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U.S. Environmental Protection Agency
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GUIDANCE

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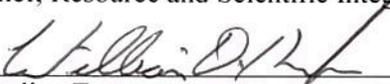
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Revision History

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1. General Information

1.1 Purpose

The intent of this FOG is to provide Region 4 On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs) with a methodology to collect defensible XRF data for lead and arsenic (approach may apply to other metals) in soil samples.

1.2 Scope/Application

The procedures contained in this document provides the methods to measure concentrations of contaminants in soil in a practical, cost-effective, and timely manner. The steps below outline the XRF FOG for lead and arsenic. By following the steps outlined, SSS has confidence XRF data collected can be defined as definitive data (See Appendix C: Case Studies). Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by Superfund management, based on their knowledge, skills and abilities and has been tested in practice and was peer reviewed. The official copy of this procedure will be scanned in to EPA's Superfund Enterprise Management System (SEMS) and published on EPA's internet. The Document Control Coordinator (DCC) is responsible for ensuring the most recent version of the procedure is placed in SEMS and for maintaining records of review conducted prior to its issuance.

1.4 Authors and Peer Reviewers

This document was prepared by Sydney Chan, Tim Frederick, Kevin Koporec, and Glenn Adams of EPA Region 4 Superfund Scientific Support Section (SSS).

SSS would like to acknowledge and thank our peers that took time to review and comment on the draft versions of this document. This document was peer reviewed by Greg Harper, Region 4; Cathy Amoroso, Region 4; Terry Tanner, Region 4; M Crowe, SESD, Region 4; Mike Neill, SESD, Region 4; Mike Beringer, Region 7; Duane Newell, ERT; Deana Crumbling, OSRTI; Michele Burgess, OSTRI; John Wheeler, ATSDR; Bryan Vasser, Tetra Tech; Quinn Kelley, Tetra Tech; Russell Henderson, OTIE; and Elizabeth Roddy, OTIE.

1.5 Executive Summary

The EPA Region 4 Superfund Scientific Support Section (SSS) has prepared this X-Ray Fluorescence (XRF) Field Operation Guide (FOG) for consideration by Region 4 On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs). The intent of this FOG is to provide OSCs/RPMs with a methodology to collect defensible XRF data for lead and arsenic (approach may apply to other metals) in soil samples. This FOG also provides the methods to measure concentrations of contaminants in soil in a practical, cost-effective, and timely manner. The previous methodology generally required the OSC/RPM to make decisions based on a single XRF reading and/or laboratory analysis from a five-point composite or a grab sample within a grid. EPA Office of Superfund Remediation and Technology Innovation (OSRTI) states statistically valid data can be collected when using the XRF by increasing the number of XRF readings on a soil sample and calculating an upper confidence level (UCL) and/or lower confidence level (LCL) on the sample bag. SSS field tests have concluded the recommended OSRTI approach to using the XRF is a viable option that OSCs and RPMs may consider for obtaining lead and arsenic concentrations in soil for decision making purposes. The steps below outline the XRF FOG for lead and arsenic. By following the steps outlined, SSS has confidence XRF data collected can be defined as definitive data (See Appendix C: Case Studies).

The Region 4 Science and Ecosystem Support Division (SESD) Operating Procedure: Field X-Ray Fluorescence Measurement (SESDPROC=107-R3) should be acknowledged in any Sampling and Analysis Plan/Quality Assurance Project Plan (SAP/QAPP) utilizing XRF. This XRF FOG does not specifically follow the process outlined in Section 4, Study Design, of SESD's protocol, but it does address the intent of the protocol. A percentage of samples should be determined in the QAPP to be analyzed by the XRF FOG process and a laboratory. The comparison of the XRF FOG data with the laboratory can be used as recommended in the SESD protocol to confirm the quality of data. However, the data quality objectives of a particular project should be determined by the RPM/OSC on a site specific basis. (EPA, 1993; EPA, 2006)

Before starting, it is important to establish a lead and/or arsenic decision point value {i.e. Regional Removal Management Level (RML), Regional Screening Level (RSL), site-specific clean-up levels, etc.}. This value is extremely important in making site-specific decisions for further analysis and/or clean-up. Please note that concentration data for total arsenic in soil collected using the XRF FOG may be higher at some sites than data reported by extraction-based analysis at a fixed laboratory (See Lessons Learned). If this happens at a site, it is recommended that the RPM and/or OSC consult with their Regional risk assessor and the laboratory to work through site-specific issue before making a final decision.

Spreadsheets developed by OSRTI are central to using the XRF FOG. The spreadsheets are periodically updated and modified with the latest applicable information. Please contact SSS for the latest versions of all spreadsheets prior to beginning field work. Example spreadsheets are included in Appendix B.

2. Quick Start Guide

Field Procedure for use of XRF in Lead and Arsenic Soil Sampling are summarized below:

- a) Collect soil samples according to SAP/QAPP. Mix and disaggregate soil sample in bowl or appropriate container, per the QAPP.
- b) Samples may need to be sieved per OLEM Guidance which recommends using soils passing a No. 100 screen size or particles less than 150 μm .
- c) Measure the soil sample's moisture content. If moisture is $\geq 10\%$, then sample should be dried to less than 10%.
- d) Determine the duration time needed for XRF reading. Typically, the Niton[®] XRF requires a minimum of 30 seconds to analyze lead and arsenic and the Innov-X XRF requires 45 seconds.
- e) Control outside variables with the XRF by confirming with a systems check, field calibration check, and a Bag Test. Consult equipment manual for instrument specific systems check directions. SSS has spreadsheets to assist with these instrument checks and Bag Test. Please contact SSS for the latest version of the spreadsheets. Perform systems check and field calibration check at the beginning of sample readings and every subsequent 5 hours.
- f) Take 4 XRF readings at different locations of each bagged soil sample through the plastic bag. Record the results in Data Spreadsheet and field logbook.
- g) Evaluate the data to determine whether additional readings are needed. If after 4 XRF readings, the relative standard deviation (RSD) $< 35\%$ then, no additional XRF readings are needed. The 95% upper confidence limit (UCL) value should be compared to the decision point.

3. X-Ray Fluorescence Field Operation Guide Procedures

When conducting a field XRF soil sample study to produce statistically defensible results, the steps below should be followed after the sample has been collected.

3.1. Sieve:

OLEM Directive 9200.1-128 recommends sieving soil samples during all lead Superfund and Resource Conservation and Recovery Act (RCRA) site investigations. When starting a soil sampling project, SSS recommends comparing sieved and non-sieved XRF results of a representative subsample. If the results are generally comparable or a ratio of un-sieved to sieved data can be determined, then sieving the remaining soil samples may not be necessary. The data quality objectives should specify the number of sieve samples and the level of comparability needed on a site-specific basis. If sieved and non-sieved XRF soil sample results are not comparable or a ratio cannot be determined, it is recommended that the remaining soil samples be sieved per the OLEM Directive. Sieving to particle fractions < 150 µm would probably require a controlled environment (i.e., mobile lab) to be conducted correctly with the set of sieves stacked from coarsest to finest to prevent packing of the soil sample. To prevent cross-contamination, the set of sieves should be decontaminated between samples and field quality control samples or equipment blanks are recommended. The decontamination procedures should be defined. Also, if XRF result values are close to the decision point or if sieved and non-sieved results are not in agreement, it is suggested that the soil sample be sieved.

3.2. Moisture Percentage:

Moisture at greater than or equal to 10% may dilute and bias the XRF results low, and Lead Technical Review Workgroup (TRW) recommendations for sampling lead sites, soil moisture be less than 10% (EPA, 2006; EPA, 2000). Therefore, the sample moisture percentage needs to be measured. This can be accomplished by using a soil moisture meter to test in the bagged soil sample. The moisture meter must have the ability to read in percentage to single digits (See Figure 1). The following guidance should be considered regarding moisture content. Please note that the moisture meter should be properly decontaminated between reading each soil sample.

- If moisture is less than 10%, the sample does not require drying and XRF results are acceptable.
- If moisture is greater than or equal to 10% and XRF result is greater than the decision point, the result may be acceptable because the sample already exceeds the decision point.
- If moisture is greater than or equal to 10% and XRF result is less than the decision point, the sample requires drying and then should be reanalyzed. This can be accomplished through solar drying methods or a portable drying apparatus. See Appendix E for example drying options.



Figure 1: Obtaining a moisture reading using General Tools DSMM500 Precision Digital Soil Moisture Meter.

3.3. Time Needed for XRF Reading:

The SSS study (Harper, 2017) revealed shorter measurement times (30 to 60 seconds) are acceptable for precision and accuracy requirements. When analyzing with a particular XRF, there was minimal or no change in result when analyzing a soil sample containing lead and arsenic for 30 seconds instead of 60 seconds. The SSS study regarding analysis time is further supported by investigations from the State of Washington Ecology Department. Its findings reveal that longer reading times allow the XRF to obtain lower detection limits (Furl, 2012). The time used should be appropriate for the instrument to ensure the detection limit is below the decision point to the analyte.

3.4. Control outside variables by confirming systems check, calibration, and by performing bag test:

| QA/QC check | Frequency | Standards used | Comparison for approval |
|-------------------|---|---|--|
| Bag Check | Each lot number | NIST 2709a, RCRA 180-661, CCRMP TILL | Spreadsheet determines effect of bag and approval for use |
| Standard Check | At the beginning of work day and every 5 hours of analysis time | NIST 2709a, RCRA 180-661, Silica/Sand Blank | The mean of the 4 readings should be within 20% of the known value of the standard |
| Duplicate Reading | Every 20 sample bags | Current sample | 2 of 3 readings should be within 95% confidence limit based on reported instrument error |

Each XRF should come with a sheet reflecting the certified values of the accompanying standards and silica blanks that are used to check the calibration of the XRF. The manufacturer's technical support can also provide certified values for standards.

a) Calibration Check

- Blank Standards: Take 4 XRF readings (reported in parts per million (ppm) unless otherwise noted) for established duration time with silica or sand blank standard provided with the instrument to ensure it is reading less than the instrument's detection limit (DL). If result reads '<LOD' (Limit of Detection), scroll down on the screen to get the numeric result (see Figure 2). Record results in Standard Spreadsheet. Ensure the average results are below DL. The mean or average are calculated in the Standards Spreadsheet (see Appendix B).
- Quantitative standards: Also known as standard reference material (SRM). We recommend NIST-certified SRMs that have certified values as close to the decision point as possible: NIST 2709a (low), RCRA 180-661 (high), CCRMP TILL (medium)

SESD suggests reconfirming calibration when the temperature has changed by more than 10 degrees F since the last confirmation. An additional Quality Assurance (QA) calibration confirmation can be conducted when sampling activities are complete. Consider checking calibrations after the XRF has been off for an extended period of time or if the battery has been changed. Standards and silica/sand blanks should be considered properly calibrated when the average readings are within 20% of known values provided with each XRF.

It is recommended that the QAPP should establish a minimum cleaning frequency of the XRF reading window. Cleaning may also be necessary when a "blank" has concentrations above the LOD. Figure 2 shows an example of readings from a silica blank.

| Ele | ppm | ±2σ |
|-----|------------|-----|
| As | <LOD= 6.4 | |
| Se | <LOD= 4.5 | |
| Rb | <LOD= 3.3 | |
| Sr | <LOD= 2.7 | |
| Zr | <LOD= 4.6 | |
| Mo | <LOD= 6.6 | |
| W | <LOD= 65.4 | |
| Au | <LOD= 7.1 | |
| Hg | <LOD= 10.3 | |
| Pb | <LOD= 9.6 | |

Figure 2: XRF screen after scrolling down when reading silica blanks or if results are less than the limit of detection (<LOD).

Any items, including clear, plastic bags located between the instrument and the sample may interfere with the XRF reading. Therefore, plastic bags need to be tested, as seen in Figures 3 and 4, to ensure they do not interfere with the analytical results (Crumbing). Each lot of plastic bags should be tested because the manufacturing process may differ slightly with each lot. SSS found that colored or tinted bags have a tendency to cause interference. The Bag Test Spreadsheet (Figure 5) will calculate the degree to which the bag interferes with the results. If the spreadsheet shows the plastic bag lot is within acceptable limits, all bags with that manufacturer's lot number can be used. The manufacturer lot number is typically found on the box (Figure 6). If the degree of interference (use the Bag Test Spreadsheet tool) from the bag is determined to be outside of acceptable limits, all bags with that lot number should not be used.



Figure 3: Reading standard **without** bag.



Figure 4: Reading standard **with** bag.

It is recommended using a manufacturer-supplied stand (see Appendix E) when possible and to maintain a ¼" thickness of soil to avoid interference from outside sources.

- b) Bag Test: To ensure the plastic bags do not interfere with the XRF soil sample results, take 4 XRF readings for established duration time with the low, medium, and high soil standard inside the plastic bag (Figure 4). Record results in Bag Test Spreadsheet. Readings from the calibration check should be used in the bag test spreadsheets for the "without bag" column. After results are entered in Bag Test Spreadsheet, the Excel calculator program will recommend whether or not the lot of plastic bags is acceptable for collecting and analyzing samples (see Figure 5).

*Note: If the bag fails at levels not applicable for the contaminant, the bag may still be used. For example, if the bag test fails at the low standard (i.e. 20 ppm) for lead but passes the medium and high standard, the bag can still be used. See Appendix D: Lessons Learned for more information.

- c) Evaluate outside variables to determine if there are calibration or bag issues that need to be addressed according to the spreadsheets.

| Medium Concentration Level | | | | | | | | | | | | | | | | | | | |
|---|------|---------------------|------|---------------------|--|---------------------|------|-----------------------|-------|---|------|---------------------|------|--|-----------------------|--|--|--|--|
| Control sample ID: USGS Sdar-M2 | | | | | | | | | | | | | | | | | | | |
| 180-706pp | | | | | | | | | | | | | | | | | | | |
| *With XRF film protector | | | | | | | | | | | | | | | | | | | |
| Target Analyte: As (click in box for drop-down list) | | | | | Target Analyte: As (click in box for drop-down list) | | | | | | | | | | | | | | |
| WITHOUT Plastic Layer | | | | WITH Plastic Layer | | | | WITHOUT Plastic Layer | | | | WITH Plastic Layer | | | | | | | |
| XRF reading # | Conc | XRF reading # | Conc | XRF reading # | Conc | XRF reading # | Conc | XRF reading # | Conc | XRF reading # | Conc | XRF reading # | Conc | | | | | | |
| 1 | 90 | 1 | 72 | 1 | 87 | 1 | 67 | 1 | 87 | 1 | 67 | 1 | 67 | | | | | | |
| 2 | 79 | 2 | 66 | 2 | 99 | 2 | 45 | 2 | 99 | 2 | 45 | 2 | 45 | | | | | | |
| 3 | 80 | 3 | 54 | 3 | 71 | 3 | 80 | 3 | 71 | 3 | 80 | 3 | 80 | | | | | | |
| 4 | 74 | 4 | 74 | 4 | 78 | 4 | 77 | 4 | 78 | 4 | 77 | 4 | 77 | | | | | | |
| 5 | | 5 | | 5 | | 5 | | 5 | | 5 | | 5 | | | | | | | |
| 6 | | 6 | | 6 | | 6 | | 6 | | 6 | | 6 | | | | | | | |
| 7 | | 7 | | 7 | | 7 | | 7 | | 7 | | 7 | | | | | | | |
| 8 | | 8 | | 8 | | 8 | | 8 | | 8 | | 8 | | | | | | | |
| SUMMARY STATISTICS | | | | | SUMMARY STATISTICS | | | | | SUMMARY STATISTICS | | | | | | | | | |
| n = | 4 | n = | 4 | n = | 4 | n = | 4 | n = | 4 | n = | 4 | n = | 4 | | | | | | |
| mean = | 80.8 | mean = | 66.5 | mean = | 83.8 | mean = | 67.3 | mean = | 83.8 | mean = | 67.3 | mean = | 67.3 | | | | | | |
| SD = | 6.7 | SD = | 9.0 | SD = | 12.1 | SD = | 15.8 | SD = | 12.1 | SD = | 15.8 | SD = | 15.8 | | | | | | |
| 2-sided 95% t-UCL = | 91.4 | 2-sided 95% t-UCL = | 80.8 | 2-sided 95% t-UCL = | 103.0 | 2-sided 95% t-UCL = | 92.5 | 2-sided 95% t-UCL = | 103.0 | 2-sided 95% t-UCL = | 92.5 | 2-sided 95% t-UCL = | 92.5 | | | | | | |
| 2-sided 95% t-LCL = | 70.1 | 2-sided 95% t-LCL = | 52.2 | 2-sided 95% t-LCL = | 64.5 | 2-sided 95% t-LCL = | 42.0 | 2-sided 95% t-LCL = | 64.5 | 2-sided 95% t-LCL = | 42.0 | 2-sided 95% t-LCL = | 42.0 | | | | | | |
| confidence interval (CI) width = | 21.3 | CI width = | 28.6 | CI width = | 38.5 | interval width = | 50.4 | CI width = | 38.5 | interval width = | 50.4 | CI width = | 38.5 | | | | | | |
| Absolute difference between the 2 concentration means = 14.3 ppm | | | | | Absolute difference between the 2 concentration means = 16.5 ppm | | | | | Absolute difference between the 2 concentration means = 16.5 ppm | | | | | | | | | |
| Difference between the 2 concentration means = 19.4 % | | | | | Difference between the 2 concentration means = 21.9 % | | | | | Difference between the 2 concentration means = 21.9 % | | | | | | | | | |
| 2-sample t-Test for a difference between concentration means | | | | | | | | | | 2-sample t-Test for a difference between value means | | | | | | | | | |
| Variances are equal (2) or unequal (3) 2 | | | | | t-Test result: 0.0441 | | | | | Variances are equal (2) or unequal (3) 2 | | | | | t-Test result: 0.1488 | | | | |
| Does the 2-sample t-Test find a difference between the means? yes | | | | | | | | | | Does the 2-sample t-Test find a difference between the means? no | | | | | | | | | |
| Initial conclusion: This bag reduces the X-ray signal; this lot of bags should NOT be used. | | | | | | | | | | Initial conclusion: This bag lot is ok to use. | | | | | | | | | |
| Mitigating factors for Pb and As: conc >1300? no abs(diff)<100? yes %diff<8? no | | | | | | | | | | Mitigating factors for Pb and As: conc >1300? no abs(diff)<100? yes %diff<8? no | | | | | | | | | |
| Is the concentration very high and the amount of difference relatively small? FALSE | | | | | | | | | | Is the concentration very high and the amount of difference relatively small? FALSE | | | | | | | | | |
| Final conclusion: Don't use this bag lot unless these concentrations are not relevant for decision-making. | | | | | | | | | | Final conclusion: This bag lot is ok to use. | | | | | | | | | |

Figure 5: Bag Test Spreadsheet.



Figure 6: Lot number on upper right corner of plastic bags box.

3.5. Taking XRF Readings for Soil Samples:

Examine bag to ensure the fines and coarse particles are still homogenized. If segregation has occurred, remix the bag by rotating the bag vertically so that the particles tumble together. Take 4 XRF readings of each bagged soil sample through the plastic bag by taking an XRF reading from the left and then one from the right side of the bag, then flip bag over and take a reading from the left and then one from the right side of the bag. Record the results in Data Spreadsheet and field logbook. (see Figure 7).

One XRF reading per soil sample is insufficient to make a statistically valid measurement. A minimum of 4 XRF readings taken in different locations of the sample are needed (Crumbling). Therefore, at least 2 readings from each side of the soil sample bag are recommended. This process should provide a statistically representative result for the sample. When the readings are entered into the Data Spreadsheet, the 1-sided t and 1-sided Chebyshev 95% UCLs are calculated. The appropriate UCL and individual XRF results can then be compared to the decision point to inform risk management decisions.

- a) If after 4 XRF readings, the relative standard deviation (RSD) <35% (ITRC, 2012) then, no additional XRF readings are needed. The 95% upper confidence limit (UCL) value should be compared to the decision point.
- b) If after 4 XRF readings, the %RSD is greater than 35%, continue flipping the bag and shooting until the %RSD is below 35% or 10 readings are taken. Typically, the 1-sided t UCL should be used for decision making. If readings are highly variable, see Appendix B for more information on using 1 sided Chebyshev UCL for decision making.
- c) If individual results are both above and below the decision point and the RSD is >35% after 10 readings, consider additional risk factors. To help make risk management decisions, additional information can be obtained by collecting additional samples and/or analyzing subsamples collected from the same bag by a laboratory. Consult SSS for further assistance.

The spreadsheet will calculate a variety of statistics. The 95% UCL for the sample that should be used to represent the sample concentration is typically the one-sided t-test calculation (See Figure 7).

| DU or Bag ID: CV-0675A-AsR-A2 | | Element: As | | % Moisture: 10.7 | |
|-------------------------------|-----------------------------------|-----------------------|-------------------------|---------------------------------|-------|
| Replicate Bag Readings | Date & Time | Run Time (sec) | Instrument Result (ppm) | Instrument Error (as 1 Std Dev) | Note? |
| Replicate reading 1 | 1546 | 30 | 35.0 | 7 | |
| 2 | 1547 | 30 | 25.0 | 5.0 | |
| 3 | 1548 | 30 | 32.0 | 6 | |
| 4 | 1548 | 30 | 25.0 | 7.0 | |
| 5 (optional) | 0 | 0 | | | |
| 6 (optional) | 0 | 0 | | | |
| 7 (optional) | 0 | 0 | | | |
| 8 (optional) | 0 | #REF! | | | |
| 9 (optional) | 0 | #REF! | | | |
| 10 (optional) | 0 | #REF! | | | |
| | | Mean | 29.3 | | |
| | | SD | 5.06 | Ttl %RSD | 17.29 |
| | | n = | 4 | | |
| | | ProUCL distribution = | | (optional) | |
| | 2-sided | Sample 95% t-LCL = | 21 | | |
| | 2-sided | Sample 95% t-UCL = | 37 | | |
| | 1-sided | Sample 95% t-LCL = | 23 | | |
| | 1-sided | Sample 95% t-UCL = | 35 | | |
| | 1-sided Smple 95% Chebyshev LCL = | | 18 | | |
| | 1-sided Smple 95% Chebyshev UCL = | | 40 | | |
| | | instrument error = | 21.55 | as %RSD | |

Figure 7: Selecting the 95% UCL from the Data Spreadsheet.

3.6. Duplicate XRF Readings:

Regular quality control checks with the XRF are recommended. Low battery, foreign material on XRF reading window, and slight movements while the XRF operator is analyzing the sample may cause variability in results. A duplicate reading should be collected every 20 soil samples. Duplicate XRF readings are performed by

collecting multiple readings in the same location on the soil sample bag without moving the placement of the bag or XRF analyzer.

Without moving the XRF, read the soil sample twice, and record results in Duplicate Spreadsheet (see Figure 8). If the two results are within the 95% confidence interval, the process is complete. If the duplicate results taken with the XRF in the same location are not within the 95% confidence interval, follow these steps:

- Confirm the correct Error Type is being used from the instrument (i.e. 1 SD or 2 SD)
- Conduct the duplicate procedure with a known certified value standard.
- If standard is within the 95% confidence interval, then repeat duplicate procedure with different area on the soil sample.
- If standard is outside the 95% confidence interval, troubleshoot XRF. Check battery level, cross-contamination, operator technique, etc. Once problem is corrected, confirm XRF calibration with the XRF standards.
- After calibration is confirmed, repeat duplicate procedure with the soil sample. If duplicates are frequently out of range, it is likely due to operator error or the XRF may need to be replaced and serviced by the manufacturer.

| Project information: | | Southside Chatt Phase II | | | | | | |
|-----------------------------|------------------------------|------------------------------|---|--|----|--|------------------------------|--|
| Operator: | | SRC | | | | | | |
| Date: | | 1/17/2017 | | Element: | Pb | | Read Time (sec): | 30 sec per filter |
| 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?) |
| RH035-FY | 315 | 11 | 2 | 304 | — | 326 | 307 | yes |
| SG111-EY | 246 | 10 | 2 | 236 | — | 256 | 243 | yes |
| AP319-EY | 126 | 7 | 2 | 119 | — | 133 | 130 | yes |
| AP290-EY | 213 | 9 | 2 | 204 | — | 222 | 219 | yes |
| CH001-16 | 141 | 8 | 2 | 133 | — | 149 | 137 | yes |

Figure 8: Duplicate Spreadsheet for quality control checks with XRF’s readings. Results are in red box.

4. Summary and Conclusions

The EPA Region 4 SSS prepared this XRF FOG for consideration by Region 4 OSCs and RPMs. The intent of this XRF FOG is to provide the OSC/RPM with a XRF methodology to collect quality XRF data for lead and arsenic in ex-situ soil samples (approach may apply to other metals). This XRF FOG is meant to add another “tool in the toolbox” for OSCs and RPMs. This XRF FOG has been field tested, but every possible field situation has not been addressed. SSS believes if this FOG is followed, the OSC/RPM should have quality data to make risk management decisions.

Disclaimer: This document is not designed to promote or endorse any brand names. If a brand name is mentioned it should be considered an example used during the field testing of this XRF FOG only.

5. References

Crumbing, D. (September, 2014), Environmental Protection Agency Office of Superfund Remediation and Technology Innovation, various personal communications, September 2014.

Environmental Protection Agency Office of Land and Emergency Management Directive #9200.1-128, (July 2016), *Recommendations for Sieving Soil and Dust Samples at Lead Sites for Assessment of Incidental Ingestion*.
<https://www.epa.gov/superfund/lead-superfund-sites-guidance#sampling>

Environmental Protection Agency Office of Superfund Remediation and Technology Innovation Directive #9360.4-21, (July 2006a), *Applicability of Superfund Data Categories to the Removal Program*.

Environmental Protection Agency, (1993), *Risk Assessment Guidance for Superfund*.

Environmental Protection Agency Office of Research and Development, (2006b), *Innovative Technology Verification Report; XRF Technologies for Measuring Trace Elements in Soil and Sediment*.
<https://semspub.epa.gov/work/HQ/190971.pdf>

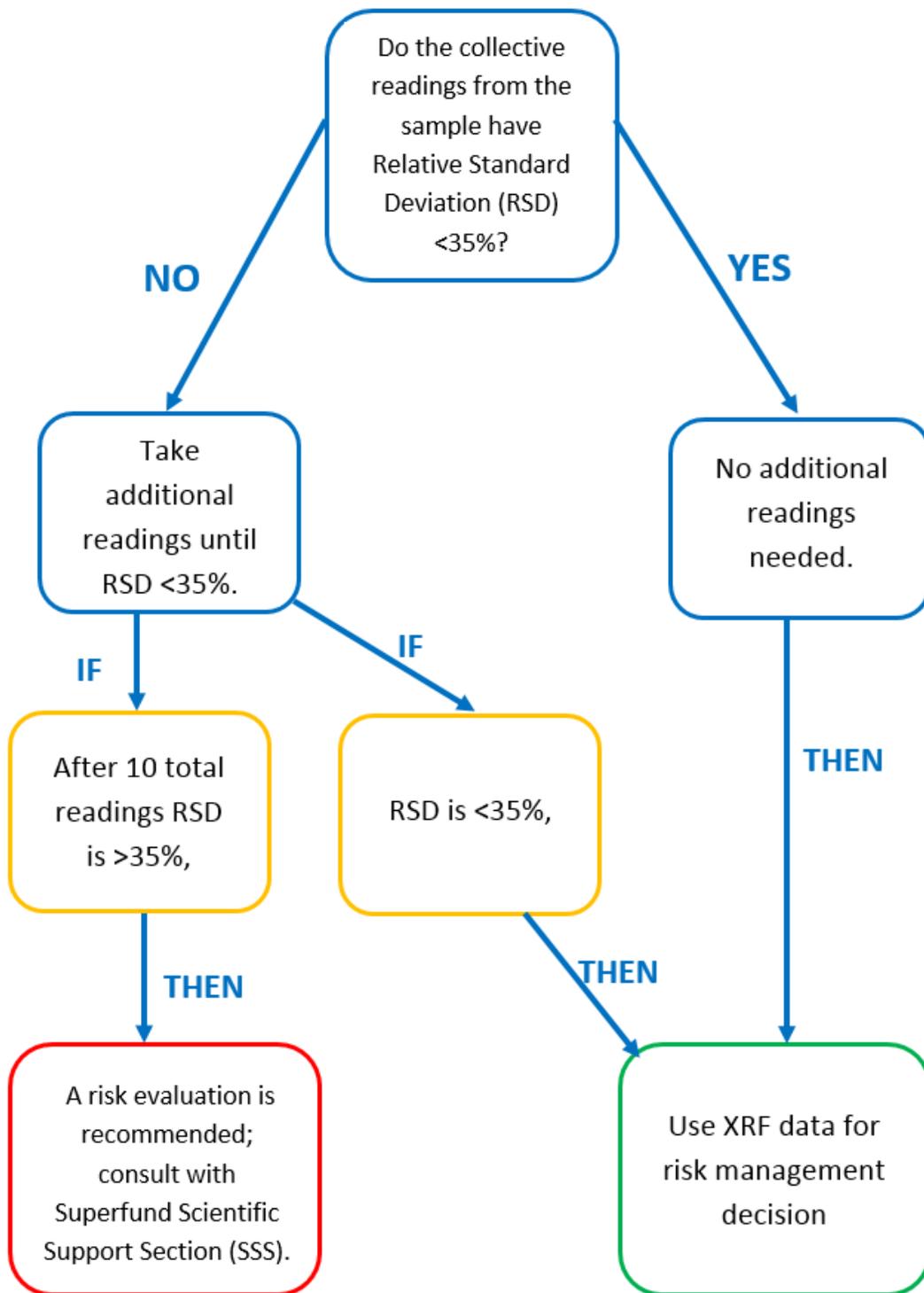
Furl, C., Mathieu, C., & Roberts, T. (2012, January) Evaluation of XRF as a Screening Tool for Metals and PBDEs in Children's Products and Consumer Goods. Publication No. 12-03-009. Retrieved from
<http://fortress.wa.gov/ecy/publications/publications/1203009.pdf>

Harper, G., et al. (2017), Environmental Protection Agency, Region 4, Superfund Division, *Study of the Effectiveness of the X-Ray Fluorescence (XRF) Analyzer on Arsenic Contaminated Soils*.

Interstate Technology & Regulatory Council (ITRC). 2012. *Incremental Sampling Methodology*. ISM-1. Washington, D.C.: Interstate Technology & Regulatory Council, Incremental Sampling Methodology Team.
www.itrcweb.org

U.S. Environmental Protection Agency (U.S. EPA). 2000. Short Sheet: TRW Recommendations for Sampling and Analysis of Soil at Lead (Pb) Sites. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC.

Appendix A: Example XRF Decision Matrix



Appendix B: Spreadsheets

| XRF Instrument Duplicate QC Calculator | | | | | | | | | |
|---|------------------------------|------------------------------|---|--|--|------------------------------|--|----------|--|
| sheet protection PW = dup | | | | | | | | | |
| This spreadsheet performs a statistical evaluation of duplicate agreement based on the counting "error" reported by the instrument. | | | | | | | | | |
| Project information: | | | | | | | | | |
| Operator: | DMC | | | | | | | | |
| Date: | 6/5/2015 | Element: | Pb | | | Read Time (sec): | 30 sec per filter | | |
| 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?) | Time | |
| SW 15 | 1192 | 13 | 1 | 1167 | 1217 | 1218 | NO | 8:27 AM | |
| SW 15 | 1192 | 13 | 1 | 1167 | 1217 | 1194 | yes | 8:28 AM | |
| SW 24 | 14.78 | 2.16 | 1 | 11 | 19 | 15.45 | yes | 12:23 PM | |
| SW 24 | 14.78 | 2.16 | 1 | 11 | 19 | 17.78 | yes | 12:23 PM | |
| SW 35 | 470 | 8.4 | 1 | 454 | 486 | 488.3 | NO | 2:31 PM | |
| SW 35 | 498 | 8.6 | 1 | 481 | 515 | 492.1 | yes | 2:38 PM | |
| SW 35 | 498 | 8.6 | 1 | 481 | 515 | 505.8 | yes | 2:39 PM | |
| SW 45 | 155 | 4.9 | 1 | 145 | 165 | 170 | NO | 4:45 PM | |
| SW 45 | 155 | 4.9 | 1 | 145 | 165 | 130 | NO | 4:46 PM | |
| | | | 1 | #NUM! | #NUM! | | | | |
| | | | 1 | #NUM! | #NUM! | | | | |
| | | | 1 | #NUM! | #NUM! | | | | |
| | | | 1 | #NUM! | #NUM! | | | | |
| | | | 1 | #NUM! | #NUM! | | | | |

Example Duplicate QC Spreadsheet

1-Sided or 2-Sided Confidence Interval:

A 1-sided confidence interval should be used when a decision needs to be made by comparing a sample concentration to the decision point (Crumbling, 2014). This comparison is focused on whether the sample concentration is either above or below the decision point, but not both. Therefore, only one side of the confidence interval is needed; the upper or lower side. The 1-sided confidence interval is usually the value most appropriate for decision making purposes in the removal program.

A 2-sided confidence interval should be used when a decision needs to be made regarding the concentration's potential range in relation to the decision point (Crumbling, 2014). This comparison is focused on the chances of the sample concentration being both above and below the decision point. Therefore, the upper and lower sides of the confidence interval are needed. This is not the case with most removal activities.

| Southside Chattanooga Background Standards and Blank Readings | | | | | Morning | | | | |
|---|------|----------------------|--------------------|-------------------|---------------------------------------|------|---------------------|--------------------|----------------------|
| Date: 1/20/17 | | | | | Standards, Blank and System Check | | | | |
| Recorded By: Sydney Chan | | | | | | | | | |
| Equipment: Thermo Scientific Niton XL3t GOLDD+ #83540 | | | | | | | | | |
| Blank: SiO2 99.995% PP 180-647 | | | | | Blank: SiO2 99.995% PP 180-647 | | | | |
| Time: 0825 | | | | | Time: 0825 | | | | |
| Reading | Time | Arsenic Result (ppm) | Standard Deviation | | Reading | Time | Lead Result (ppm) | Standard Deviation | |
| 1 | 0826 | <LOD = 2.9 | | Average = #DIV/0! | 1 | 0826 | <LOD = 3.6 | | Average = |
| 2 | 0828 | <LOD = 2.9 | | | 2 | 0828 | <LOD = 3.6 | | |
| 3 | 0829 | <LOD = 2.9 | | | 3 | 0829 | <LOD = 3.7 | | |
| 4 | 0831 | <LOD = 2.9 | | | 4 | 0831 | <LOD = 3.7 | | |
| * Run time 30 seconds per beam | | | | | * Run time 30 seconds per beam | | | | |
| Blank: SiO2 99.995% PP 180-647 | | | | | Blank: SiO2 99.995% PP 180-647 | | | | |
| Time: 0825 | | | | | Time: 0825 | | | | |
| Reading | Time | Copper Result (ppm) | Standard Deviation | | Reading | Time | Nickel Result (ppm) | Standard Deviation | |
| 1 | 0826 | <LOD = 11.4 | | Average = #DIV/0! | 1 | 0826 | 31 | 14 | Average = *did not p |
| 2 | 0828 | <LOD = 11.6 | | | 2 | 0828 | <LOD = 20 | | |
| 3 | 0829 | <LOD = 11.6 | | | 3 | 0829 | 27 | 13 | |
| 4 | 0831 | <LOD = 11.1 | | | 4 | 0831 | <LOD = 19.3 | | |

Example Standards Check Spreadsheet conducted with blank, high, and low SRMs.

Project: [Redacted]
 Property ID: [Redacted]
 Particle Size Fraction in Bag: s100
 Operator: [Redacted]
 Date: [Redacted]

| DU or Bag ID: | | Element: | | As | |
|---------------|---------|-----------------------------------|-------------------------|---------------------------------|---------|
| Bag Readings | Time | Run Time (sec) | Instrument Result (ppm) | Instrument Error (as 2 Std Dev) | Note? |
| 1 | | 30 | | | |
| 2 | | 30 | | | |
| 3 | | 30 | | | |
| 4 | | 30 | | | |
| 5 (optional) | | | | | |
| 6 (optional) | | | | | |
| 7 (optional) | | | | | |
| 8 (optional) | | | #REF! | | |
| 9 (optional) | | | #REF! | | |
| 10 (optional) | | | #REF! | | |
| | | Mean | NA | | |
| | | SD | NA | Ttl %RSD | #VALUE! |
| | | n = | 0 | | |
| | | ProUCL distribution = | | (optional) | |
| | 2-sided | Sample 95% t-LCL = | #VALUE! | | |
| | 2-sided | Sample 95% t-UCL = | #VALUE! | | |
| | 1-sided | Sample 95% t-LCL = | #VALUE! | | |
| | 1-sided | Sample 95% t-UCL = | #VALUE! | | |
| | | 1-sided Smple 95% Chebyshev LCL = | #VALUE! | | |
| | | 1-sided Smple 95% Chebyshev UCL = | #VALUE! | | |
| | | instrument error = | #DIV/0! | as %RSD | |

Example Excel Data Spreadsheet

XRF Bag Entry

XRF Bag Entry

| | | | |
|-------------------------------|----------------------|-------------------------------------|----------------------|
| Project ID | <input type="text"/> | Operator | <input type="text"/> |
| Property ID | <input type="text"/> | | |
| Bag ID | <input type="text"/> | Sample Nomenclature: JH019-SF-EY | |
| Particle Size Fraction in Bag | Raw | | |
| Date and Time | <input type="text"/> | Readings Run time | 30 |
| % Moisture | 0 | | |
| Reading 1 Time | 0 | | |
| Reading 1 Arsenic Result | 0 | Reading 1 Arsenic SD | <input type="text"/> |
| Reading 1 Lead Result | 0 | Reading 1 Lead SD | <input type="text"/> |
| Reading 2 Time | 0 | | |
| Reading 2 Arsenic Result | 0 | Reading 2 Arsenic SD | <input type="text"/> |
| Reading 2 Lead Result | 0 | Reading 2 Lead SD | <input type="text"/> |
| Reading 3 Time | 0 | | |
| Reading 3 Arsenic Result | 0 | Reading 3 Arsenic SD | <input type="text"/> |
| Reading 3 Lead Result | 0 | Reading 3 Lead SD | <input type="text"/> |
| Reading 4 Time | 0 | | |
| Reading 4 Arsenic Result | 0 | Reading 4 Arsenic SD | <input type="text"/> |
| Reading 4 Lead Result | 0 | Reading 4 Lead SD | <input type="text"/> |
| Arsenic Mean | 0 | Arsenic 95% UCL | 0 |
| Arsenic St Dev | 0 | Arsenic %RSD | #Num! |
| Lead Mean | 0 | Lead 95% UCL | 0 |

Example Microsoft Access Data Form

Appendix C: Case Studies

Study of the Effectiveness of the X-Ray Fluorescence (XRF) Analyzers on Arsenic Contaminated Soils

The *Study of the Effectiveness of the X-Ray Fluorescence (XRF) Analyzers on Arsenic Contaminated Soils* was based on the collection of 30 discrete soil samples with arsenic levels ranging from 5 ppm arsenic to 335 ppm arsenic (un-sieved *ex situ* XRF readings). The soil samples were collected from an actual arsenic-contaminated CERCLA site. Multiple laboratory analyses and *ex situ* XRF readings were conducted on the 30 discrete soil samples. A statistical comparison of the XRF readings to the laboratory analytical results was completed for each soil sample. The statistical analysis was used to determine the precision, accuracy, and statistical reliability of XRF field screening procedures.

The means of the un-sieved and sieved XRF readings were compared to the mean un-sieved ICP-MS results and a correlation was calculated. The R-squared for the un-sieved XRF/un-sieved ICP-MS data was 0.83. The R-squared for the sieved XRF/un-sieved ICP-MS data was 0.93. These findings show that the XRF data, especially sieved soils, correlate well with laboratory data and can be assumed to reflect accurate results.

The means of the un-sieved and sieved XRF readings were compared to the mean un-sieved ICP-AES results and a correlation was calculated. The R-squared for the un-sieved XRF/un-sieved ICP-AES data was 0.84. The R-squared for the sieved XRF/un-sieved ICP-AES data was 0.91. These findings show that the XRF data, especially sieved soils, correlate well with laboratory data and can be assumed to reflect accurate results.

The statistical analysis was used to determine the precision, accuracy, and statistical reliability of XRF field screening procedures. The statistical analysis presented in the study showed the XRF data collected during this study was both accurate and precise. The study showed when the XRF is used to evaluate arsenic contaminated soils while using the XRF Field Screening Procedure and statistical spreadsheets developed by Office of Superfund Remediation and Technology Innovation (OSRTI), the XRF results can be as accurate as laboratory analysis.

Appendix D: Lessons Learned

Please note during calibrations, SSS suggests measuring the time shown on the XRF versus “real time”, the time on your watch. For example, real time is 40 seconds versus XRF “nominal” time of 30 seconds. If there is a significant difference, the XRF may need to be sent to the manufacturer for calibration.

When running calibration checks with SRMs, Nickel always comes back above LOD when running the silica SRM. Nickel should read <10, but generally averages around 30. Because any decision point pertaining to Nickel should be higher than 30, the LOD should not affect the decision making process.

It should be noted, that concentration data for total arsenic in soil collected using the XRF FOG may be higher at some sites than data reported by extraction-based analysis at a fixed laboratory. It is important to clarify that this does not necessarily reflect a bias or error in either the XRF or the fixed laboratory data. The XRF could be reporting total arsenic which is higher than the total inorganic arsenic digested in the laboratory and/or the XRF data could be a result of an interference like high lead concentrations can sometimes cause. Either way, if this happens at a site, it is recommended that the RPM and/or OSC consult with their Regional risk assessor and the laboratory to work thru site specific issues before making a final decision.

SESD recommends the use of a manufacturer-supplied test-stand when using “cupped” samples. It allows the operator to more consistently align the sample cup under the instrument prior to measurement, and gives a consistent “back-stop” for the analysis. A consistent (non-metal) back-stop should also be used for the bagged samples, since whatever is under the bag could impact the measurement.

SSS recommends having a designated data management collector along with a customized spreadsheet. Currently, SSS uses Microsoft Access to keep all completed soil sample spreadsheets in one, uniform database. With multiple persons containing individual spreadsheets on their respective computers, the transfer of data to a combined location can cause some files to be missed or older versions transferred.

If it is not practical to sufficiently dry samples in the field, SSS recommends drying samples overnight. SSS has successfully used inexpensive electric smokers for this purpose (See Appendix E).

Using stainless sieves may be difficult and time consuming in the field. SSS has successfully used disposable, polyester sieve mesh to reduce decontamination time. Also, sieving contaminated soils may require the use of Personal Protective Equipment (PPE) including respiratory protection and a portable fume hood to minimize exposure.

The Bag Check procedure can be a very time consuming process. SSS recommends bag checking prior to the start of the project to ensure bags for the project have been approved. SSS has found that colored or tinted bags have a tendency to interfere with the X-ray and generally does not pass the bag check.

This is intended to be a living document, if you encounter issues or make improvements to the method, please share with SSS.

Appendix E: Pictures



XRF stand connected to the computer with XRF screen replicated.



XRF stand with XRF attached.



Drying ovens with soil samples inside (above)



Soil samples being dried alternatively by Florida's sunshine.



Soil samples being sieved under a fume hood.



Stacked disposable sieves capturing the fraction



Sieved soil samples properly labeled and waiting XRF coarse readings.



Subsamples taken from the parent fines soil sample.



Decontamination of surface soil samplers.



Surface soil samples drying after decontamination process.