing Instrument Precision and Bias* to determine any obvious bias or precision problems with the instrument.

At this point, the operator is most concerned with selecting a run time that will meet the project's desired detection levels. For example, if the instrument is reporting arsenic results as non-detects (<LOD) at concentrations where the project needs to report concentration, the operator should increase the measurement time for the filter used for arsenic to lower the LOD.

A general guideline is that the instrument should, at a minimum, be able to report quantified results at a concentration that is at most one-half of the action level. However, non-detect values are problematic if the data will be used for risk assessment or other quantitative calculations. Large numbers of non-detect data should be avoided, if possible, by extending the XRF's read time. As explained above, the general guideline is that the operator has to quadruple the XRF run time to reduce an LOD by half.

Perform instrument duplicate measurements on two CRM samples of different concentrations for project target analytes as a baseline measure of instrument precision/variability; this is a function of electronic stability.

Use *Procedure 02.1.1: Assessing Instrument Precision and Bias* along with the Instrument Duplicates Calculator tool to evaluate precision. If the instrument fails the test for precision, contact the instrument vendor to arrange for a replacement. As a guideline, if no more than two out of 10 measurements are outside QC limits, the instrument is performing acceptability. Change run time for CRMs by collecting data at the different measurement time period along with running the instrument using the previous measurement time to establish adequate performance. A CRM control chart is specific to the measurement time used to establish the chart.

Appendix D - Considerations for the Number of CRMs and/or LCSs Required for Control Charts

For quantitative use of the data (meaning the data will use the number values reported by the XRF for statistical calculations), a minimum of two LCSs that contain relevant concentrations for the project's target analytes are required.

For qualitative uses of XRF data (project decisions will be based on whether results are non-detect, medium, or high concentration), only one LCS is required. Examples of qualitative uses of XRF data are:

- The detection limit for a certain target analyte is near or higher than the action level. Samples giving ND results will be sent for fixed lab (ICP) analysis.
- If a sample concentration is high enough so that the XRF gives numerically stable results for this analyte, it is known that the sample will exceed the action level.
- A common example of an application using this qualitative data is whether the sample exceeds some disposal action level.
- The one LCS should have a concentration near the disposal action level. Ordinal use of the data is acceptable (if x out of y results exceed z, sample considered to exceed).
- Another CRM should be used to monitor the non-detect status. It is only necessary to run the non-detect CRM seven times prior, and one time per day at start of day. No plotting is required. Keep the LCS QC data in database for periodic review and for XRF performance documentation.

Ideally the LCSs should be used for Quality Control (QC) using the procedures described in *XRF Procedure 2.1.2: Creating and Using XRF Control Charts*. This section provides guidance on the selection and use of CRMs and LCSs.

1) The three concentration ranges around an action level (AL) can be expressed as below
   a) Less than (<) AL = below the action level; generally more than 25% below the action level. Examples:
      i) AL = 400 ppm; <AL would be less than 300 ppm (400 – 0.25x400 = 400 – 100)
      ii) AL = 10 ppm; <AL would be less than 7.5 ppm (10 – 2.5)
   b) @AL = at or near the action level; "near" means within approximately 25% of the action level either above or below. Examples:
      i) AL = 400 ppm. @AL would be a concentration between 300 and 500 ppm.
      ii) AL = 10 ppm; @AL would be a concentration between 7.5 and 12.5 ppm.
   c) Greater than (>)AL = above action level; generally more than 25% above the action level, but not more than 10 times the action level. Examples:
      i) AL = 400 ppm; >AL would be more than 500 ppm (400 + 0.25x400 = 400 + 100), but less than 4000 ppm.
      ii) AL = 10 ppm; >AL would be more than 12.5 ppm, but less than 100 ppm.
   d) The same math applies to all action levels, whether risk-based, disposal-based, or other.
   e) These are guidelines only. Mild exceedances of the 25% or 10-times limit are allowable to find available CRMs.
2) Note that if there are three suitable LCSs and Pb is the only target analyte, then three control charts will be generated.

a) If there are three suitable LCSs and Pb and As are target analytes, then there will be six control charts.
b) However, if there are more than one target analyte and the same three CRMs do not contain the needed concentrations for all the analytes, more than three CRMs may be needed to get the concentrations required for quality control. However, six control charts are still needed if the analytes are Pb and As.
c) CRMs that have low concentrations of As and Pb will likely have non-detected Cd concentration. Additional CRMs with suitable Cd concentrations may be needed. Purchasing CRMs that have target elements in the desired ranges should be considered. Companies offering these materials can easily be found on the Internet.

3) If project DQOs plan to use the XRF to report quantitative data for target analytes typically having low concentrations (such as Cd), two LCSs must have detectable concentrations.
   a) It is acceptable for the <AL concentrations to be near the instrument's detection limit as long as more than 50% of the XRF's measurements are detections.
   b) Another LCS will have a concentration at or near the risk-based decision threshold.
   c) If accurate quantification of high concentration data are important (perhaps for making real-time decisions about soil disposal), then a third LCS should have a concentration near that decision threshold.
4) The time invested to locate and obtain reference materials better suited to project data needs will ensure data collected are of adequate quality to meet project needs. Even if using rental XRF instruments, it may make sense to obtain a set of QC reference materials that better reflect project data quality objectives and ultimate decisions the data support for the project.

Wilcox XRF Procedure 02.1.1- Assessing Instrument Precision and Bias

This Procedure contains seven sections:

1.0 Purpose
2.0 Application
3.0 References
4.0 Associated Procedures
5.0 Equipment
6.0 Decontamination
7.0 Procedure

1.0 Purpose
This procedure provides instructions for gathering and evaluating the data set used to assess instrument precision and bias during the instrument evaluation period. This procedure is part of a group of XRF procedures that are performed as part of the Quality Control (QC) and Data Validation for the XRF.

2.0 Application
This procedure explains how to assess instrument precision and bias by comparing instrument readings to certified reference standards. The procedure is required during a baseline instrument evaluation and is part of a group of procedures for evaluating instrument performance subordinate to XRF *Procedure 02.1: Instrument Evaluation Period*. This procedure incorporates the data output characteristics for the Niton XL3t GOLDD Ultra but is applicable to any XRF instrument used for measuring the concentrations of metals in soil with the XRF. This procedure requires that during the instrument evaluation period, a dataset for evaluating precision and bias will have been generated for use in this analysis.

3.0 References

None

4.0 Associated procedures
- XRF procedure 01: General XRF Operation and Maintenance *(under development)*
- XRF procedure 02: XRF Quality Control and Data Validation
- XRF procedure 02.1.1: Assessing Instrument Precision and Bias
- XRF procedure 02.1.2: Creating and Using XRF Control Charts
- XRF procedure 02.1.3: Using the XRF Bag Checker and Calculator Tool
- XRF procedure 02.1.4: Converting a Spreadsheet into a Readable PDF File

5.0 Equipment
- XRF instrument (Niton XL3t GOLDD Ultra, or equivalent), power cords and data transfer cables
- Laptop or desk computer with Excel software installed
- QC Check materials
    - Laboratory control samples (LCS) in sample cups

- XRF Logbook

6.0 Decontamination
The QC check materials (Certified Reference Materials (CRMs)) are contained in a plastic sample cup covered with a thin plastic film. The film must be kept clean and protected. Generally there should be no need for decontamination of the XRF in a laboratory setting. However, in some instances the sample cup may leak or dust may accumulate on the instrument or stand and will require removal with a laboratory wipe.

7.0 Procedure

7.1 Introduction

The operator will need to select at least five CRMs with concentrations that cover the potential concentration range of interest for project specific target analytes. If the project specific concentration range is narrow and five CRMs cannot be identified or obtained, fewer can be used as long as there are at least three CRMs. The calibration checking procedure must not be done on less than three CRMs. However, if only three CRMs are used, the chances are reduced that the performance evaluation will be successful. Since an unsuccessful or inconclusive instrument evaluation wastes much time and effort, at least five CRMs are preferred. Data from these five CRMs will be used to check the calibration of the instrument and verify its linear range (how high and low the instrument can reliably measure).

For the Wilcox project, three CRMs will be used:

JSAC 0462
RCRA
NIST 2711a

The target analyte for the CRMs is lead.

Appendix A in XRF Procedure 02.1 Instrument Evaluation Period describes selecting CRMs for the project; Appendix B in XRF Procedure 02.1 describes how many CRMs and LCSs are needed.

7.2 Using the CRM Data Sets to Evaluate Instrument Precision and Bias

Evaluating the instrument bias is the same as checking the instrument's calibration. Note that XRF instruments are calibrated at the factory and the user can not adjust or change internal calibrations, although it may be possible for user-specified equations or factors to be entered into the instrument's software. User-specified equations are developed from CRM regressions, and serve to mathematically alter the output from the internal calibration. The instrument's precision is determined by evaluating the relative standard deviation (RSD) for the CRM data sets.

1. Approximately 30 CRM measurements collected during other instrument evaluation tasks, should be available to the analyst for use in this procedure. Download the raw data from the XRF, or other spreadsheet, into a new spreadsheet. The raw data will look something like the spreadsheet illustrated in Figure 1.

2. The spreadsheet will likely contain data from several CRMs, and data rows will be intermixed. Use the **Sort** function in Excel to group the rows by CRM ID (column J in Figure 1), so that all the readings from a single CRM (and only that CRM) are in adjacent rows.

3. Once grouped, insert at least five extra rows between each different CRM data set to create space for statistical analysis of the columns of data, as illustrated in Figure 2 below. Only target analytes require statistical analysis (although all analytes in the spreadsheet example below have the statistics shown).

    a. Figure 3 below shows 35 runs of a USGS CRM (middle rows were compressed to accommodate to the page size). The certified values for the USGS CRM are shown at the top of the USGS group, and the ratio of the average to the certified value is at the bottom (pink highlight). Drawing a border below the last data run makes it easier to pick out important information when looking at a long spreadsheet.
    b. Adding the certified values (pink highlight) to the spreadsheet is also helpful. The ratio of the CRM's results average to the CRM's certified value (pink highlight) is a helpful indicator of potential bias. Ratios less than 1.0 indicate that the average of results is less than the certified value, and ratios greater than 1.0 indicate results were above the certified value. Note that some CRMs have certified values for only a few analytes

4. Enter the formulae for mean, standard deviation, and %RSD below the data set for each analyte. Figure 4 illustrates the equations used for the statistics calculations in an Excel format.

    Note that if a newer version of Excel is used, there is more than one option for the Standard Deviation (SD) function:

    The P designates a population standard deviation, and the S is for a sample standard deviation. For this analysis use the sample (S), not the population SD.

	A	E	F	G	H	I	J	K	L	X	Y	Z	AA	AB	AC	AD	AE	AF	
1	Index	Duration	Units	Sigma Value	Sequence	Flags	SAMPLE	LOCATION	INSPECTOI	Sb	Sb Error	Sb CPS/ua	Sn	Sn Error	Sn CPS/ua	Cd	Cd Error	Cd CPS/ua	Pd
25	24	90	ppm	1	Final					< LOD	4.27	0	< LOD	3.7	0	< LOD	4.16	0	< L
26	25	90	ppm	1	Final		USGS	ERT	DMC	59.89	3.55	0	< LOD	4.21	0	< LOD	4.72	0	< L
27	26	90	ppm	1	Final		RCRA	ERT	DMC	< LOD	5.3	0	< LOD	4.81	0	477.3	6.05	0	
28	27	90	ppm	1	Final		NIST 2709a	ERT	DMC	< LOD	4.96	0	< LOD	4.32	0	< LOD	4.76	0	< L
29	28	90	ppm	1	Final		SiO2	ERT	DMC	< LOD	4.26	0	< LOD	3.73	0	< LOD	4.14	0	< L
30	29	90	ppm	1	Final		NIST 2709a	ERT	DMC	< LOD	5	0	< LOD	4.35	0	< LOD	4.81	0	< L
31	30	90	ppm	1	Final		RCRA	ERT	DMC	< LOD	5.21	0	< LOD	4.67	0	483.2	5.98	0	
32	31	90	ppm	1	Final		USGS	ERT	DMC	57.66	3.61	0	< LOD	4.32	0	< LOD	4.81	0	< L
33	32	90	ppm	1	Final		SiO2	ERT	DMC	< LOD	4.3	0	< LOD	3.7	0	< LOD	4.15	0	< L

Figure 1: Example Spreadsheet with Downloaded XRF Data (unsorted)

169	80	6/5/2015 12:31	RCRA	DMC	3.91	1.24	316.13	2.69	72.71	1.38	6.73	2.38	60.87	1.64	16.32	2.48	476.12	8.42	9.47	5.89	446.1	5.17	439.48	7.9
170	138	6/5/2015 14:53	RCRA	DMC	2.71	1.23	337.27	2.74	73.9	1.37	<LOD	3.43	62.97	1.63	14.6	2.43	467.02	8.3	<LOD	8.6	460.1	5.17	463.77	7.88
171	189	6/5/2015 17:09	RCRA	DMC	3	1.22	300.43	2.63	72.28	1.37	<LOD	3.4	59.8	1.61	9.56	2.37	465.06	8.35	<LOD	8.69	452.2	5.19	436.96	7.85
172				mean =	2.5	KM	306.3		74.6		5.3	KM	62.5		14.5		486.2		8.6	KM	443.4		443.6	
173				SD =	2.1		16.1		9.8		1.8		13.3		2.6		53.1		4.6		69.9		58.6	
174				%RSD =	84.4		5.3		13.1		33.5		21.3		17.9		10.9		54.0		15.8		13.2	
175				l value =													0.97				0.89		0.89	
176																								
177			USGS SRM		Mo		Zr		Sr		U		Rb		Th		Pb		Au		Se		As	
178			Certified value:		13.2		270		143		2.63		145		14.4		761		1.2		1.8		78	
179	Reading No	Time	Sample ID	Operator	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Au	Au Error	Se	Se Error	As	As Error
180	5	5/27/2015 9:44	USGS SdAR-M2	Travis A.	14.46	1.28	236.35	2.45	134.5	1.81	8.84	3	141.4	2.33	24.65	3.01	823.94	9.93	<LOD	4.29	4.37	1.54	69.52	7.63
181	28	5/27/2015 12:37	USGS SdAR-M2	Travis A.	12.4	1.26	227.13	2.43	134.9	1.8	<LOD	4.43	145.26	2.23	25.4	2.96	791.94	9.64	<LOD	4.24	5.27	1.52	81.53	7.47

Inserted Rows

Figure 2: Example Sorted Spreadsheet with Rows for Statistical Summaries for Each RCM

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X
176																								
177				USGS SRM	Mo		Zr		Sr		U		Rb		Th		Pb		Au		Se		As	
178				Certified value:	13.2		270		143		2.63		145		14.4		761		1.2		1.8		78	
179	Reading No	Time	Sample ID	Operator	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Au	Au Error	Se	Se Error	As	As Erro
180	5	5/27/2015 9:44	USGS SdAR-M2	Travis A.	14.46	1.28	236.35	2.45	134.5	1.81	8.84	3	141.4	2.33	24.65	3.01	823.94	9.93	<LOD	4.29	4.37	1.54	69.52	7.6
181	38	5/27/2015 13:37	USGS SdAR-M2	Travis A.	13.4	1.26	237.13	2.43	134.9	1.8	<LOD	4.42	145.36	2.32	25.4	2.96	791.94	9.64	<LOD	4.34	5.37	1.52	81.53	7.4
182	93	5/27/2015 17:20	USGS SdAR-M2	Travis A.	12.31	1.25	238.04	2.42	133.1	1.78	10.24	2.99	144.04	2.32	26.31	2.97	801.88	9.66	8.14	3.02	5.01	1.56	83.42	7.4
183	101	5/28/2015 11:59	USGS SdAR-M2	Travis A.	13.36	1.25	248.61	2.45	137.5	1.79	6.28	2.94	145.97	2.31	20.08	2.89	818.52	9.68	<LOD	4.27	4.75	1.51	70.63	7.4
184	152	5/28/2015 17:04	USGS SdAR-M2	Travis A.	13.35	1.26	246.2	2.45	135	1.78	10.12	2.98	142.44	2.3	23.8	2.93	807.98	9.66	4.54	2.89	3.79	1.49	72.77	7.4
185	166	5/28/2015 17:54	USGS SdAR-M2	Travis A.	14.28	1.25	250.41	2.43	134.6	1.76	9.05	2.92	142.06	2.27	23.22	2.89	804.54	9.52	<LOD	4.34	2.68	1.49	81.97	7.3
186	174	5/29/2015 7:35	USGS SdAR-M2	Travis A.	15.1	1.27	232.39	2.41	132.1	1.79	6.87	2.96	143.22	2.32	16.57	2.88	802.08	9.74	<LOD	4.32	4.47	1.52	74.34	7.5
187	221	5/29/2015 13:36	USGS SdAR-M2	Travis A.	13.79	1.26	235.61	2.43	137.7	1.82	5.91	2.95	143.41	2.32	23.88	2.95	793.55	9.67	4.45	2.92	2.92	1.5	85.82	7.5
188	232	6/1/2015 8:23	USGS SdAR-M2	DMC	15.41	1.26	240.28	2.42	135.7	1.78	<LOD	4.36	146.1	2.31	22.28	2.91	809.54	9.66	5.47	2.94	5.8	1.53	74.72	7.4
189	266	6/1/2015 11:53	USGS SdAR-M2	DMC	13.76	1.26	239.95	2.44	135.1	1.8	9.92	2.98	139.88	2.3	23.99	2.96	809.78	9.74	5.71	2.98	3.38	1.53	74.47	7.5
190	304	6/1/2015 17:27	USGS SdAR-M2	DMC	13.10	1.27	250.80	2.42	134.1	1.79	5.77	2.93	144.73	2.32	22.83	2.93	821.07	9.76	4.93	2.90	4.72	1.54	87.32	7.3
191	312	6/2/2015 8:44	USGS SdAR-M2	DMC	13.10	1.26	256.04	2.41	134	1.77	5.83	2.91	141.83	2.28	15.33	2.9	830.93	9.77	3.92	2.90	4.31	1.53	84.23	7.4
192	347	6/2/2015 11:11	USGS SdAR-M2	DMC	14.32	1.26	231.7	2.3	134.6	1.6	10.1	3.03	143.34	2.33	20.00	2.93	803.83	9.70	0.46	3.02	<LOD	2.3	73.30	7.3
193	369	6/2/2015 15:05	USGS SdAR-M2	DMC	13.03	1.26	233.83	2.32	130.4	1.82	7.1	2.93	143.03	2.33	13.00	2.94	822.03	9.3	<LOD	4.36	<LOD	2.21	78.08	7.0
194	380	6/2/2015 15:42	USGS SdAR-M2	DMC	13.21	1.26	240.02	2.47	133.4	1.82	<LOD	4.44	144.84	2.33	24.26	3	800.72	9.83	3.70	3.02	<LOD	2.3	87.38	7.0
195	434	6/2/2015 17:30	USGS SdAR-M2	DMC	14.08	1.27	242.24	2.43	133.3	1.8	<LOD	4.34	141.03	2.23	21.77	2.93	803.51	9.74	3.33	2.93	3.26	1.52	72.2	7.
196	442	6/3/2015 8:13	USGS SdAR-M2	DMC	12.32	1.23	232.17	2.4	132.2	1.78	8.00	2.93	140.8	2.23	23.14	2.94	800.20	9.71	<LOD	4.23	3.31	1.53	73.03	7.4
197	473	6/3/2015 10:30	USGS SdAR-M2	DMC	13.43	1.23	237.23	2.42	133.4	1.78	3.77	2.93	143.44	2.31	18	2.9	827.43	9.81	<LOD	4.23	3.33	1.47	70.30	7.3
198	522	6/3/2015 13:23	USGS SdAR-M2	DMC	13.39	1.27	243.43	2.42	133.3	1.78	8.00	2.93	144.13	2.32	24.36	2.90	803.33	9.71	0.0	2.97	3.1	1.51	73.00	7.4
199	533	6/3/2015 14:11	USGS SdAR-M2	DMC	14.07	1.24	237.41	2.33	134.4	1.70	<LOD	4.26	143.3	2.20	20.03	2.93	800.71	9.33	<LOD	4.31	3.33	1.3	77.8	7.3
200	577	6/3/2015 16:27	USGS SdAR-M2	DMC	13.03	1.20	242.11	2.42	130.3	1.73	<LOD	4.33	143.37	2.3	13.32	2.84	813.12	9.71	<LOD	4.33	3.33	1.43	77.30	7.4
201	621	6/3/2015 18:32	USGS SdAR-M2	DMC	17.4	1.3	234.43	2.31	133.3	1.6	0.36	2.90	141.34	2.31	23.87	2.96	813.33	9.84	<LOD	4.4	3.33	1.33	70.08	7.3
202	630	6/4/2015 8:03	USGS SdAR-M2	DMC	13.21	1.20	240.33	2.42	134	1.78	<LOD	4.32	141.40	2.28	21.27	2.92	813.83	9.73	<LOD	4.27	3.01	1.3	84.0	7.4
203	657	6/4/2015 10:30	USGS SdAR-M2	DMC	14.00	1.20	242.14	2.44	134.3	1.73	0.30	2.93	144.37	2.32	24.03	2.97	824.83	9.73	<LOD	4.33	3.71	1.51	71.03	7.3
204	724	6/4/2015 12:04	USGS SdAR-M2	DMC	13.17	1.26	231.13	2.43	133.1	1.73	0.33	2.90	144	2.32	23.30	2.93	790.0	9.03	<LOD	4.33	3.34	1.50	92.37	7.3
205	727	6/4/2015 12:11	USGS SdAR-M2	DMC	11.71	1.23	240.34	2.40	130.1	1.61	13.43	3.02	133.37	2.3	26.21	2.90	793.02	9.03	3.33	2.93	2.06	1.43	90.33	7.4
206	732	6/4/2015 13:02	USGS SdAR-M2	DMC	14.23	1.26	236.7	2.40	134.6	1.62	3.34	3.03	147.17	2.36	23.3	3.02	817.83	9.31	<LOD	4.4	3.36	1.33	83.31	7.
207	760	6/4/2015 13:23	USGS SdAR-M2	DMC	13.3	1.3	240.43	2.3	134.1	1.61	8.02	3.02	143.01	2.30	22.44	2.93	817.14	9.31	4.30	2.93	3.33	1.33	77.02	7.0
208	837	6/4/2015 17:42	USGS SdAR-M2	DMC	10.33	1.32	233.23	2.36	134.4	1.63	0.37	3.02	143.36	2.30	10.03	2.94	816.13	9.36	0.16	3	<LOD	2.27	83.43	7.0
209	3	6/5/2015 8:04	USGS SdAR-M2	DMC	13.32	1.27	271.32	2.34	133.4	1.78	7.34	2.94	144.07	2.3	20.88	2.3	812.42	9.07	7.71	2.93	3.33	1.33	76.38	7.4
210	68	6/5/2015 11:31	USGS SdAR-M2	DMC	16.98	1.3	241.84	2.48	133.7	1.81	7.77	3.01	143.4	2.35	21.92	2.98	812.67	9.89	<LOD	4.46	3	1.54	91.39	7.6
211	79	6/5/2015 12:28	USGS SdAR-M2	DMC	15.13	1.27	253.82	2.48	134.8	1.78	5.4	2.9	140.31	2.28	30.43	2.99	788.93	9.57	<LOD	4.38	5.75	1.55	81.61	7.4
212	83	6/5/2015 12:37	USGS SdAR-M2	DMC	16.34	1.27	262.57	2.49	132.6	1.76	<LOD	4.26	142.4	2.26	21.62	2.89	807.57	9.6	5.78	2.96	5.57	1.54	75.9	7.
213	137	6/5/2015 14:50	USGS SdAR-M2	DMC	14.52	1.29	257.27	2.54	134.4	1.82	<LOD	4.48	145.85	2.36	22.21	2.98	809.09	9.89	4.83	3	5.96	1.58	82.55	7.6
214	187	6/5/2015 17:05	USGS SdAR-M2	DMC	12.78	1.25	240.85	2.43	134.6	1.78	10.91	2.99	143.35	2.31	20.51	2.91	818.32	9.73	6.97	2.95	<LOD	2.22	76.21	7.5
215	188	6/5/2015 17:07	USGS SdAR-M2	DMC	12.2	1.25	239.13	2.43	131.4	1.77	<LOD	4.38	145.61	2.32	21.98	2.93	806.7	9.7	<LOD	4.35	<LOD	2.21	70.27	7.4
216				mean =	14.4		244.8		134.4		6.9	KM	143.5		22.5		810.9		5.1	KM	3.9	KM	76.4	
217				SD =	1.3		9.2		1.6		2.4		1.9		3.2		10.3		1.1		1.3		7.4	
218			USGS SRM	%RSD =	9.1		3.7		1.2		34.3		1.3		14.1		1.3		21.0		32.6		9.7	
219			data set ave/Certified value =		1.09		0.91		0.94		2.63		0.99		1.56		1.07		4.23		2.16		0.98	

Figure 3: Example Sorted Spreadsheet with All CRM Data and Certified Values

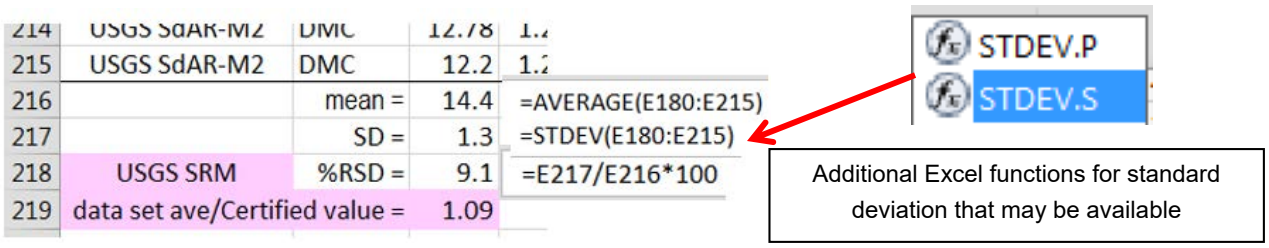


Figure 4: Equations Used for Statistics Calculations

5. After grouping the CRM data sets and calculating the statistical values, examine the project target analytes. For the next step, it is helpful to **Copy** the statistics for the target analyte(s) and **Paste Value** into a new worksheet. Arrange the certified values and the average value into a small table, illustrated in Figure 5.

SRM	certified value	ave XRF reading
NIST 2781	7.82	17.96
NIST 2702	45.3	52.8
JSAC 0465	550	519
JSAC 0466	1093	1007
NIST 2711a	1400	1296

Figure 5: Comparison of CRM Results to Certified Values

6. Create a linear regression graph from the data table, as illustrated in Figure 6. Include a Line of Perfect agreement (1:1 slope). Include the equation of the line and the R^2 value on the graph.

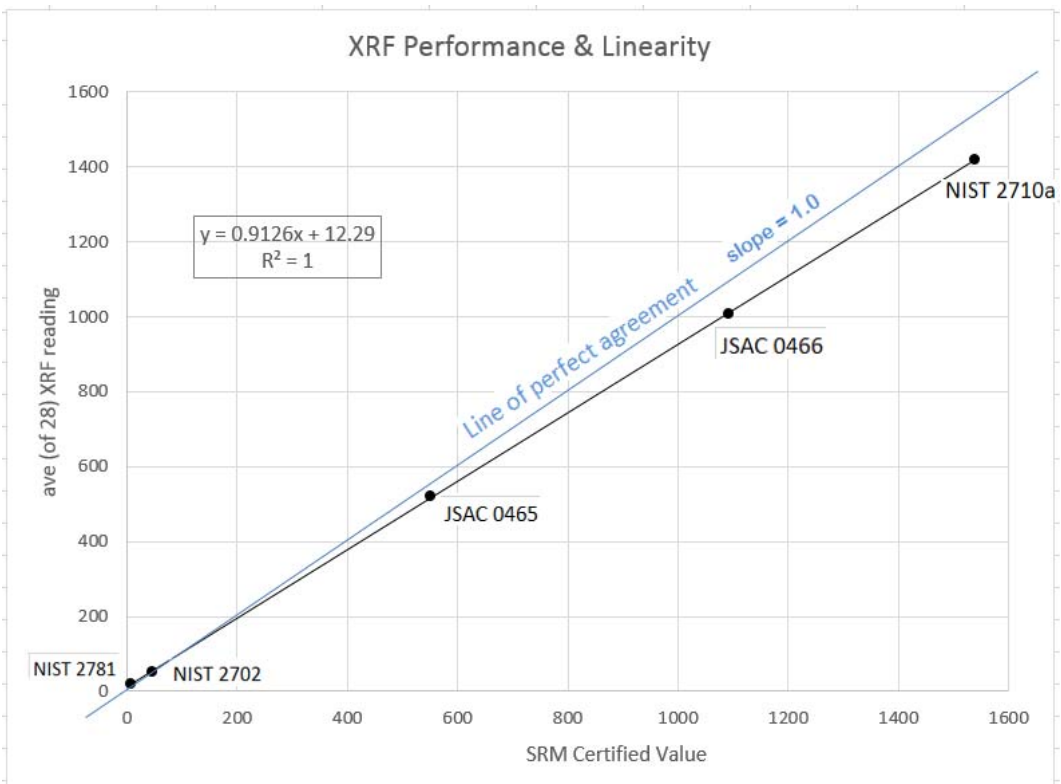


Figure 6: Linear Regression Graph, Certified Value vs. XRF Measurements

In the example shown, the high R^2 value and closeness of the CRM regression line to the data points at the lowest and highest concentrations show that the linearity of the CRMs data sets is excellent. However, the calibration curve in Figure 6 is biased slightly low compared to the perfect fit line with a slope of 1.0.

7.3 Conducting a precision test for duplicate samples

XRF instrument duplicates assess the reading-to-reading precision of the XRF instrument. Instrumental precision can be affected by a low battery, extraneous material stuck on reading window, a torn read window membrane, and operator mishandling. The following procedure and associated Excel worksheet, *Instrument Duplicator Calculator.xls* can be used to record and assess the results of XRF instrument duplicate quality control check.

Before starting the procedure, determine whether the instrument error value as reported by the XRF instrument represents either 1 or 2 standard deviation (SD) for the instruments counting statistics. This information can be obtained from the instrument setup menu, the manual, or from the manufacturer.

This procedure should be done using field samples in plastic bags, when possible. If no samples are available, use an LCS cup.

1. Take the 1st reading of what will be the duplicate set. A colleague may record the concentration value and the error reported by the instrument into the preprogrammed "duplicate calculator sheet" at that time, or wait to enter the results until after the 2nd of the duplicate readings are taken. In either case, do not move the sample bag after the 2nd reading until the duplicate reading is determined to be within control limits!

2. Do not move the sample bag at all between the duplicate readings.

3. Enter the 1st instrument reading and its error into the spreadsheet calculator.
    a. Be sure to enter the error correctly as a 1 or 2, depending on whether the instrument reports its counting "error" as 1 or 2 SD.
    b. The spreadsheet will calculate the 95% Upper and Lower bounds for the confidence interval (CI) around the 1st value using the instrument's counting SD.
    c. Note that the CI is based on the z-distribution (perfectly normal), not the t-distribution (nearly normal).
    d. The z-distribution is used because the CI is based on instrument counting statistics, which are likely to have a perfectly normal distribution.

4. Enter the 2nd result of the duplicate pair. Acquisition times must be the same for the 1st and 2nd measurement.

5. The calculator will determine whether the 2nd reading lies between the Upper and Lower Confidence Limits calculated from the 1st reading and populate "yes" or "no" in Column I: "Is the duplicate result within the statistical Confidence Interval?"
    a. If "yes," the bagged sample may be moved and proceed to the next analysis.
    b. If "no." do not move the bagged sample. Continue to Corrective Action below.

Sample ID	1st Result of Duplicate Pair	Error as Reported by the XRF	Error Type (1 - 1 SD; 2 - 2 SD) (Notes 5 & 6)	Lower Bound of 95% Confidence Interval		Upper Bound of 95% Confidence Interval	2nd Result of Duplicate Pair	*Do the duplicates agree? (Is the duplicate result within the statistical Confidence Interval?)*
USGS	68.8	7.5	1	54	–	83	63.4	yes

Figure 7: Example data entered into the XRF Duplicate QC Calculator.

If the 1st duplicate result is not within acceptable limits for the original reading ("No" is populated in column I) follow the following corrective action procedure:

1. Re-enter the result and error from the 1st reading into the row immediately under the previous row. For "Sample ID," enter "Rerun X", where X is the ID for the sample currently being analyzed.

2. Take a 3rd reading (a 2nd duplicate reading). The bagged sample can be moved after this reading.

3. Enter this 3rd reading in the "2nd Result of Duplicate Pair" column in the row with the re-entered results from the original reading. Determine whether the 3rd reading is within the 95% confidence interval for the original reading.

4. If it is within the confidence interval, all is well and normal activities can resume. It is possible that the initial duplicate was "out" due to random error.
    a. Note that with 95% confidence, 5 out of 100 duplicate readings may be "out."
    b. However, keep in mind that it is also possible that the operator's technique could be improved, such as ensuring the sample is steady and "square" on the test stand.

5. If the 3rd reading is also outside the confidence interval, and a field sample in a plastic bag was used, inspect the plastic bag for creases or dimples at the read location.
    a. If it appears that readings were taken through damaged plastic, choose a defect-free area of the bag, and repeat the duplicate procedure.
    b. If the duplicate now agree, the issue is resolved. If the duplicates again do not agree, use an LCS (or other CRM) cup to run the duplicate.

6. If the CRM control duplicates are within limits, select another field sample to perform the duplicate analysis (start from Step #1 above) in a defect-free area of the bag.
    a. If the problem persists with field samples only, suspect a problem with operator technique, a soil matrix interference or interference from the plastic bag.
    b. Observe the operator to rule out a problem with the operator's technique.
    c. If subsamples will be sent to an offsite lab for comparison, evaluate the possibility of a soil matrix interference by examining the XRF spectrum and selecting that sample (and perhaps other samples of the same matrix) for ICP analysis on an exact same 1 - 1.5 gram of soil that has also been shot by the XRF.

7. If the XRF spectrum appears normal, a problem with the plastic bag material needs to be ruled out. Verify that the bag's lot number had been tested using the Bag Checker and Calculator tool.xls
    a. If not, run the bag checks.
    b. If the bag's lot number had previously been checked, recheck another bag from the same lot number. If there seems to be a problem with the plastic material, change bag brand or a new lot number of the same brand.

8. If the CRM control(s) are also "out of control," troubleshoot the instrument by checking the battery, checking for cross-contamination, a torn window membrane, poor operator technique, or any other possible problems that might be noticeable from the outside of the instrument.
    a. If any correctable problems are found and resolved, restandardize or restart the instrument and rerun all start-up QC controls to establish acceptable instrument performance.

9. If no problem can be found, turn off the instrument for a few minutes, then restart and perform all restart procedures and QC.
    a. If the problem recurs and ambient conditions are extreme (hot, cold, humid), turn off the instrument. Take it into normal temperatures and humidity. Allow the instrument to equilibrate for 3-4 hours or overnight. Restart the instrument.

b. If the problem is still present or if it recurs, confer with an XRF expert to explore other trouble-shooting measures or send the instrument to the manufacturer for repair.

10. If LCSs are in-control, and everything else about the XRF instrument is working, but sample duplicates are frequently "out" (> 5% of the time), then the reason is probably operator technique.
    a. Corrective action is to counsel or retrain the operator, and/or modify the operator and bag positioning when taking a reading. An unstable test stand or loose analyzer in the stand may also cause wobbles in the XRF.
    b. Increase the frequency of sample duplicates until certain that the operator is able to use the XRF properly to generate reproducible results.

11. Record all non-conformances and corrective actions on the "Troubleshooting Log" worksheet in *Instrument Duplicator Calculator.xlsx*.

Wilcox XRF Procedure 02.1.2- Creating and using XRF Control Charts

This project-specific procedure contains eight sections and one Appendix:

1.0 Purpose
2.0 Application
3.0 References
4.0 Associated Procedures
5.0 Equipment
6.0 Decontamination
7.0 Procedure
8.0 Tools and Forms
Appendix A - Instructions for Using the Excel Tool: Template for Creating an XRF Control Chart

1.0 Purpose

This procedure provides instructions for creating and using control charts to validate XRF performance in real-time during XRF deployment.

2.0 Application

This procedure explains how to perform one of the tasks required during a baseline instrument evaluation (XRF *Procedure 02.1: Instrument Evaluation Period*). This procedure is applicable to any work that involves measuring the concentrations of metals in soil with the XRF. The preparation and use of control charts is required for all XRF applications. The purpose of creating an XRF control chart is to demonstrate that the system is in control when taking concentration measurements of samples. Control charting is a way to visually track performance to determine when a procedure is not meeting data-quality objectives. Control charts indicate when a procedure is headed out of control, so the analyst can pause, eliminate the source of the problem, and prevent the out-of-control situation.

This procedure requires that during the instrument evaluation period a data set for creating the control chart will have been generated.

There are several commercial tools available to create a control chart and the operator may use any tool available that meets the project needs and is consistent with the applications described in this procedure. This procedure includes instructions for using the *Control Chart Creator Excel Tool* in Attachment A. This simple tool is provided for convenience and is not required to be used for compliance with the procedure.

3.0 References

Wheeler, Donald J, 2016. The Levey-Jennings Chart, *Quality Digest*, Published: Monday, February 1, 2016, Available at: http://www.qualitydigest.com/inside/statistics-column/020116-levey-jennings-chart.html

4.0 Associated Procedures

- XRF procedure 01: General XRF Operation and Maintenance *(under development)*

  - XRF procedure 01.1: Operation of the TIIB Niton XL3t GOLDD+ Ultra *(under development)*
  - XRF procedure 01.2: Sample Processing
  - XRF procedure 01.3: Taking XRF Readings on Soil in Plastic Bags
  - XRF procedure 01.4: Subsampling and Analysis for Comparability Assessment
- XRF procedure 02: XRF Quality Control and Data Validation
  - XRF procedure 02.1: The Instrument Evaluation Period
  - XRF procedure 02.1.1: Assessing Instrument Precision and Bias
  - XRF procedure 02.1.3: Using the XRF Bag Checker and Calculator Tool
  - XRF procedure 02.1.4: Converting a Spreadsheet into a Readable PDF File

5.0 Equipment

- XRF instrument (Niton XL3t GOLDD+ Ultra, or equivalent), power cords and data transfer cables
- Laptop or desk computer with Excel software installed
- QC Check materials
  - Laboratory control samples (LCS) in sample cups
- XRF Logbook

6.0 Decontamination

The QC check materials (Certified Reference Materials (CRMs)) are contained in a plastic sample cup covered with a thin plastic film. Generally there should be no need for decontamination of the XRF in a laboratory setting. However, in some instances the sample cup may leak or dust may accumulate on the instrument or stand and will require removal with a laboratory wipe or puff of air.

7.0 Procedure

As part of tasks included in the instrument evaluation at least two standard reference materials will have been selected with relevant concentrations to use as LCSs during project deployment. For a discussion of choosing CRMs for a particular project and how many CRMs and LCSs are needed, as well as the schedule for collecting the LCS data see Appendix B in *XRF Procedure 02.1: Instrument Evaluation Period*.

The purpose of control charts is to closely monitor instrument performance so that developing problems will not lead to reporting poor quality XRF data.

Although field-portable XRF instruments are built to withstand the rigors of field deployment, there are still things that can go wrong. If undetected and uncorrected, these things can cause XRF data to be imprecise or biased. A partial list of things that can affect the bias and/or precision of XRF data are

- Batteries running down: Depending on the XRF unit, weakening batteries can begin affecting data before the normal indication that batteries need to be replaced. This problem has been observed as downward trends on the control chart that slightly precede a battery warning from the instrument.

- Torn XRF window membrane: This is prone to occur when measuring *in situ* soil containing small, sharp rocks. A torn window could allow dust to enter sensitive electronics and will disrupt the optimal internal temperature the XRF tries to maintain.

- XRF instruments are rated to operate under a wide range of temperature conditions (-5° to 50° C) however, extreme changes in ambient conditions such as rapid changes in temperature of the samples or instrument can cause humidity to form on sample bags and instrument membrane, which will affect readings.

- Jarring of the instrument or test stand strong enough to alter the alignment of the detector, the X-rays optics, etc.

- Improper operator technique: Wobbling of a hand-held XRF during a reading slightly changes the distance between the soil target and the detector while the XRF is counting, which create data imprecision.

- Electronic wear within the instrument that could create electronic instabilities.

Anything that alters the performance of the XRF so that LCS readings go outside the acceptable QC limits or creates a trend in the data also alters the quality (precision and bias) of the XRF data. When the control chart indicates a potential problem, sample analysis stops and troubleshooting of the instrument performed immediately.

7.1 Generating The LCS Data Used to Prepare the Control Charts

During the instrument evaluation period, LCS data sets will be generated having these characteristics:

1. About 30 readings (no less than 25 readings) generated on each LCS over a period of 7 or more working days (4 readings over the course of an 8-9 hour day, with an instrument restart in the middle of each day).
2. Data generated by different XRF operators during the data collection period, if possible.
3. It is imperative that the readings are not rushed For the following reasons:
    - The LCS readings must capture the full range of instrument and operator variability.
    - LCS readings should be taken over time, not back-to-back as this will artificially reduce the variability (the degree of differences) in the Evaluation data set.
    - Artificially reducing the variability will produce control chart lines (at ±2 and ±3 Standard Deviations (SDs) that are too close together (i.e., the ranges between them are too narrow).
    - If these ranges are too narrow, LCS readings will be out-of-control more often than they should when taking readings in production mode.
    - This will cause unnecessary delays during site work to repeat LCS readings or take corrective action when none is actually required.
    - The purpose of LCS charts is to identify a condition that something might be wrong with the instrument, and using a narrow range of conditions will signify a warning condition even when there is nothing wrong.

4. The data set should include all analytes reportable from the XRF and this data should be maintained electronically, although control charts will be prepared only for the target analytes. For the Wilcox site the analyte of interest is lead.
5. A single control chart is unique for
   - a specific instrument,
   - a specific CRM/LCS,
   - a specific analyte, and
   - a specific sample measurement time.
6. For example, a control chart might be designated for **NIST 2709a, Pb, and 30 second measurement time**. If a 15 second measurement time is used to generate a Pb result from the NIST 2709a LCS, that data point cannot be plotted on the 30 second control chart.

For the Wilcox project, three CRMs will be used as LCSs:

JSAC 0462
RCRA
NIST 2711a

The target analyte for the CRMs is lead.

LCSs do not need to have the same measurement time as the samples being run in the batch. The LCSs must have the same measurement time as specified on the control chart being used.

7.2 Creating the Control Charts

Appendix A provides detailed instructions for preparing a Control Chart using the Excel-based tool provided as part of this procedure. The instructions below provide a general overview of the process. Other software may be available for creating control charts.

1. Gather the QC data generated during the “Instrument Evaluation Period.” Only the target XRF elements for the project need to have a control chart prepared.
2. Record the project and instrument information into a data entry sheet.
3. As necessary, arrange the rows and columns of the spreadsheet containing the Instrument Evaluation data to make it is easy to copy and paste the following:
   a. Reading Number
   b. Data Collection date and time
   c. XRF result, and
   d. the XRF “error” reported with each result
4. The “error” reported by the instrument must be identified. Instruments may be set to report error as 1 or 2 standard deviations, so it is important to determine and note the reporting convention.
5. A minimum of 25 data points is required to construct a control chart. After the data is pasted, calculate the mean and standard deviation for the result data set. From these values, calculate two and three standard deviations on each side of the mean, and use those values (along with the mean) to place five horizontal lines on an Excel chart with the Y-axis representing concentration and the X-axis representing LCS readings (to be filled in during control chart use).

6. Some manual refinement of the y-axis will often be desirable.
7. After the control chart has been refined, the chart can be printed directly to a paper printer (color-printing is helpful, but not required) and/or to a pdf file.
8. A lined sheet should be stapled to the control chart to provide additional space to document XRF activities related to instrument maintenance, QC exceedances/non-conformances, troubleshooting of problems, and corrective actions taken. A suggested layout for the sheet is provided as an attachment to this procedure.
9. An example of the completed control chart is shown in Figure 1.

7.3 Using the Control Charts During XRF Deployment

The process for preparing and interpreting Control Charts is described below.

1. LCS results for target analytes are plotted on their control charts immediately upon generation. The plotted point is accompanied by the operator's initials, date and time, as illustrated in the figures below.

Figure 1: Example Control Chart and CRMs used for LCS

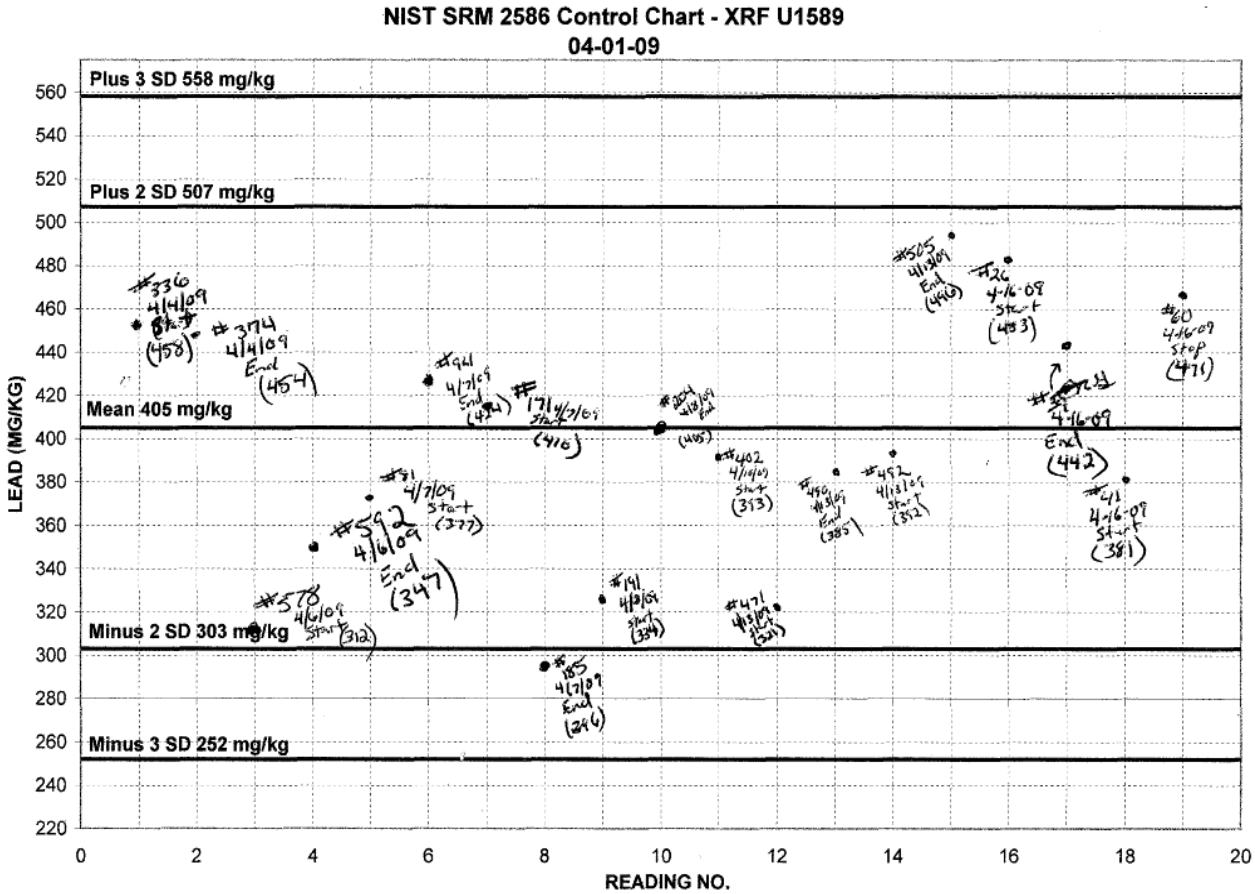


Figure 2: Example Control Chart Detail

2. Based on the control results, there are three possible states for instrument performance:

   a. **<u>In-control:</u>** Instrument performance is within the acceptance limits.

      - Samples may be reported if bounded by in-control LCSs

   b. **<u>Uncertain status:</u>** There is an indication that an out-of-control state may be developing, but more measurements are needed to confirm whether the actual state is in-control or out-of-control.

      - Samples run after the last "in-control" QC check may not be reported until the "uncertain" status is resolved and instrument performance is verified as being "in-control."

      - After instrument performance is verified as being in-control, those samples do not need to be rerun before reporting.

   c. **<u>Out-of-control:</u>** It is confirmed that instrument performance is unacceptable and an out-of-control state exists.

- Sample results generated while the instrument was in an out-of-control state (i.e., all samples run after the last "in-control" QC check) may not be reported.
- Activities to bring the instrument back into control must be taken. This might be as simple as changing the batteries and restarting the instrument, or may require systematic troubleshooting of the instrument.
- New samples may not be run until the instrument is back "in-control."
- All samples run since the previous "in-control" QC checks must be rerun.

d. In summary,

- All reported XRF results must be bounded by in-control QC samples.
- Out-of-control QC problems must be resolved before more samples can be analyzed.
- Samples analyzed after the previous in-control QC must be reanalyzed after an out-of-control situation has been resolved.

3. Triggers for the various performance states

a. **In-control state**

- LCS results plot within the ±2 SD lines.
- LCS results plot randomly above and below the mean line.
- Conclusions and actions: All appears to be functioning normally; continue routine operations

b. **Uncertain state**

- An LCS result plots between a 2 SD line and its corresponding 3 SD line.
- Conclusions: this could indicate an emerging problem or it could only be random variation.

  Because the range between the ±2 SD lines represents 95% of the data population that was generated during the instrument evaluation period, there is a 5% chance that an LCS will randomly exceed a 2 SD line even though nothing is wrong with the instrument.

  As discussed in Section 7.1, *Generating the LCS Data Used to Prepare the Control charts,* if LCS readings were not spaced sufficiently during the instrument evaluation period, exceedance of a 2 SD line will occur more often than 5% of the readings, incurring unnecessary delays and extra work during deployment.

- Action to take when an LCS reading falls between a 2 SD line and its corresponding 3 SD line

  1. Do not analyze more samples. Do not report results from the samples run after the previous in-control LCSs up to this point.

  2. Immediately rerun the LCS.

  3. If the repeat LCS reading plots within the ±2 SD lines, and there are no issues with any of the other LCSs, the instrument performance state returns to **in-control** and routine activities can resume. Note the reading and corrective action on the Non-conformance Log Sheet accompanying the control chart. The frequency of "false alarms" should be tracked**.**

     The samples run after the previous in-control LCSs and before the problem LCS reading do not need to be rerun to be reported.

  4. If the repeat LCS reading again plots outside the ±2 SD lines, and there are no issues with any of the other LCSs, examine the problem LCS for damage to the sample cup membrane or alterations of the sample in the cup (mold, mildew, or moisture).

     a. If damage is found, the LCS cup will need to be repaired or replaced.

     b. If using three LCSs and one is removed due to damage, only two LCSs will be available until the third LCS is returned to service. This is sufficient to allow routine operation to continue.

     c. If only using two LCSs and one is removed due to damage only one will be available for determining instrument control, which is not sufficient. Until such time as the other LCS can be returned to service, a set of instrument duplicate readings can be used to check instrument precision. Select a bagged sample with the approximate concentration as the missing LCS and collect duplicate readings without rotating the sample. Use the Instrument Duplicate Calculator tool, as described in *XRF procedure 02.1.1: Assessing Instrument Precision and Bias* to determine if the instrument precision is within an acceptable range. Record the results of the instrument precision check on the Non-conformance log.

     d. If the LCS's CRM is replaced by a different batch of the same CRM, it is possible that the new CRM may not fit the statistical data range of the original cup. If that happens, continue running the new cup, and note each exceedance of the 2 or 3 SD lines in the Non-conformance log. When 25 or more data points for the new LCS have accumulated, create a control chart for the new LCS.

        1) Once the LCS is repaired or replaced the instrument returns to an **in-control state**. Previously run samples do not need to be rerun.

e. If damage to the cup is not found, the instrument is now in an **out-of-control state.** Perform an inspection of the instrument for a torn or dirty window membrane.

1) If found, rectify any obvious instrument problems.

a. Rerun all LCSs. If they are within the 2 or 3 SD lines, return to **in-control** and routine operation.

b. If the rerun LCSs are not within the 2 or 3 SD lines, the instrument is **out-of-control**. Shut it down and restart the instrument using standard procedures.

c. Do not report results from any samples run after the previous in-control LCSs.

2) If no obvious problems can be found, the instrument is **out-of-control.** Shut it down and restart the instrument with all standard startup procedures and QC. If the results plot within the 2 or 3 SD lines, it returns to an **in-control state**. Rerun all samples run after the previous in-control LCSs. Report the new results.

3) If the problem remains, the instrument remains **out-of-control**.

- Action to take when an LCS reading plots outside the ±3 SD lines. The probability that the 3 SD lines are exceeded by chance is less than 1% (about 0.3% to be exact)

1. Do not analyze more samples. The instrument status is **uncertain**. Immediately check the LCS cup for damage and the instrument for a defect as discussed above in Section (4) (a) and (b) above.

2. If no problems are observed with the LCS cup or instrument, consider whether it was possible that the reading itself was “bad” because of instability of the instrument during the reading.

a. This is more likely to happen when LCS measurements are made with the instrument held by hand rather than in an XRF stand. Even a momentary distraction of the operator holding the instrument can cause a “bad” reading.

b. If the LCS cup was read in a stand, ensure it was properly centered over the instrument window. If the stand is set up in a temporary trailer, consider if the trailer was jolted during the measurement time.

c. If these are possibilities, repeat the reading on the LCS.

d. If the new reading is within the 2 SD lines, return to an **in-control state**.

3. If the new reading is not within the 2 SD lines, or the out-of-control reading cannot be attributed to a non-instrument problem, the instrument is **out-of-control.**

a. Troubleshoot the instrument as discussed in the sections above and Section 5) below.

c. **Out-of-control state**

- If seven consecutive readings are on one side of the mean line (i.e. all above the mean or all below the mean), the instrument is **out-of-control.**
- In most cases, this occurs when the batteries are starting to lose power, but the instrument's warning to change batteries has not turned on. The control chart usually resembles the figure below.

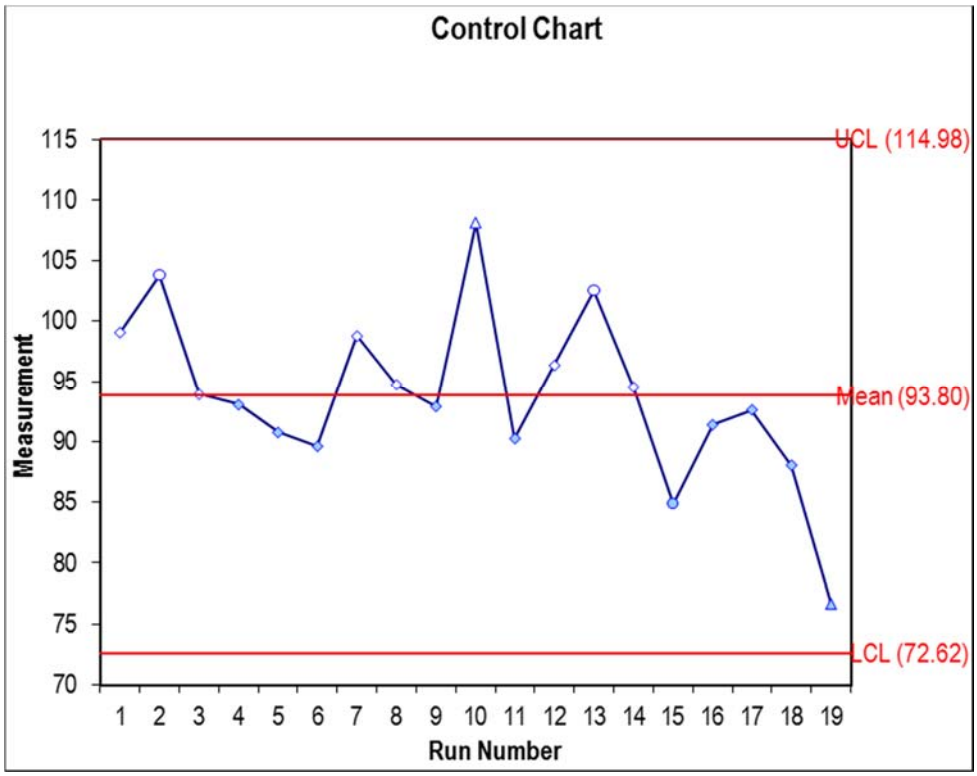


Figure 3: Example Control Chart Showing the Effect of Low Battery

- Action: replace batteries. Restart instrument using routine procedures and QC checks.
- When the instrument is back **in-control**, rerun all samples analyzed by the XRF after the previous in-control LCSs.
- Log all non-conformances and note all corrective actions on the Non-conformance Log Sheet.

4. Frequency of running and plotting the LCS set

Selection of LCS frequency is a matter for some discretion. One consideration is how many samples would need to be rerun if an end-of-batch LCS is out-of-control. In general, it is wise to run LCSs at a higher frequency early in the project to establish that both staff and equipment are running smoothly. After stability in the measurement system is demonstrated, the frequency at which the LCS set is run is generally every 6 to 10 sample bags.

Consider that each sample bag will have at least four readings, and could have as many as 10 readings. If there is high matrix heterogeneity and concentrations are close to the action level such that 8-10 readings are needed, the LCS set might be run more often perhaps every 6 or 7 sample bags. If heterogeneity is low and/or concentrations are far from the action level, perhaps only four to six readings are needed, and the LCS set can be run every 10 sample bags.

5. Troubleshooting an XRF can include the following actions

    - check the battery
    - check for a dirty window and cross-contamination
    - check for a torn window membrane
    - check for poor operator technique
    - If any correctable problems are found and resolved, restandardize or restart the instrument and rerun all start-up QC controls to establish acceptable instrument performance.
    - If no problem can be found, turn off the instrument for a few minutes. Restart and perform all routine restart procedures and QC.
    - If the problem recurs and ambient conditions are extreme (hot, cold, humid), turn off the instrument and take the following actions:
        - Take it into normal temperatures and humidity.
        - Allow the instrument to equilibrate for 3-4 hours or overnight.
        - Restart the instrument and perform all routine procedure and QC.
- If the problem is still present or if it recurs under normal operating conditions,
    - confer with an XRF expert to explore other trouble-shooting measures, and/or
    - send the instrument back to the rental company or to the manufacturer for repair.

8.0 Tools and Forms

This procedure contains one Tool as worksheets in an Excel file

- Excel Control Chart Creator: *XRF Procedure 2.1.1 Creating and Using XRF Control Charts Tools.xlsx*

This procedure also contains and appendix that describes the process for using the Excel Control Chart Creator Tool.

Appendix A – Instructions for Using the Excel Tool: Template for Creating an XRF Control Chart

Purpose of this Excel Tool

This tool assists with preparing the control charts used during XRF deployment as described in *XRF procedure 02.1.2: Creating and Using XRF Control Charts* for producing hard-copy paper control chart(s) for real-time evaluation of XRF Laboratory Control Sample (LCS) QC data (as a part of real-time validation of XRF performance). This tool is provided as a convenience for the user. Other control chart tools are available and may be used.

Step-by-Step Instructions: Getting Started

This procedure assumes that the instrument has already gone through the "Instrument Evaluation Period," either because it is a rental instrument or because it was purchased new for your organization.

1) As part of the Instrument Evaluation, about 30 readings have been generated over 1-2 weeks on each LCS QC sample that might be used. That data was downloaded from the XRF instrument into a spreadsheet. A copy of the original spreadsheet (a "working spreadsheet") will be used to supply the data to be entered into this Control Chart tool.

2) To make it easier to identify data to be used in the control charts, delete rows and columns from the working spreadsheet that contain information not directly relevant to producing the control chart(s). That means that data for all elements that are not target analytes for the project can be deleted.

3) After removing irrelevant data, the following columns should remain:
   - Reading Number, or equivalent (a sequential number generated by the instrument identifying a unique reading made by the instrument);
   - Read/data collection Date and Time (either as two columns or as a single column, depending on how the XRF outputs the data);
   - The Sample ID (which will be the LCS ID), and
   - The XRF reading results with their associated reading error (two columns for each target analyte), as shown below for a single LCS.

	A	B	C	D	E	F	G
1	Reading No	Date & Time	LCS ID	As	As Error	Pb	Pb Error
2	1	11/3/2014 7:47	NIST 2709a	8.79	1.78	16.04	2.19
3	2	11/3/2014 11:51	NIST 2709a	10.71	1.76	13.1	2.11
4	3	11/3/2014 13:04	NIST 2709a	9.29	1.8	16.9	2.21
5	4	11/3/2014 16:41	NIST 2709a	9.06	1.82	17.25	2.24
6	5	11/4/2014 7:31	NIST 2709a	10.88	1.8	16.82	2.17
7	6	11/4/2014 11:47	NIST 2709a	8.95	1.78	14.81	2.19

4) The working spreadsheet will likely contain data from two or more LCSs, and their data rows will be intermixed. Use the sort function to group the rows by LCS ID, so that all the readings from a single LCS (and only that LCS) are in adjacent rows.

Step-by-Step Instructions: Working with the Control Chart Tool

1) Save a new copy of the Excel template file. Rename the new copy using the LCS name and the element being evaluated in this file. If more than one XRF instrument is being used, add the XRF ID to avoid confusion.

Example file name: "XRF Control Chart-NIST2710a-Pb-InnovX1.xlsx"

2) Enter the indicated project and instrument information on the right-hand side of the "Data Entry" sheet. Note that some sheets in the workbook and parts of the "Data Entry" sheet are protected to avoid accidental alteration of automatic calculations.

Region/Project:	Pb Example			
Other project information:				
Operator:	DMC			
Date Chart Prepared:	3/10/2015			
LCS ID:	NIST 2709a			
Element:	Pb			
Read time for target element:	30	sec	Is this a rental?	no
			If yes,	
XRF Brand:	Niton		Date rental XRF rec'd:	
XRF Model:	XL3t 955 GOLDD+ Ultra		Rented from (company):	
XRF's serial number:	92959		Contract number:	
XRF's unique ID/name:	TIIB Ultra			
No. of XRF filters used:	3			
Read time for main filter:	30	sec		
Read time for Low filter (if applicable):	30	sec		
Read time for Light filter (if applicable):	30	sec		
Total read time:	90	sec		

3) Consider the effect of filters applied with the XRF Instrument:
    - Some XRFs have “filters” that allow a single instrument to read a wider range of elements.
    - Any particular element is read using only one of the filters. For example, Pb and As and many other elements are read on a filter often called the “main filter.” But Cr may be read using a different filter (which may be called the “Low filter” or low range filter). Mg, Ca, S, Al and some other “light” atomic mass elements can be measured on the “light filter.”
    - Which filters are used during an XRF analysis, and how long each filter reads, is programmable in the instrument.
    - The total measurement time is the sum of the measurement times for all filters used.
    - Note that in the above example, all three filters were used. However, the read time for Pb is only 30 seconds, not the 90 seconds that represents the total read time for all three filters.

4) The measurement time for an LCS does not have to be the same as the measurement time used on project samples, as long as the measurement time for samples was selected to be sufficient to manage instrument error to the degree needed. This is discussed more thoroughly in *XRF procedure 0.2.1: Instrument Evaluation*.
    - The measurement time for target analytes in LCSs during project deployment must be the same as the measurement time used to generate the 25 to 30 readings of target analyte data during the Instrument Evaluation Period.
    - The measurement time to be used when reading LCSs should be noted on the Control Chart to avoid using the wrong read time.

    Example: If a control chart was set up from Pb data generated by 30 second measurement times during Instrument Evaluation, but during deployment the LCS measurement time was 15 seconds, it is quite possible that the result from the 15 second reading will be outside of the control limits set by a 30 second read time. This is because analytical variability in XRF results decreases as measurement time increases.

5) When the data have been organized in the working spreadsheet, copy the “Reading No.” column from the data spreadsheet into the “Reading Number” column on the “Data Entry” sheet.

Enter the (LCS) Control Data Set Collected During the

Instrument Evaluation Period

(Enter at least 25 results, but no more than 50)

	use if date & time separate		use if together			
Reading Number	**Collection Date**	**Collection Time**	**Collection Date & Time**	**XRF Result**	**Instrument Error**	**Is the "Error" configured as 1 or 2 SD?**
1			11/3/14 7:47 AM	16.04	2.19	**Enter 1 or 2:** 1

6) The “Data Entry” page must have at least 25 results entered for the tool to run, and can accommodate up to 50 results.

7) Copy the Date and Time column(s) into either the two designated columns or into the single column, depending on how the XRF download is set up.

8) The two columns for the XRF result and its error are normally side-by-side, so they can be copied and pasted together.

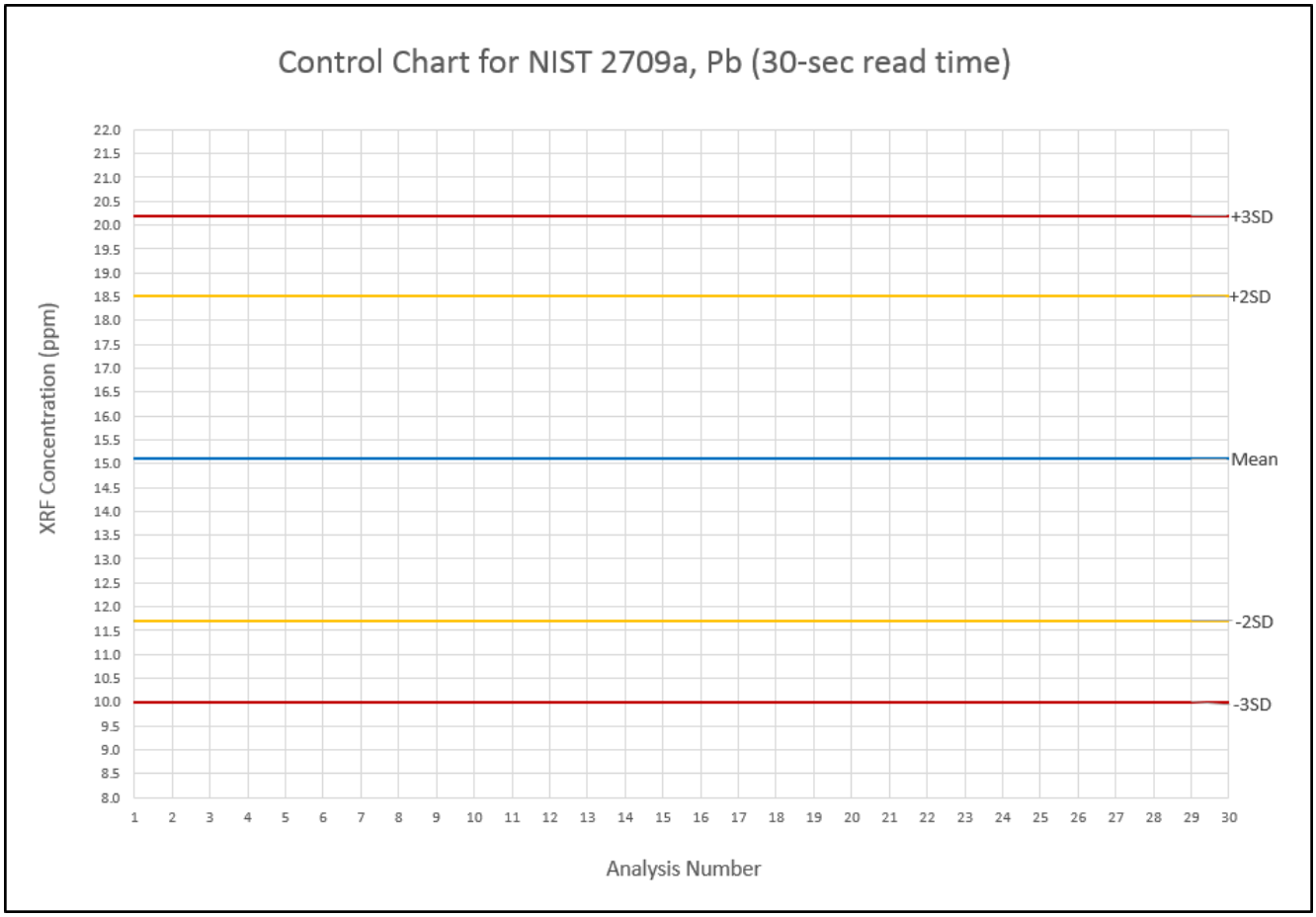
9) Enter a 1 or 2 in the “Error configuration box”. This is a required field.

10) Once these data are entered, the spreadsheet does several things to create the blank control chart shown in the figure below:
    - The “Statistics for the Instrument Evaluation LCS Data Set” box (just above the graph) populates the three entries there (Mean, Std. Dev. and 1 Std. Dev. Error).
    - The entries for “data set mean” and “data set Std. Dev.” in that box are used to generate the five lines for the graph. Those lines are the mean, + 2 SDs, - 2 SDs, + 3 SDs, and - 3 SDs.
    - Note that the “Average Instrument Error (as 1 SD)” entry is currently for research purposes only.
    - The standard deviation lines appear on the Control Chart graph.
    - Control chart configuration settings appear in the “Optimization of Excel defaults for the y-axis” box just below the auto-generated line data block, to the right of the graph.

11) The five lines are placed on the chart according to how the Excel program automatically scales the y-axis of the graph.
    - Usually, the choices made by Excel must be optimized to make the Control Chart easy to use.

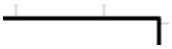
- Suggestions for optimizing the y-axis are presented in the box: "Optimization of Excel defaults for the y-axis."

Figure A-1: Example Control chart prepared using the Excel Control Chart Creator

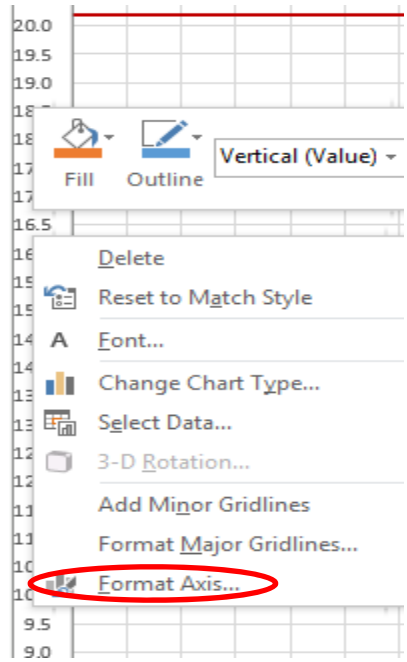


Step-by-Step Instructions: Optimizing and Printing the Control Chart

1) The following steps describe how to optimizing the scale of the y-axis by formatting the y-axis in Excel.

   a) Click on the chart near a border so that the chart is "selected." If it was successfully selected, the chart border will go from looking like this:  to looking like this:

b) Place the cursor over the y-axis of the chart and right-click the mouse. A dialogue box similar to the one on the right will open.



c) Place the mouse cursor on “format axis” at the bottom of the dialogue box and left click to select.

d) A dialogue box for formatting the vertical axis will open. This box will look different depending on the version of Excel (e.g., Excel 2007 vs. Excel 2013). But the following three elements are always present and are the only ones that might need to be changed.

   i) Maximum axis value
   ii) Minimum axis value
   iii) Major Units

e) The default setting for each of these is “auto” which allows Excel to make the selection.

f) To change these three values, select the “fixed” radio button, and/or simply enter the desired values into the box.

g) First try entering the suggestions in the “Optimization of Excel defaults for the y-axis” box. An example is shown below.

Optimization of Excel defaults for the y-axis		
+3SD to -3SD range	10.2	See "Instructions" sheet for more details.
chart's y-axis approx max	22	<---- use this approx to set the max value for the y-axis
chart's y-axis approx min	8	<---- use this approx to set the min value for the y-axis
approx y-axis step	0.55	<---- use this approx to select from the choices below:
common choices for the y-axis step are: 0.2, 0.5, 1, 5, 10, 20, 50		

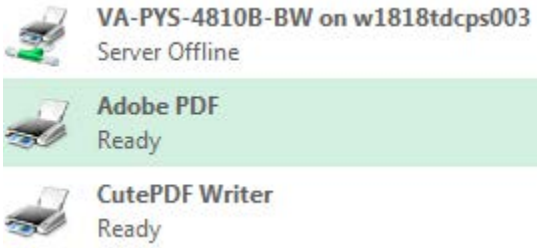
- The min and max values are self-explanatory. The value for the “approx. y-axis step” equates to the Excel dialogue box entry for “Major Units” and sets the closeness of the horizontal grid lines.
- The suggested value in the “Optimization” box is derived from calculation and may need to be rounded up or down to one of the “common choices for the y-axis step.”
- Evaluate the appearance of the y-axis on the chart. Ideally,
  - The area bounded by the + 3 SD and the - 3 SD lines should be roughly centered, with some room to plot points slightly above and below the 3 SD lines.
  - The concentration values along the y-axis should be easy to read and not cluttered.

- It should be easy to interpolate where to plot points that fall between Major Unit lines.
- If the suggestions in the optimization box don't give the desired appearance, select appropriate values.

2) Excel offers two options for saving and printing the Control Chart. The Excel file is saved, and the Control Chart can be printed to a paper printer directly from Excel. Alternatively, the Control Chart can be "printed" to a PDF file which is saved. The PDF file can be printed to paper at a later time instead of printing from Excel.

   a) Printing to paper
      i) Select the chart as in Section 1) a) above.
      ii) Select File/Print on Excel's main menu.
      iii) Select the desired printer (color printing is useful, but not required).
      iv) Make sure "Print Selected Chart" is selected in the Print dialogue box.
      v) Make sure "Landscape orientation" is selected for the paper.
      vi) The size of the chart in the Excel file has been set so that the chart will fill most of the page.
      vii) Click "Print."

   b) Printing to a PDF file
      i) Either Adobe Acrobat Pro (or similar) or CutePDF Writer must be installed on the computer. Some versions of Excel allow saving files as pdf.
         (1) Adobe Acrobat Reader cannot be used to do this.
         (2) CutePDF Writer is free and can be downloaded from the web. Search on "CutePDF Writer." It installs as a "printer."
         (3) Similarly, Adobe Acrobat Pro installs an "Adobe PDF" printer in the printer selection list.
         (4) These programs allow using the printer menu to select the program as if it were a physical printer, except that the output is a PDF file, rather than paper.



(5) The process is the same as for printing to paper (above), except that one of the PDF writers is selected from the drop-down list of printer options.

(6) When “Print” is clicked, the Adobe program (including Adobe Acrobat Reader) will open to show the “printed” page. It will also prompt to name the file and select where to save it.

(7) There can be a time delay between clicking “Print” and Adobe Reader opening and/or being prompted to save the file, depending on the complexity of the item being printed to PDF.

Wilcox XRF Procedure 02.1.3 Assessing Interference from Plastic Sample Bags

This Standard Operating Procedure (SOP) contains seven sections:

1.0 Purpose
2.0 References
3.0 Associated SOPs
4.0 Equipment
5.0 Decontamination
6.0 Procedure
7.0 Tools and Forms
This procedure includes one tool, XRF *Procedure 2.1.3 Plastic Bag Checker and Calculator Tool.xlsx*.

1.0 Purpose

This procedure provides instructions for using an Excel calculator to verify that a specific lot number of plastic bags does not pose significant interference to X-rays passing through it, i.e., the plastic bag will not bias the target analytes' concentrations significantly high or low. This procedure is part of a group of SOPs that are subordinate to XRF Procedure 02: XRF QC and Data Validation.

2.0 Application

This procedure explains how to evaluate the potential for interference from the plastic bags used as sample containers for soil during XRF analysis. The procedure is required prior to using any sample bag and is normally conducted during a baseline instrument evaluation. It is part of a group of procedures for evaluating instrument performance subordinate to *Procedure 02.1: Instrument Evaluation*. This procedure is applicable to all XRF analysis when samples are contained in plastic bags.

3.0 References

None

4.0 Associated SOPs

- XRF SOP 02: XRF Quality Control and Data Validation
- XRF SOP 02.1: The Instrument Evaluation Period *(under development)*
- XRF SOP 02.1.1: Assessing Instrument Precision and Bias
- XRF SOP 02.1.2: Creating and Using XRF Control Charts
- XRF SOP 02.1.4: Converting a Spreadsheet into a Readable PDF File

5.0 Equipment

- XRF instrument (Niton XL3t GOLDD Ultra, or equivalent), power cords and data transfer cables
- Laptop or desk computer with Excel software installed
- QC Check materials
    - Laboratory control samples (LCS) in sample cups
- XRF Logbook

- Plastic bags that will be used for sample analysis

6.0 Decontamination
The QC check materials (Certified Reference Materials (CRMs)) are contained in a plastic sample cup covered with a thin plastic film. The film must be kept clean and protected. Generally there should be no need for decontamination of an XRF in a laboratory setting. However, in some instances the sample cup may leak or dust may accumulate on the instrument window or stand platform and will require removal with a laboratory wipe or puff of air.

7.0 Procedure

7.1 Introduction

There are several advantages to using plastic bags to hold soil samples for XRF analysis, especially in the field or a field lab setting. Plastic bags are inexpensive and much easier to use than XRF cups, and can generally be purchased at local food or department stores. Unlike XRF cups, a plastic bag allows remixing of a segregated sample, and multiple readings can be taken from across the bag and on the both sides of the bag. In conjunction with a preprogrammed calculator tool, multiple readings allow control over mild to moderate soil heterogeneity using statistics, and an expression of statistical confidence in the result is possible for the concentration determined for the sample soil inside the bag.

However, plastic bags can significantly bias XRF readings of the soil inside by absorbing or scattering the X-rays as they enter or leave the bag. The degree of bias created by plastic bag interference varies greatly depending on the type of plastic (e.g., polyethylene and polypropylene), whether “virgin” plastic was used in the manufacture, the thickness of the plastic bag walls, and potentially variables such as temperature or molding process during manufacturing.

For this reason, plastic bags used for XRF analysis must be checked prior to use to establish that no significant interference is present for the target analytes of the XRF project. The absence of interference must be confirmed at two concentration levels (a high and a low). This is easily done by placing one (1) layer of the plastic bag over the reading surface of an CRM material and taking several readings to calculate statistics. The statistics for the CRM with the plastic layer is statistically compared to CRM results without the plastic layer.

Even if a particular brand and make of plastic bag has been shown to be adequate, each unique lot number of that brand must be checked to verify that the manufacturing process for that lot number did not introduce an interference for that lot number. (A “lot number” refers to a “batch” of items all produced at the same time and under the same conditions. The lot number is always stamped or inked on the box, although you may have to look carefully to see it.)
To increase the likelihood that a particular bag will “pass” the bag checker test, choose a type of bag that is as thin, smooth and clear as possible. Do not buy bags that have surface texturing or colored plastic. Do not attempt to disaggregate soils in the reading bag since this will damage the bag. The bag must be free of crinkles or dimples where read by XRF.

If it is uncertain whether a particular bag will pass the interference test, buy only one (1) box and test it. If it passes, go back to the store and purchase enough of the same lot number to finish

the project. Any box from a different lot number must be checked. Only one (1) bag from each lot number needs to be checked.

7.2 Using the Calculator

An Excel calculator has been developed to facilitate the testing and evaluation of plastic sample bags for interference (*Procedure 2.1.3 Plastic Bag Checker and Calculator Tool.xlsx*). The steps for using the calculator are presented below. Note that this information is included in the calculator/spreadsheet.

1. Fill out the indicated information on the spreadsheet:

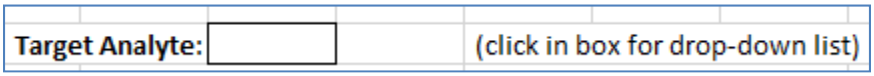
Date of this testing:	
Project:	
Operator:	
ID of the XRF instrument being tested:	
Plastic bag brand and name/make:	
Bag material & wall thickness:	
Bag lot number:	
Where this bag lot was purchased:	
Control sample ID:	
Read time (sec):	

   Control Sample ID refers to the CRM ID used for testing bags. There will be one CRM for low concentration testing and one CRM for high concentration tests.

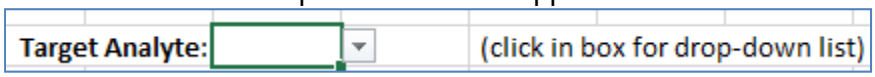
2. The tool can simultaneously assess up to four different analytes. Each analyte has a pair of data entry columns for recording concentrations without the plastic bag and with the plastic bag:

Target Analyte:		(click in box for drop-down list)	
WITHOUT Plastic Layer		**WITH Plastic Layer**	
XRF reading #	Conc	XRF reading #	Conc
1		1	
2		2	
3		3	
4		4	
5		5	
6		6	
7		7	
8		8	
	SUMMARY STATISTICS		

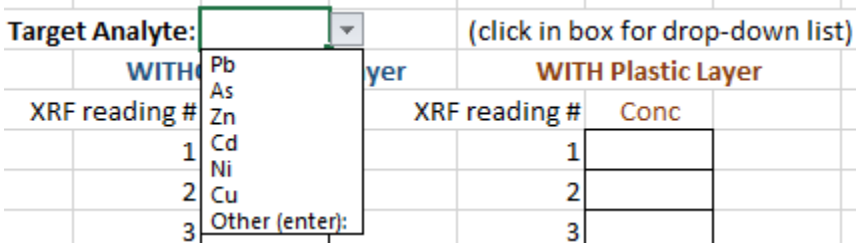
3. For each pair of data columns, enter the target analyte in the space provided above the pair:



Clicking on the box causes the drop-down arrow to appear:



Clicking the arrow causes a pick-list to appear for common potential analytes:



4. Two concentration levels, a **Low Concentration Level**, and a **High Concentration Level**, for the target elements are used. Four (4) measurements are taken initially with and without one layer of plastic bag covering the reading surface of the CRM cup. To take a reading with the plastic film, the single layer of plastic bag is placed on the test stand over the reading window and the CRM cup is placed on top of the plastic layer.

   If the CRMs are also being used as LCSs, the last four readings from the routine LCS QC checks may be used as the “without” data, rather than taking four new readings on the CRM cups specifically for the Bag Checker tool. If this is done, indicate it on the spreadsheet with a Y or N in the indicated box, as shown below.

5. Enter the four readings for the low and high concentration measurements in the appropriate columns, and the calculator will run the statistics. The spreadsheet will provide an **initial** assessment of the bag lot including instructions if an additional four readings using the plastic bag are needed for statistical support. If ambiguity is not removed after a total of 8 readings in the "WITH Plastic Layer" column, do not use that lot number of bag.

6. A **final** determination for whether the bag passes the tests will be clear when one of the following the statements appears:
   - “This bag lot is OK to use”, or
   - “OK to use this bag since these concentration differences do not appear to be significant for decision making.”

7. Use a new Calculator file for each bag lot number checked.

8. Retain the completed spreadsheet as a record of quality control for the bag lot.

7.0 Tools and Forms

This SOP contains one Tool as worksheets in an Excel file (Wilcox XRF *Procedure 2.1.3 Plastic Bag Checker and Calculator Tool.xlsx*):