UPPER COLUMBIA RIVER

FINAL
Soil Amendment Technology Evaluation Study
Phase III & IV Work Plan:
Test Plot Field-scale Implementation & Test Plot Monitoring

Prepared for

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TITLE AND APPROVAL SHEET

SOIL AMENDMENT TECHNOLOGY EVALUATION STUDY
PHASE III & IV WORK PLAN:
TEST PLOT FIELD-SCALE IMPLEMENTATION & TEST PLOT MONITORING

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ACRONYMS AND ABBREVIATIONS

ALS	ALS Environmental Laboratory, Kelso, Washington
ANOVA	analysis of variance
CCT	Confederated Tribes of the Colville Reservation
COC	chain-of-custody
DQO	data quality objective
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
GPS	global positioning system
IC	incremental composite
ITRC	Interstate Technology and Regulatory Council
IVBA	*in vitro* bioaccessibility
NRMRL QMP	National Risk Management Research Laboratory Quality Management Plan
OSU	The Ohio State University
QA	quality assurance
QC	quality control
RI/FS	remedial investigation and feasibility study
RPD	relative percent difference
SATES	Soil Amendment Technology Evaluation Study
SDG	sample delivery group
SOP	standard operating procedure
SPLP	synthetic precipitation leaching procedure
TAI	Teck American Incorporated
TAL	target analyte list
UCR	Upper Columbia River

UNITS OF MEASURE

°C	degree(s) Celsius
ft	foot or feet
g	gram(s)
in.	inch(es)
mg	milligram(s)
µg/L	microgram(s) per liter
µm	micrometer(s)
mg/kg	milligram(s) per kilogram
mm	millimeter(s)
mS/m	millisiemen(s) per meter
lb(s)	pound(s)
tons/A	dry U.S. tons per acre

1. PROJECT OVERVIEW

The Soil Amendment Technology Evaluation Study (SATES) is designed to identify and field test a soil amendment technology or technologies that could appropriately and cost-effectively reduce the long-term potential for human exposure to lead in shallow upland soils in the Upper Columbia River (UCR; hereinafter, the Site[1]) (USEPA 2016). This study is being conducted as part of the UCR remedial investigation and feasibility study (RI/FS) Teck American Incorporated (TAI) is conducting under U.S. Environmental Protection Agency (EPA) oversight, as required by the Settlement Agreement between TAI and EPA, dated June 2, 2006. The SATES data quality objectives (DQOs), background, purpose, scope of work, and participants in the study are detailed in the following EPA-approved documents:

- Final Work Plan for the Soil Amendment Technology Evaluation Study Phase I: Test Plot Characterization and Initial Amendment Alternatives Evaluation (hereinafter the Phase I Work Plan; Ramboll 2017a)
- Addendum—Soil Amendment Technology Evaluation Study (SATES) Final Work Plan for the Soil Amendment Technology Evaluation Study, Phase I: Test Plot Characterization and Initial Amendment Alternatives Evaluation (Ramboll 2017b).

SATES is subdivided into four phases:

- Phase I – Test plot characterization and amendment alternatives screening
  - Phase IA – Test plot screening and selection (Part 1) and baseline soil characterization (Part 2)
  - Phase IB – Soil amendment technology screening and design
- Phase II – Bench-scale treatability testing
- Phase III – Test plot field-scale implementation (field-scale pilot testing)
- Phase IV – Test plot monitoring.

This work plan establishes guidelines for the work to be performed in Phases III and IV, hereinafter referred to as field-scale pilot testing.

1.1 OBJECTIVES OF FIELD-SCALE PILOT TESTING

The objectives of the field-scale pilot testing are to:

- Assess feasibility of amendment application;

[1] The Site as defined within the June 2, 2006, Settlement Agreement is the areal extent of hazardous substances contamination within the United States in or adjacent to the Upper Columbia River, including the Franklin D. Roosevelt Lake, from the U.S.-Canada border to the Grand Coulee Dam, and those areas in proximity to the contamination that are suitable and necessary for implementation of response actions.

- Evaluate whether specific soil amendments show potential to reduce the *in situ* bioaccessibility of lead in Site soils;
- Measure changes in key soil chemical and physical properties;
- Measure changes in plant diversity and density; and
- Use the monitoring data to reduce uncertainty about the selection and potential implementation of soil treatment technologies as a remediation strategy.

1.2 SCOPE OF FIELD-SCALE PILOT TESTING

Phases III and IV will be conducted in tandem, starting with the field application of select soil treatment amendments on the test plots (Phase III), followed by periodic monitoring with soil sample collection and analysis (Phase IV) to gather the data needed to assess the effects of the soil treatments on soil conditions under ambient field conditions. The results will be used to identify the soil treatment amendment(s) that most effectively meet the DQOs as described in the Phase I Work Plan (Ramboll 2017a). The Phase II bench-scale testing (Ramboll 2019b) was conducted between September 2019 and March 2020 to review the efficacy of five individual amendments and four amendment combinations (see Section 2.1.1 of this work plan).

Based on the preliminary Phase II bench test results, and with discussion and input from members of EPA and the SATES technical team on the results, the study objectives, and acceptability criteria, three soil treatment amendments were selected for evaluation in the field pilot study: 1) soluble phosphate; 2) an organic compost-enriched potting soil (hereinafter "compost"); and 3) the combination of soluble phosphate and biochar. The scopes for Phases III and IV are summarized briefly below. Additional details are provided in Sections 2.0 and 3.0, respectively.

Field testing of the selected soil treatments will occur within UCR decision units 258, 401, and 441 (see Figure 1-1) at test plots 258-3, 401-1, 401-2, and 441-1 (see Figure 1-2 through 1-4), all of which are located on Confederated Tribes of the Colville Reservation (CCT) tribal allotments. Four subplots are located within each test plot, and field testing of the selected soil treatments will occur at the subplot level. Soils at these locations were initially characterized during the 2014 UCR residential soil sampling study (CH2M HILL 2016), and then studied in further detail as part of SATES Phase I to develop a better understanding of the chemical characteristics and physical properties of the soils within the test plots (Ramboll 2019a). Phase III involves applying each of the selected soil treatments to one of the three subplots within a single test plot and then maintaining the untreated subplot as a control for the field study.

Phase IV is designed to monitor the effects of the selected soil treatments on soil properties in the test plots relative to the objectives outlined in Section 1.1 and the SATES DQOs. Phase IV will involve periodic soil sample collection and analysis, as described in this work plan. Periodic vegetation monitoring began prior to Phase I and will continue through Phase IV to evaluate how

changes in soil conditions affect plant diversity and density following field application of the selected amendments.

The field work described in this work plan will be conducted in accordance with the culture resource coordination plan (CRCP) provided in Appendix A. The CRCP was prepared for the UCR RI/FS to provide relevant background information about Site-related cultural resources, to define measures and specific requirements to protect resources, and to define procedures for consulting with the appropriate state, federal, and tribal parties with interests in the cultural resources of the Site. The CRCP also specifies the requirements for providing notifications to the appropriate entities when an inadvertent discovery occurs in the course of ground-disturbing field work. Proposed sampling methods for the UCR RI/FS, including those planned for the field-scale pilot testing described herein, are summarized in the CRCP and in the cultural resource monitoring protocol summarized in Standard Operating Procedure 2 (SOP-2) provided in Appendix B.

1.3 SCHEDULE

Phase III is scheduled to be completed by early fall 2020, followed by Phase IV monitoring commencing later in fall 2020 and continuing through approximately October 2023.

2. PHASE III – IMPLEMENTATION OF FIELD-SCALE TESTS

This section summarizes the Phase III application of amendments to the test plots for field-scale testing. It discusses the process for selecting amendments to advance to the field-scale pilot test and requirements for amendment application to the test plots.

2.1 AMENDMENTS SELECTED FOR FIELD-SCALE TESTING

Nine soil treatment amendments and amendment combinations were tested during the Phase II bench-scale treatability testing (bench-scale tests), consistent with the Phase II work plan (Ramboll 2019b). The amendments listed below were tested in Phase II:

Individual Amendments

- Soluble phosphate
- Wood ash
- Biosolids
- Biochar
- Compost

Combination Amendments

- Soluble phosphate + biosolids
- Soluble phosphate + biochar
- Soluble phosphate + compost
- Wood ash + biosolids

The bench-scale test results were used to select which amendments should be advanced to the field-scale pilot application on the test plots (Ramboll 2017a). Of the nine amendments tested in the Phase II bench tests, three were selected for field-scale application and testing – soluble phosphate, compost, and the combination of soluble phosphate and biochar. More specifically, available Phase II bench test results[2] were examined to determine how each soil treatment option performed in the tests and how each amendment application rate (e.g., low and high application rates, per the Phase II Work Plan [Ramboll 2019b]) affected lead and arsenic bioaccessibility in the test soil and effects on other soil properties in the laboratory setting.

A multicriteria decision model (i.e., the Analytic Hierarchy Process [Saaty 1987]), designed to facilitate structured decision making, was used to help and prioritize the various soil treatment

[2] The test results available for evaluation and consideration in the amendment selection process were from three sets of bench testing samples: 1) samples collected prior to the start of the tests (baseline, collected at time point zero [t_0]); 2) samples collected at the one-month time point (t_1); and 3) samples collected at the four-month time point (t_2). Samples collected in March 2020 at the end of the six-month-long test (i.e., t_3 samples) could not be analyzed at that time because the OSU laboratory conducting the tests and chemical analyses was shut down soon after sampling and sample preparation for analysis in response to the novel coronavirus outbreak. The t_3 samples were stored, pending analysis in the future upon reopening of the laboratory.

options that were tested in Phase II. TAI, EPA, and the SATES technical team and other stakeholder representatives provided input to capture different viewpoints and preferences in the model to rank the treatment options in order of acceptability for use in the field study, then the aggregated results were integrated with the laboratory bench test results to develop weighted scores for the various treatment options. The results were used to help guide technical team discussions to collaboratively develop a short list of soil treatment options likely to perform well in meeting the DQOs and that were identified by TAI, EPA, and the SATES technical team as acceptable for use on the test plots for the field-scale testing. Ultimately, the amendments selected for advancement to the field study were recommended based on the following additional factors:

- Project DQOs including accessibility of amendments to local residents (USEPA 2016);
- Best performance in reduction of bioaccessible lead in the available Phase II bench-scale treatability test results[2];
- Preliminary results from an EPA study evaluating the effects of biochar amendment on gastrointestinal lead bioavailability in UCR upland soils (Plunkett 2019);
- Local availability of amendments.

Soluble phosphate was selected because it was one of the most effective treatments for decreasing in vitro bioaccessibility (IVBA) of lead. The compost medium tested performed well at decreasing IVBA in the laboratory tests and is likely to enhance plant growth where applied on the test plots. The combined amendment of biochar and soluble phosphate also performed well at decreasing IVBA in the laboratory tests and had positive preliminary results from a recent EPA laboratory study (Plunkett 2019). In addition to showing promise toward achieving the soil treatment objectives defined for SATES as demonstrated in the laboratory tests, the soluble phosphate, compost, and biochar materials used in the Phase II bench tests are readily available to consumers in the local area and are expected to be available in the quantities needed for the field pilot tests. A mixture of triple super phosphate and potash will be used for the soluble phosphate treatment; G&B Organics Potting Soil will be used for the compost treatment; and Black Owl Supreme biochar will be used with soluble phosphate for the combination treatment.

For field testing, compost and biochar amendments will be applied on the soil surface at rates corresponding to the low rates used in the laboratory bench tests, while soluble phosphate will be applied on the soil surface in a liquid solution at a rate corresponding to the high rate used in the laboratory bench study.

2.2 FIELD-SCALE PILOT TEST APPLICATION

2.2.1 Application Plan

In each test plot, three of the four subplots will receive amendments for pilot testing and the fourth subplot will be randomly assigned as a control. The amendments will be randomly assigned to subplots, with no replication within the same test plot. The application rate requirements for each amendment are shown in Table 2-1. Application rates are given in weight per area or volume per area to facilitate application. Amendment placement requirements are described further in SOP-1 in Appendix B.

Although the surficial application of amendments to the test plots is not expected to cause disturbance to the surficial soil layer, the application of amendments and subsequent surficial soil sampling may affect plants growing in the test locations in the short term. The soil sampling methods associated with the SATES field study will involve disturbance of the surficial soil layer (0 to 3 in. depth). Therefore, TAI and its field team will coordinate with the CCT to assess the effects of the planned work and identify ways to avoid, minimize, or mitigate any adverse effects on historic and cultural properties, as described in the CRCP included in Appendix A and in accordance with SOP-2 in Appendix B.

2.2.2 Preapplication Amendment Sampling

To confirm that the amendments supplied for field-scale testing are suitable for use in this study, representative composite samples of each medium will be collected from the proposed source stock and analyzed for the following parameters (see Table 2-2):

- Total target analyte list (TAL) metals, by EPA Method 6010 (except mercury)
- Mercury by EPA Method 7471B
- Semi-volatile organic compounds by EPA Method 8270, biochar and compost only

Water that will be applied to the subplots alone or in solution with phosphate will be sampled during application, and analyzed for the following parameters:

- TAL metals, by EPA Method 6010 (except mercury)
- Mercury by EPA Method 7470B
- Temperature, pH, and electrical conductivity

Procedures for the preapplication amendment sample collection for laboratory analysis are provided in SOP-3 in Appendix B.

2.2.3 Quality Control Requirements for Amendment Application

Accurate and even placement of soil treatment amendments within the test plots is critical to ensure the accuracy of amendment dose for experimental results. To that end, the contractor retained by TAI to apply the amendments (hereinafter the "application contractor") will be responsible for accurate and even placement on each subplot. The application contractor will be required to prepare an Amendment Placement Quality Management Plan (APQP) that describes the placement methods for each of the amendments selected for the field-scale testing and addresses requirements for placement accuracy and evenness, as described below and in SOP-1. Verification of placement accuracy and evenness and other aspects of the APQP will be conducted in the field by TAI and/or a designated representative, along with representatives of EPA, CCT, and/or Citizens for a Clean Columbia, if desired.

2.2.3.1 Accuracy of Amendment Application

It is important that each amendment is applied only to the intended subplot and is not over-sprayed or spilled onto another subplot; over-spraying or spills could adversely affect results from the experiment. Thus, the contractor's APQP must include a means to physically control and constrain the distribution of the amendments within the boundaries of the intended subplots (e.g., tarps, plywood sheets, or other materials). The interior edge of each subplot is bordered by a 4-ft buffer zone; care must be taken to ensure that the amendments are not placed beyond this buffer.

2.2.3.2 Evenness of Amendment Application

The application contractor will be required to apply the amendment materials at the prescribed application rates (Table 2-1). Care should be taken to ensure even placement around tree trunks, under bushes, and large debris such as fallen branches. Ten or more evenly-spaced measurements should be recorded within each subplot to verify the application rates (i.e., mass of solid amendment media or amount of liquid amendment dispersed per unit area). For the solid media (i.e., compost and biochar), the contractor will be required to obtain at least ten randomly spaced as-placed weight/unit volume measurements. For the soluble phosphate amendment application, the concentration and volume of the phosphate solution dispersed per unit area must be measured during application and documented. For example, the measurement of liquid amendments could be done using flow meters, or by dividing the subplots quadrants with measured volumes of liquid applied to each quadrant, or other means to be determined by the application contractor that can be used to verify the evenness of amendment application.

2.2.4 Field Documentation

Documentation of the amendment application process and the verification methods and measurements will be recorded as described in SOP-4 (see Appendix B), utilizing field logbooks, field data forms, and photographs.

3. PHASE IV – TEST PLOT MONITORING AND DATA COLLECTION

This section summarizes the Phase IV monitoring program that will be used to characterize the changes in soil conditions over time at each test plot on the subplots with applied soil treatment amendments (treated subplots) and the control subplots. Monitoring will include periodic soil sample collection and analysis and vegetation monitoring on the test plots for the duration of the field testing phase to evaluate changes on the treated subplots relative to the baseline conditions initially measured in August 2017 and ongoing conditions in control plots. CCT will perform the vegetation monitoring. Details for soil sample collection, quality control (QC), and sample management, shipping, and custody are in the SOPs provided in Appendix B.

3.1 MONITORING FREQUENCY

Phase IV monitoring will be conducted for three years after the soil treatment amendments have been applied to the test plots. Assuming that Phase III is implemented by early fall of 2020, the targeted timeframes for Phase IV monitoring events are October 2020, April 2021, and July 2021 in the first year, then semi-annually thereafter in October 2021, April and October 2022, and April and October 2023. Monitoring is planned for three years after the soil treatment amendments have been applied to the test plots. Vegetation growth and health will be determined using a combination of measures such as percent cover, density, species richness, and diversity. TAI will coordinate with CCT to schedule vegetation monitoring surveys in advance of each soil sampling event to avoid disturbance of the vegetation prior to soil sampling and to facilitate accurate counts of the plant species observed on the test plots.

One optional round of soil sampling may be conducted in July in the second or third year of Phase IV to be able to verify trending changes in or changes in percent IVBA lead and arsenic and/or metal concentrations in the surface soil that may be indicated by data from the preceding Phase IV monitoring events. A decision whether to conduct the additional sampling event will be based on an evaluation of the soil conditions indicated by the available soil quality results and the vegetation monitoring data. This decision will be made in consultation with the SATES technical team.

3.2 SOIL SAMPLE ANALYSES

The data requirements for Phase IV can be found in Table 3-1. The treated subplot samples and control subplot samples will be collected using incremental composite sampling methods and analyzed for the following parameters, as summarized in Table 2-2:

- Bioaccessible lead and arsenic by EPA Method 6010B, with sample aliquots extracted at pH 1.5 and at pH 2.5

- Electrical conductivity (soil salinity) measured by electrode
- Soil pH by the Thomas (1996) method
- Mehlich III extractable lead and phosphorus by the Mehlich (1984) method and EPA Method 6010
- Mercury by EPA Method 7471B acid/permanganate digestion
- Mineralizable nitrogen by the Waring and Bremner (1964) method
- Oxalate extraction McKeague and Day (1993) method
- Synthetic Precipitation Leaching Procedure (SPLP) TAL metals and phosphorus by EPA Method 1312 Western U.S. (pH 5.00)/6010
- Total arsenic and lead by EPA 3051A (sample preparation) and EPA 6010
- Total TAL metals (except mercury) by EPA 3051A (sample preparation) and EPA 6010 – first monitoring event and last monitoring event during Phase IV
- Total carbon and nitrogen by the Bremner and Mulvany (1982) and Nelson and Sommers (1996) methods
- Total organic carbon by the Heanes (1984) method.

All of the analyses except for bioaccessible and total lead and arsenic will be conducted on the < 2 mm soil fraction; however, for the bioaccessibility and total arsenic and lead analyses, soil sample aliquots will be sieved so that the analyzed aliquots consist of the soil particles < 150 μm..

Additional optional x-ray diffraction analysis for further assessment of lead and arsenic mineralogy (speciation) are included on Table 2-2, for samples that will be selected based on the Phase IV monitoring results. Samples to be evaluated for mineralogy will be selected in consultation with and at the discretion of the SATES technical team based on the available Phase IV monitoring results. If lead and arsenic mineralogy will be evaluated, samples will be selected in consultation with the SATES technical team and submitted to EPA in February 2022 and 2023. Mineralogical analysis will be conducted using synchrotron analysis by EPA's National Risk Management Research Laboratory Quality Management Plan Method L18735 with Athena software data analysis.

3.3 SOIL SAMPLING PROCESS DESIGN

Soil sampling planned for the Phase IV monitoring portion of the field-scale testing will involve initially collection of incremental composite (IC) samples from each of the treated subplots and each control subplot during each sampling event outlined in Section 3.1.

Additionally, during or soon after the final sampling event proposed for October 2023, discrete samples will be collected from the subplots over a deeper soil profile (0 to 12 in. depth) for total

TAL metals analysis. Discrete samples will be collected for each 2-in. depth horizon consistent with discrete sample collection approach that was used in Phase IA, Part 1 (Ramboll 2017a). The discrete sample data will be used to evaluate how the soil treatments have affected metals concentrations relative to the baseline data collected in Phase IA test plot characterization portion of the study. Additional parameters may be analyzed as well and will be selected based on the monitoring results obtained from sampling events conducted in 2021 and 2022. TAI will prepare a work plan addendum that describes the study design and the sampling and analysis plan for discrete sample collection, for implementation in 2023. This work plan addendum will be prepared in the last half of 2022 after the initial monitoring data have been reviewed and a preliminary analysis of discernable changes in the soil characteristics or chemistry in response to the applied treatments has been completed. TAI will present these results to the SATES technical team for discussion and recommendations for this part of the Phase IV monitoring design. The proposed analysis of depth-discrete data is discussed in Section 3.11.1.3 of this work plan.

3.3.1 Advance Preparation and Requirements for Field Personnel

The field sampling team will have the necessary knowledge and experience to perform the field activities described in this work plan. Such knowledge includes experience using tape measures and a compass to perform field measurements necessary to layout the sampling grids and sampling points, the specified sampling gear, soil sample collection and the IC sampling method, preparing the required field documentation, and following sample custody, storage, packaging, and shipping procedures.

The soil sampling described in this work plan will require compliance with the Cultural Resource Coordination Plan in Appendix A and the procedures described in SOP-2 in Appendix B.

Field personnel will be familiar with this work plan and will participate in site and equipment orientation prior to initiating each monitoring event.

3.3.2 Soil Sample Locations for Incremental Composite Sampling

IC samples will be collected in test plots 258-3, 401-1, 401-2, and 441-1 (Figures 1-1 through 1-4). Each test plot is subdivided into four 50-ft by 50-ft subplots that are designated as subplots A, B, C, D (Figure 3-1). As discussed in Section 2, within each test plot, three subplots will be treated with the selected amendments and the fourth subplot will be maintained as a control for the field study. The corners of each test plot and subplot are marked with durable flush-with-ground yellow plastic markers, and the interior boundary of each subplot is bordered by a 4-ft buffer. Soil samples will be collected within the main subplot areas only.

Procedures for laying out the sampling grid and positioning each IC sample point are detailed in SOP-5, provided in Appendix B. SOP-5 allows for tape measures and compasses to be used instead

of using a hand-held global positioning system (GPS) device to measure and map each sampling location due to poor satellite reception at the test plot sites, as observed during the Phase I sampling efforts. Poor satellite reception can cause a loss in GPS accuracy of 6 ft or more. Because proposed sampling stations are scoped to be approximately 8 ft apart, a GPS error of 6 ft or more might result in resampling a previously sampled location. SOP-5 provides instructions to the field personnel should they find a Phase IV sampling station (or stations) is positioned at a previously sampled location, and provides for Phase IV monitoring locations to be shifted a small distance, if necessary, to avoid resampling at any point or points within a subplot.

3.3.3 Incremental Composite Sampling Methodology

At each subplot, one IC surficial soil sample will be obtained by collecting 30 soil increments from the measured grid and sampling points measured within each subplot as described in Section 3.3.1. Each increment will be collected from 0 to 3 in. depth.[3] Samples will be analyzed for IVBA lead and arsenic, and other soil chemistry and physical properties that may affect or be affected by the amendments applied to the treated subplots, as summarized in Table 2-2. The IC sampling method is described in detail by the Interstate Technology and Regulatory Council (ITRC) and consists of single-point increment samples composited and subsampled according to a detailed SOP prior to laboratory analysis (ITRC 2012). IC field sampling collection is described in SOP-6 in Appendix B. The laboratory's IC processing is detailed in Appendix C.

The points where increment samples will be collected from each subplot will shift to a new, nearby location for each monitoring event, to avoid resampling locations that were sampled either during the Phase IA test plot characterization effort or during a prior Phase IV monitoring event. The coordinates targeted for collecting IC sample increments during each monitoring event are provided in Table 3-2 and in Table B-2 in Appendix B.

Field QC samples will include triplicate and replicate samples. Field replicate samples will be collected from co-located samples at each of the 30 increment locations, and both of the increment sets will be developed and submitted as separate IC samples that will be homogenized by the ALS laboratory in Kelso, Washington, to prepare the samples for the chemical analyses listed in Tables 3-3a and 3-3b. ALS will label, package, and ship, under the required chain-of-custody procedures for this project, prepared soil samples to OSU for the analyses to be performed by the OSU laboratory. For each Phase IV monitoring event, two field replicate samples (approximately 15 percent of the total number) will be collected for homogenization and analysis. Analytical results for the field replicates will be used to evaluate precision of field techniques and the homogeneity of the IC samples.

[3] For the purpose of measuring soil sample depths, 0 in. begins at the base of the loose duff layer.

As recommended in the ITRC IC sampling guidance (ITRC 2012), one triplicate IC sample (one primary IC sample plus two replicate IC samples), selected randomly, will be collected during each Phase IV sampling event. This frequency is supported by a previous review of the Phase IA Part 1 lead data, which indicated a low coefficient of variability in all test plots (Ramboll 2019a). The triplicate increments will be collected in the same manner as the sample increments, but should not be collected from the same locations as the sample increments (or other triplicate increments). Triplicate samples will be developed and submitted as separate IC samples. Efforts should be taken to ensure that all increments for each triplicate sample are collected in different locations to ensure the ability to evaluate sample and small-scale variability within a specific area being sampled (i.e., a decision unit). Triplicate sample results are used to calculate a 95 percent upper confidence interval for the mean concentration that helps quantify the uncertainty in the estimate of the mean for the decision unit, which in this case is a subplot. Triplicate IC samples will be analyzed using the same test methods as the primary samples (see Table 2-2). Relative percent difference (RPD) between replicates will be reviewed after each sampling event.

The sampling procedures and requirements for maintaining the chain-of-custody (COC) and documentation, preservation, and shipping of samples to the analytical laboratory are summarized in sections 3.5 and 3.6, below, and detailed in the following SOPs provided in Appendix B: SOP-6 – Incremental Composite Surface Sample Collection, SOP-7 – Sample Labeling, SOP-8 – Sample Custody, and SOP-9 – Sample Storage, Packaging, and Shipping.

3.3.4 Sample Point Selection

Starting with the IC sampling methodology described in the Phase IA Data Summary Report (Ramboll 2019a), a grid of 30 points was established for each subplot. For each new sampling event conducted during Phase IV monitoring, the grid will be shifted to a new orientation within the subplot area to avoid resampling any point that was previously sampled either during the SATES Phase IA test plot characterization effort or during a previous Phase IV monitoring event. The procedures for properly positioning the sampling grid and sample points for each monitoring event are detailed in SOP-5 in Appendix B. To avoid accidental re-sampling of any point, each location that is sampled will be marked with an untreated 2.5-in.-long wooden dowel with saw-cut ends buried approximately 0.5 in. below the surface as a marker. Areas that were previously disturbed by test pits dug during the Phase IA test plot characterization are marked by a metal rod with brightly-colored brass or plastic cap and will be located using a metal detector, marked with a pin flag or other temporary marker, and avoided during the Phase IV sampling efforts. If a point falls on a previous test pit or a wooden marker from prior sampling, it will be shifted slightly to an alternate point to avoid re-sampling, as described in SOP-5. Coordinates for the alternate location and rationale for the change will be recorded in the field logbook.

3.3.5 Minimum Sample Mass

The field testing objectives cannot be met without the collection of sufficient soil mass for laboratory analysis. Minimum sample sizes for the IC samples and each increment comprising them were conservatively calculated as described in this section.

The minimum mass required for the IC samples are given in Table 2-2. These amounts were calculated similarly to the EPA quality assurance project plans (QAPPs) for the 2014 UCR residential and upland soil studies (SRC 2014, Ramboll 2016). As described in those QAPPs, for purposes of estimating the required mass, it was assumed that the < 2 mm particle size fraction would be approximately 80 percent of the soils collected[4]. The < 150 μm particle size fraction is assumed to comprise 5 percent of the soil. To calculate the minimum mass of soil to be collected in the field, the mass of the soil required for the laboratory was divided by either 0.8 or 0.05 depending on the fraction needed for analysis (< 2 mm and < 150 μm, respectively).

The volume of soil needed to be collected in the field to meet the minimum requirements is dependent on the soil densities that will be encountered in the field. The sampling method planned for Phase IV will allow collection of appropriate mass of soil for sample analysis. Collected sample masses can be predicted using the following equation:

$$M = \varrho \times n \times D \times \pi \times (\theta/2)^2$$

Where:

M = targeted mass of sample (g)
ϱ = soil bulk density (pounds per cubic foot)
n = number of increments
D = sampling depth (cm)
θ = diameter of circular sample corer

3.4 SOIL SAMPLE DESIGNATION SYSTEM

This section describes the sample labeling requirements for the Phase IV monitoring samples. Further details are provided in SOP-7 (Appendix B).

[4] This proportion was estimated in the 2014 Upland Study Field Sampling Plan (TAI 2014) using average grain size data from the National Uranium Resource Evaluation data set (USGS 2004). The assumption that 80 percent of the composite sample would pass through the 2 mm sieve was determined by summing two thirds of the average proportion of sand (60 percent), and all silt and clay (40 percent).

3.4.1 Monitoring Samples

In the test plots, each subplot has been designated with an alphabetical identifier (A, B, C, and D; see Figures 3-2 through 3-5). Starting with the subplot identifier, soil samples will be coded with the following information:

- IC for incremental composite soil sample, WP for potable water
- Test plot number
- Subplot letter
- Six-digit date (MMDDYY)
- Three-letter code for the amendment applied to a treated subplot and for the control, as follows:
  - CTL = control
  - PHO = soluble phosphate
  - CPS = compost-based potting soil
  - PBI = soluble phosphate and biochar combination

For example, an IC soil sample collected on October 21, 2020 from test plot 258-3, subplot A with the soluble phosphorus treatment, would be designated by the identification number "IC-258-3A-102120-PHO". If multiple containers are sent from the laboratory in which to collect one sample (this may occur for water samples), append the following suffixes to the end of the sample code: -1, -2, -3, etc.

3.4.2 Field Quality Assurance and Quality Control Samples

Field quality assurance and quality control (QA/QC) samples, which will be collected and prepared as triplicate IC soil samples and duplicate potable water samples, will be labeled as described below.

Triplicate IC samples will be labeled with the prefix "IC1-", "IC2-", and "IC3" included in the sample identification number (e.g., **IC1**-258-3A-102120-PHO, **IC2**-258-3A-102120-PHO, **IC3**-258-3A-102120-PHO).

Field replicate IC soil samples will be labeled with the same designator as the original sample and then the suffix "-R" will be added to end of the sample ID (e.g., IC-258-3A-102120-PHO**-R**).

Duplicate potable water samples will be labeled with the prefix "WP1-", to identify the parent sample and "WP2-" to identify the duplicate sample.

3.5 SAMPLE HANDLING AND CUSTODY REQUIREMENTS AND PROCEDURES

3.5.1 Field Custody Procedures

The objective of field sample custody is to ensure that samples are not tampered with or modified from the time they are collected through transport and transfer to the analytical laboratory. Persons will have custody when the samples collected are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area (e.g., accessible only to authorized personnel), they will be deemed to be in the custody of such authorized personnel. Field custody documentation consists of both field logbooks, custody seals, and field COC forms. Details of sample custody management, requirements, and documentation are provided in SOP-8 in Appendix B.

3.5.2 Field Logbooks

Field logbooks will be used to record the data collecting activities that are performed. Entries in the logbook will describe as much detail as possible so that personnel who go to the Site could reconstruct a particular situation without reliance on memory. Field documentation requirements for the SATES soil sample collection activities are detailed in SOP-4 in Appendix B.

3.5.3 Sample Labeling

The following information must be written on each sample label (see SOP-7 in Appendix B):

- Project name
- Date collected
- Time collected
- Location
- Name of sampler
- Analysis(es) to be performed
- Sample identification number

3.5.4 Chain-of-Custody Forms

Completed COC forms are required for all samples submitted to the laboratory for analysis and/or for archiving. COC forms will be prepared in the field by the sampling crew. These will contain the unique sample identification number, sample date and time, sample description, sample type, preservation (if any), and required chemical analyses. The original COC form will accompany the samples to the laboratory. Copies of the COC will be made prior to shipment (or multiple copy

forms will be used) for field documentation. The COC forms will remain with the samples at all times. The samples and signed COC forms will remain in the possession of the sampling crew, as described in Section 3.5.1 and SOP-8, until the samples are delivered to the express carrier (e.g., FedEx), hand delivered to the laboratory, or placed in a secure and locked storage location.

Sample labels will be completed for each sample using waterproof ink, following the labeling requirements given in SOP-7 in Appendix B. Completed sample labels will be securely affixed to each sample container and covered with clear tape.

If any samples are split with a government agency or other party, a separate COC form will be prepared for those samples and marked to identify the party with whom the samples are being split. The person relinquishing the sample(s) to the other entity should request the signature of the individual receiving the sample(s) to acknowledge the sample transfer, and the date and time the samples were relinquished by the sampling personnel to the receiving entity is to be recorded on the COC form. If the representative is unavailable or refuses, this information will be printed in ink by the field sampling supervisor or other sampling personnel in the "Received By" space.

3.5.5 Sample Packing, Handling, and Shipping

Sample packaging and shipment procedures are designed so that the samples will arrive at the laboratory intact and with the completed COC form. Detailed requirements are provided in SOP-9 in Appendix B.

The guiding principles that will be followed during sample preparation for shipping to the laboratory are to ensure that each of the following requirements are met: samples are not contaminated by water intrusion or other substances; samples will remain at the appropriate temperature until arrival at the laboratory; samples are accompanied by the COC forms in a secure location inside the shipping container (e.g., a cooler with ice); and all samples are carefully packaged to avoid breakage during transport, or separation of the shipping label from the shipping container. Both samples and wet ice will be double-bagged inside plastic freezer bags with a zipper closure. Enough ice will be used to maintain the temperature required for sample preservation inside an insulated cooler (4°C ± 2°C) until the samples can be packaged and shipped to the laboratory, or for up to two days in case of shipping delays.

Samples will be hand delivered or delivered by an express carrier to the analytical laboratory within 24 hours after the samples were collected. All sample shipments will be accompanied by the completed COC form(s) identifying the contents in the sample cooler(s); the original COC form will accompany the shipment and the sampler will retain a copy of the COC form for the sampling office records. If the samples are sent to the laboratory by a common carrier, a bill of lading will be used. A bill of lading is required for all time-sensitive less-than-truckload freight at FedEx and

UPS. Commercial carriers are not required to sign the COC form because the forms are sealed inside the sample cooler when the samples are shipped. Air bills will be retained as part of the permanent record for the project.

Custody seals and packing materials for filled sample containers will be provided by the analytical laboratory when the sample supply order is filled. As described in SOP-9 in Appendix B custody seals are to be placed across the opening of sample coolers prior to shipping to protect the integrity of samples and a layer of transparent packaging tape placed over the seals to prevent breakage before the samples reach the destination laboratory.

3.5.6 Laboratory Custody Procedures

3.5.6.1 General

Upon sample receipt, laboratory personnel will be responsible for sample custody. The original field COC form will accompany all samples requiring laboratory analysis. The laboratory will use COC guidelines described in EPA guidance documents.

Samples will be kept secured in the laboratory until all stages of analysis are complete. All laboratory personnel having samples in their custody will be responsible for documenting and maintaining sample integrity.

3.5.6.2 Sample Receipt and Storage

Immediately upon sample receipt, the receiving laboratory sample custodian will verify the integrity of the custody seal, open the cooler, and compare the contents against the field COC form. The laboratory will immediately notify the Technical Team Coordinator and/or Quality Assurance Coordinator if a sample container listed on the COC form or air bill (if multiple coolers of samples were shipped together) is missing, a sample container is received broken, the sample is in an inappropriate container, water is present on the bottom of the cooler indicating ice melt and leakage, or the sample has not been preserved by appropriate means. The laboratory sample custodian will be responsible for logging the samples in, assigning a unique laboratory identification number to each sample, labeling the sample bottle with the laboratory identification number, preparing and delivering a Sample Acknowledgement Form to the Technical Team Coordinator and/or Quality Assurance Coordinator, and moving the sample to an appropriate storage location to await analysis. The technician will check sample temperature upon receipt and will store the samples in a refrigerated area at 4 ± 2 °C. The project name, field sample code, date sampled, date received, analysis required, storage location and date, and action for final disposition will be recorded in the laboratory tracking system, which will note that samples will be maintained by the laboratory until disposal is authorized in writing by EPA. Relevant custody documentation will be placed in the project file.

3.5.6.3 Sample Analysis

Analysis of an acceptable sample will be initiated by a work sheet that will contain pertinent information for analysis. The routing sheet will be forwarded to the analyst, and the sample will be moved into an appropriate storage location to await analysis. The Analytical Laboratory Quality Assurance Manager or a designated document control officer will file COC forms in the project file. Samples will be organized into sample delivery groups (SDGs) by the laboratory. Field duplicates are considered field samples for the purposes of SDG assignment. All field samples assigned to a single SDG will be received by the laboratory over a maximum of seven calendar days and must be processed through the laboratory (preparation, analysis, and reporting) as a group. If reanalysis of a sample is required it may be re-run separately from the original SDG and the resulting data will be reported within the SDG in which the samples were re-run.

Every SDG must include a minimum of one method blank and one matrix spike/matrix spike duplicate (or matrix spike/laboratory duplicate) pair; each SDG will, therefore, be self-contained for all of the required QC samples. Project samples to be used for matrix spike/matrix spike duplicates will be noted on the COC form. Information regarding the sample, analytical procedures performed, and the results of the testing will be recorded in a laboratory notebook by the analyst. These notes will be dated and identify the analyst, the instrument used, and the instrument conditions.

3.5.6.4 Sample Storage Following Analysis

Unused portions of samples submitted to ALS and OSU for analysis will be securely stored and maintained by ALS in archive until disposal is authorized in writing by EPA. The laboratory will be responsible for the eventual and appropriate disposal of the samples and will inform the Analytical Chemistry Laboratory Coordinator before any samples for this project are disposed.

3.5.7 Sample Containers and Preservation

Appropriate sample containers, preservation methods, and laboratory holding times for the samples are shown in Tables 3-3a and 3-3b. A sufficient number of sample containers and supplies will be requested from the laboratory to allow for collection of additional sample mass to be used for laboratory quality assurance (QA) and QC (QA/QC) analyses for 5 percent of samples.

The analytical laboratory will supply appropriate sample containers in advance of each sampling event. Sample containers will be purchased clean, consistent with the requirements of EPA Office of Solid Waste and Emergency Response Directive 9240.05A. Field personnel will be responsible for properly labeling and packing containers and preserving samples, as described in sections 3.5.3 and 3.5.5, and detailed in SOP-7 and SOP-9 in Appendix B.

3.6 SAMPLING EQUIPMENT DECONTAMINATION PROCEDURES

Decontamination of reusable sample equipment will be performed between collection of individual soil increments and between sample locations within the subplots to reduce the potential for cross-contamination using two decontamination methods: dry decontamination will be completed between soil increments collected for the one IC sample, and full decontamination will be completed between separate IC samples. Project-specific decontamination procedures are detailed in SOP-10 in Appendix B.

3.7 POST-SAMPLING SITE RESTORATION

After soil sampling has been completed, the small holes created at each sample point will be plugged with a 2.5-in.-long wooden dowel similar in diameter to the sampling hole and with saw-cut ends, then covered with vegetation removed prior to sampling, duff, vegetation debris, or local soil. These wood plugs will mark each increment location to prevent the location from being re-sampled during future sampling events.

Stakes, flagging, and other temporary markers used during a sampling event will be removed at the end of each event. Semi-permanent markers at the subplot corners and at the location of the test pits excavated previously (in SATES Phase IA) within each subplot will remain in place.

3.8 CHANGES AND CORRECTIVE ACTIONS

In the event that unanticipated or changed circumstances occur in the field, the field supervisor will institute the necessary corrective actions, complete a corrective action record (an example is included in the field forms contained in Appendix D), and ensure that the appropriate procedures are followed. If corrective actions require a deviation from this work plan, these changes will be documented on a field change request form (Appendix D). Changes will be noted in the field logbook by the field supervisor and a change request form will be completed for the project files and submitted to EPA. Problems that cannot be easily resolved or that might affect the quality or usability of the data collected will be brought to the attention of the TAI project coordinator, the project senior technical advisor, and EPA. EPA will be notified of any problems encountered that may affect the final outcome of the monitoring effort.

3.9 HEALTH AND SAFETY

The health and safety plan addendum for the field effort for the study is included in Appendix E. This is an addendum to the general UCR Site-specific health and safety plan (TAI 2009).

3.10 MANAGEMENT OF INVESTIGATION-DERIVED WASTES AND MATERIALS

Investigation-derived wastes include soils, decontamination water sampling supplies, and personal protective equipment. These wastes are generated during sampling, and other sampling activities. The intent of managing investigation-derived wastes is to ensure that impacted materials and media are not allowed to contaminate non-impacted materials and media. Where necessary to promote the safe, efficient, and environmentally protective performance of work, management of investigation-derived materials and wastes will be performed consistent with EPA guidance Guide to Management of Investigation-Derived Wastes, 9345.3-03FS (USEPA 1992). Disposable equipment (including personal protective equipment) will be containerized, appropriately labeled during the sampling events, and disposed of accordingly. Water generated during equipment decontamination will be containerized, temporarily stored at a designated staging area in scalable containers and disposed or recycled appropriately based on analytical results from prior UCR sampling events.

3.11 DATA EVALUATION

This section summarizes how the data collected in Phase IV will be summarized and evaluated, and describes the deliverables that will be prepared during and at the conclusion of the field-scale pilot testing.

3.11.1 Data Reporting

Following each monitoring event, the laboratory will summarize and report the analytical results in standard electronic data deliverable (EDD) format. The data deliverable will include a laboratory report and sample and instrument QC documentation necessary for data validation as detailed in SOP-11 in Appendix B.

3.11.2 Data Analysis

The soil chemistry data and vegetation monitoring results will be analyzed based on the effectiveness and applicability of each amendment using the SATES DQOs to guide the analysis. This will include evaluation of the following soil treatment effects:

- Changes in lead and arsenic bioaccessibility
- Completeness of bioaccessibility reduction reactions
- Changes in leachability of other metals
- Changes in key soil quality parameters
- Changes in vegetation characteristics
- Changes in lead and arsenic mineralogy

The evaluation methods are described in the following subsections.

3.11.2.1 Lead and Arsenic Bioaccessibility Changes

Statistical evaluations will be done incrementally through Phase IV to assess the progress and effects of soil treatments over time. The first evaluation will be done after the first full year of sample data have been collected (January 2022), and then annually every year after through early 2024. Variations in percent bioaccessible lead and arsenic between treated subplots and the control subplots will be evaluated using a one-way analysis of variance (ANOVA[5]) to determine statistical differences in measured changes. The results will be used to rank the soil treatments from the most effective at reducing bioaccessibility to the least effective and will also be used to identify changes or trends observed during field testing that may suggest benefit to adding a sampling event in the subsequent year (discussed in Section 3.1). Measurements that will be used for this analysis include the following: 1) total lead and arsenic concentrations; 2) lead and arsenic bioaccessibility (*in vitro* bioaccessibility or %IVBA) using EPA Method 1340 protocol with a pH 1.5 for extraction; and 3) lead and arsenic bioaccessibility using a modified EPA Method 1340 protocol with a pH 2.5 for extraction.

Total lead and arsenic will be determined for each treatment being tested based on the analytical results from each treated or control subplot for total lead. These results and the results of bioaccessible lead and arsenic analysis for both the pH 1.5 and pH 2.5 extracts from each subplot at each monitoring event will be used to calculate percent lead and arsenic bioaccessibility using the following equation:

$$\%\ bioaccessibility = 100\ x \frac{IVBA\ [Pb] or\ [As]}{(total\ [Pb]\ or\ [As]\ extracted\ at\ pH\ 1.5\ or\ 2.5)}$$

Where:

IVBA [Pb]	=	bioaccessible lead, mg/kg
IVBA [As]	=	bioaccessible arsenic, mg/kg
total [Pb]	=	lead concentration determined by EPA Method 6010
total [As]	=	arsenic concentration determined by EPA Method 6010

A comparison of the treated subplot and control sample results to the baseline results collected in Phase IA will be used to calculate the change in percent bioavailability of lead and arsenic for each subplot. Using percent change in bioavailability normalizes for differences in total lead and arsenic content and allows comparisons between the control plots and the treated subplots.

[5] An ANOVA compares the means between groups and determines whether any of those means are statistically significantly different from each other.

3.11.2.2 Completeness of Bioaccessibility Reduction Reactions

After each year of sampling, a one-way ANOVA will be performed for lead and arsenic bioaccessibility results for each amendment and control. This will allow a determination of whether there is a statistical difference between the baseline conditions and current soil conditions at each monitoring event (as defined in section 3.1), and also between monitoring events. For example, a result showing initial reaction at the first monitoring event but no significant statistical difference between the two following monitoring events would indicate the bioaccessibility reduction reaction has slowed or stopped. A result showing a significant difference between the second and third monitoring events would indicate that at least at six months since field amendment application the reactions associated with the amendment application are continuing.

3.11.2.3 Leachability of Other Metals

The leachability of other metals and phosphorus in the soils tested will be evaluated by SPLP analysis for TAL metals and phosphorus. A one-way ANOVA will be performed for TAL metals and phosphorus concentrations in SPLP extract for each soil treatment application and the control to determine if any of the soil treatments caused an increase in the leachability of metals in the field. Leachable metals and phosphorus will be expressed as a percent of total metals or phosphorus, as follows: 100 x [SPLP metal (or SPLP phosphorus)/total metal (or total phosphorus)]. Total metals and phosphorus will be determined for each field treatment replicate sample. The average total metals and phosphorus from the replicated soil samples will be used to calculate the percent SPLP. The total metals and phosphorus results from the baseline samples will be considered during data evaluation.

During or soon after the final Phase IV sampling event, when the last set of IC samples will be collected, an additional set of depth-discrete sampling will be carried out in each of the subplots to further evaluate the leachability of metals in the test plot soils. As discussed in Section 3.3, TAI will develop a proposed sampling and analysis plan for depth-discrete sampling in the second half of 2022, and will submitted it to EPA and the SATES technical team for review, discussion, and subsequent approval prior to conducting this additional sampling.

3.11.2.4 Key Soil Quality Parameters

A one-way ANOVA will be used to determine statistical differences in pH, nutrient concentrations, total and organic carbon, and total carbon-to-nitrogen ratio across the treatment and control subplots by using the data from the baseline and subsequent monitoring events. Identification of significant changes in these parameters, and of the potential effects on soil quality and plant growth at the Site will be considered in the ranking of the amendments.

3.11.2.5 Lead and Arsenic Mineralogy

If lead and arsenic mineralogy will be analyzed, samples will be selected based on the results of the bioaccessibility analysis results. Samples from treated subplots that indicate significant reductions in the bioaccessibility of lead and arsenic have occurred, as compared to the control and baseline data, will be selected for mineralogical analysis to assess changes in lead and arsenic mineralogy that may occur during field testing. Mineralogical analyses will be conducted by EPA using synchrotron analysis by EPA's National Risk Management Research Laboratory Quality Management Plan Method L18735 with Athena software data analysis.

4. QUALITY ASSURANCE AND QUALITY CONTROL

4.1 QUALITY CONTROL REQUIRMENTS

QC requirements for the Phase III and Phase IV field-scale pilot testing are described in Section 10 of the SATES Phase I Work Plan (Ramboll 2017a) , which is included as Appendix F of this work plan and incorporated by reference. These requirements include QA objectives and criteria (Section 10.2), field QC checks (Section 10.3), analytical laboratory QC checks (Section 10.4), data precision assessment procedures (Section 10.5), data accuracy assessment procedures (Section 10.6), and data completeness assessment procedures (Section 10.7).

4.2 INSTRUMENT AND EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

Laboratory and field instrument and equipment documentation procedures include details of observed problems, corrective measures, routine maintenance, and instrument repair. Procedures for instrument and equipment testing, inspection, and maintenance are described in Sections 11.1 (field) 11.2 (laboratory) of the Phase I Work Plan (Ramboll 2017a). Preventive maintenance of equipment will generally follow manufacturers' guidelines. Laboratory and field systems managers are responsible for the routine maintenance of instruments.

Inspection and acceptance requirements for laboratory supplies and consumables are described in Section 12.2.1 of the Phase I Work Plan. All supplies used in the laboratory will be available when needed. The supplies and consumables required for the various analyses are noted in the laboratory SOPs, which are also in the Phase I Work Plan.

4.3 INSTRUMENT CALIBRATION FREQUENCY

Field and laboratory equipment calibration procedures and frequency requirements are described in Sections 12.1 and 12.2, respectively, of the Phase I Work Plan (Ramboll 2017a) that is provided in Appendix F of this work plan. Instrument calibration will follow the specifications provided by the instrument manufacturer or specific analytical method used. When analyses are conducted according to EPA or other standardized methods, the calibration procedures and frequencies specified in the applicable method will be followed. For analyses governed by SOPs, see the appropriate SOP for the required calibration procedures and frequencies. Records of calibrations will be filed and maintained by the field or laboratory personnel and will be subject to QA auditing. Care will be taken to verify the correct concentration, use, and documentation of reference media and materials.

4.4 DOCUMENTATION AND RECORDS

Procedures for laboratory documentation and records are described in Section 6.2 of the Phase I Work Plan (Ramboll 2017a). Workbooks, bench sheets, instrument logbooks, and instrument printouts will be used to trace the history of samples through the analytical process and to document important aspects of the work, including the associated QC checks. Information regarding the sample, analytical procedures performed, and the analytical results will be recorded by the analyst on laboratory forms or log files. All laboratory records will be retained as part of the permanent record for the project.

Procedures for laboratory reporting are described in Section 6.3 of the Phase I Work Plan. The laboratory will prepare Level 2 data packages (modified reporting) for all samples, which is used for analyses performed following standard EPA-approved methods and QA/QC protocols. Required elements for the Level 2 data packages include:

- Chain-of-custody documentation
- Case narrative
- Final parameter concentration for all samples
- Preparation or extraction and analysis dates and times
- Method blanks
- Surrogate recoveries
- Inductively coupled plasma/mass spectroscopy serial dilution percent difference
- MS/MSD recoveries and RPD
- Laboratory duplicate RPD
- Laboratory control sample recoveries.

Analytical results will be reported by the laboratory in EDD format within 30 working days from the date of sample collection (standard turnaround), except when requested otherwise. SOP-11, provided in Appendix B of this work plan, specifies the EDD format requirements.

Sampling and analysis contractors will transfer all project documentation to Ramboll, and project records will be stored and maintained in accordance with Ramboll and TAI requirements.

4.5 DATA MANAGEMENT

Procedures for data management are described in Section 14 of the Phase I Work Plan (Ramboll 2017a). The UCR RI/FS data management plan and its final amendment (Exponent 2019) establish standard procedures for the management of all documents and environmental data (field and laboratory) generated for the UCR RI/FS. The final repository for sample information is the UCR project relational database housed at http://teck-ucr.exponent.com.

All data manually entered into the laboratory information management system will be proofed at the analytical chemistry laboratory prior to being released. All data collected from each laboratory instrument, either manually or electronically, will be reviewed and confirmed by analysts before reporting.

Laboratory data will be entered directly into the project database through an electronic upload at the laboratory or through conversions of laboratory EDDs to the appropriate format for upload, as managed by the database administrator. The electronic data will then be made available for download and review by the data validator. Data qualifiers will be entered into the spreadsheet and subsequently loaded into the database along with electronic validation reports.

4.6 ASSESSMENT AND RESPONSE ACTIONS

Procedures for assessment and response actions are described in Section 15 of the Phase I Work Plan (Ramboll 2017a). Performance and systems audits will be completed. As a participant in state and federal certification programs, the laboratory is audited by representatives of the regulatory agency issuing certification, in addition to undergoing its own internal audits.

Corrective actions may be required when analytical data are not within the objectives specified in the work plan. Corrective action procedures involve the prompt investigation, documentation, evaluation, and correction of data collection and/or analytical procedures. Corrective action may be initiated in the laboratory, at a minimum, under the following conditions:

- Procedures defined by this work plan have not been followed
- Predetermined data acceptance standards are not met
- Equipment is not in proper working order or calibrated
- Sample and test results are not completely traceable
- QC requirements have not been met
- Issues have emerged from performance or systems audits.

Project personnel will continuously monitor ongoing work performance in the normal course of daily responsibilities. Corrective action will be initiated upon identification of the problem. Depending on what level this occurs (e.g., analyst, supervisor, or during data review or QC review), it will be brought to the attention of the analytical laboratory QA manager and the laboratory director. Final approval of any action deemed necessary is subject to the approval of the laboratory director. If previously reported data are affected by a situation requiring correction or if the corrective action impacts a project budget or schedule, the action will directly involve the project manager and QA coordinator. Corrective action may include sample re-extraction, re-preparation, reanalysis, cleanup, dilution, matrix modification, or other activities. If a corrective

action is necessary, a Corrective Action Record form (Appendix D of this work plan) should be filled out and submitted to the TAI Project Coordinator.

5. REPORTS TO MANAGEMENT

The Task Quality Assurance Coordinator will audit the implementation of the work plan QA/QC requirements. Each project component will result in some type of QA report or, by its absence, will indicate that no significant QA or QC deviations occurred. Items that may result in a QA report include:

- Changes or updates to the work plan
- Deviations from work plan specifications
- Results of system and performance audits
- Significant QA/QC problems, recommended solutions and results of corrective actions
- Limitations on the use of measurement data.

5.1 FIELD REPORTS

Reporting of the quality of field sample collection and field measurements will be the responsibility of the field team leader designated by the technical team coordinator. Information from the field logbooks will be compiled, and a summary report on field activity QA will be prepared for the project file.

5.2 LABORATORY REPORTS

The laboratory will maintain QA records related to the analyses performed, QC, and corrective actions. This information will be made available to the project manager upon request. Routine reporting will include documenting all internal QC checks performed for this project.

6. DATA REDUCTION AND REVIEW

After field and laboratory data have been obtained, the data will be subject to the following:

- Reduction or manipulation mathematically or otherwise into meaningful and useful forms
- Data validation
- Review
- Organization, interpretation, and reporting.

6.1 FIELD DATA

6.1.1 Field Data Reduction

Information collected in the field through visual observation, manual measurement, and/or field instrumentation will be recorded in field notebooks, data sheets, and/or on forms. Such data will be reviewed by the appropriate Task Manager for adherence to the Work Plan and the QA/QC requirements for consistency. Concerns identified as a result of this review will be discussed with the field personnel, corrected if possible, and (as necessary) incorporated into the data evaluation process.

6.1.2 Field Data Review

Field data calculations, transfers, and interpretations will be conducted by the field personnel and reviewed for accuracy by the appropriate task manager and the QA coordinator. Logs and documents will be checked for:

- General completeness
- Readability
- Use of appropriate procedures
- Appropriate instrument calibration and maintenance
- Reasonableness in comparison to present and past data collected
- Correct sample locations
- Correct calculations and interpretations

6.2 LABORATORY DATA

6.2.1 Laboratory Data Reduction

The calculations used for data reduction will be in accordance with the analytical methods. Whenever possible, analytical data will be transferred directly from the instrument to a

computerized data system. Raw data will be entered into permanently bound laboratory notebooks. The data entered must be sufficient to document all factors used to arrive at the reported value. Concentration calculations for chromatographic analyses will be based on response factors. Quantitation will be performed using internal standards for gas chromatograph/mass spectrometry methodology. Concentration calculations for metals and wet chemistry, if appropriate, will be based on linear regression. Unless otherwise specified, all values will be reported uncorrected for blank contamination.

6.2.2 Laboratory Data Review

Data will be subject to multi-level review by the laboratory. The laboratory project manager will review all data reports prior to release for final data report generation. The QA Manager will review the final data reports and the laboratory director will review a cross section of the final data reports prior to shipment to the environmental consultant. If discrepancies or deficiencies are present in the analytical results, corrective action will be taken, as discussed in Section 15.3 of the Phase I Work Plan (Ramboll 2017a). Deficiencies discovered as a result of internal data review, as well as the corrective actions to be used to rectify the situation, will be documented on a corrective action form. This form will be submitted to the project manager and QA coordinator for further distribution, as necessary.

7. DATA VERIFICATION AND VALIDATION

Data validation is a systematic review process for judging the analytical quality and usefulness of a specific set of chemical data, and is necessary to ensure that data of known and documented quality are used in making environmental decisions that meet DQOs. The data validation process compares a body of data to the requirements in a set of documented acceptance criteria to ascertain its completeness, correctness, and consistency.

Soil data generated in Phase IV will be validated by a third-part validator using EPA's National Functional Guidelines (USEPA 2017). These procedures and criteria may be modified, as necessary, to address project-specific and method-specific criteria, control limits, and procedures. Data validation will consist of data screening, checking, reviewing, and editing to document analytical data quality and to determine whether the quality is sufficient to meet the SATES DQOs. The data validator will verify that reduction of laboratory measurements and laboratory reporting of analytical parameters is in accordance with the procedures specified for each analytical method and/or as specified in this work plan. Upon receipt of laboratory data, the following procedures will be executed by the data validator:

- Evaluate the completeness of the data package.
- Verify that field chain-of-custody forms were completed and that samples were handled properly.
- Verify that holding times were met for each parameter. Holding time exceedances, if they occur, will be documented.
- Verify that parameters were analyzed according to the methods specified.
- Review QA/QC data (i.e., confirm that duplicates, blanks, and laboratory control samples were analyzed for the required number of samples, as specified in the method, and verify that duplicate RPDs are acceptable).
- The data validator will review reference material documentation and verify the correct ranges of reference materials were used and reported.
- Investigate anomalies identified during review, including reported measurements that are presented without defined RPDs (such as soil moisture). When anomalies are identified, they will be discussed with the project manager and/or the laboratory manager, as appropriate. Level 4 data packages may be requested to evaluate anomalies. Deficiencies discovered as a result of the data review, as well as the corrective actions implemented in response, will be documented and submitted in the form of a written report as specified in Section 18.1 of the Phase I Work Plan (Ramboll 2017a) to include the following topics, as applicable to each method:
    - Assessment of the data package
    - Description of any protocol deviations

- Failures to reconcile reported and/or raw data
- Assessment of any compromised data
- Overall appraisal of the analytical data
- Table of site name, sample quantities, matrix, and fractions analyzed
- Impact to decisions made using deficient data

Qualified results do not necessarily invalidate data. The goal to produce the best possible data does not necessarily mean that data must be produced without QC qualifiers. Qualified data can provide useful information. During the review process, laboratory qualified and unqualified data are verified against the supporting documentation. Based on this evaluation, qualifier codes may be added, deleted, or modified by the data reviewer. Results will be qualified with codes in accordance with the National Functional Guidelines (USEPA 2017):

Concentration (C) qualifiers

U The analyte/compound was analyzed for but not detected. The associated value is the compound quantitation limit.

J The compound was positively identified; however, the associated numerical value is an estimated concentration only.

Quantitation (Q) qualifiers

For inorganics analytes:

B The compound has been found in the sample as well as its associated blank, its presence in the sample may be suspect.

E The reported value is estimated due to the presence of interference.

N Spiked sample recovery not within control limits.

Validation qualifiers

U The analyte was detected at or above the associated detection limit.

U* The analyte should be considered not detected because it was detected in an associated blank at a similar concentration.

J Quantitation is approximate because of limitations identified during data validation.

UJ This analyte was not detected, but the detection limit is probably greater because of a low bias identified during data validation.

UB Compound considered non-detect at the listed value due to associated blank contamination.

EMPC Chromatographic peaks are present in the expected retention time window; however, the peaks do not meet all of the conditions required for positive

identification. The detection limit represents the estimated maximum possible concentration if the analyte was present.

R Unusable result; unknown whether analyte is present or absent in this sample.

All data users should be aware of the following points:

1. The "R" flag means that the associated value is unusable. In other words, due to significant QC problems, the analysis is invalid and provides no information as to whether the compound is present or not. "R" values indicate data rejected as part of the validation process and will not be included in the data analyses for the study.
2. No compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data but any value potentially contains error. Resolution of issues regarding laboratory performance or deliverables will be handled between the laboratory and the data validator. Suggestions for reanalysis may be made by the QA Coordinator at this point.

Data validation reports will be kept in electronic format (PDF) at the environmental consultant's office. In addition, data validation reports will also be maintained in the UCR project database maintained by Exponent.

8. REFERENCES

Bremner, J.M. and C.S. Mulvaney. 1982. Nitrogen—total. In: *Methods of Soil Analysis, Part 2: Chemical and microbiological properties*. A.L. Page, R.H. Miller, and D.R. Keeney (eds). Agronomy Monographs, 9, 2nd ed. American Society of Agronomy and Soil Science Society of America, Madison, Wisconsin. pp. 595–624.

Exponent. 2019. Final Upper Columbia River data management plan, amendment no. 1. Prepared by Exponent, Bellevue, WA, for Teck American Incorporated. June.

Heanes, D.L. 1984. Determination of total organic-C in soils by an improved chromic acid digestion and spectrophotometric procedure. *Commun. Soil Sci. Plan.* 15(10):1191–1213.

McKeague, J.A. and J.H. Day. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* 46(1):13–22 (from Appendix A).

Mehlich, A. 1984. Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. *Comm. Soil Sci. Plant An.* 15: 1409–1416.

Nelson, D.W. and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. In: *Methods of Soil Analysis, Part 3: Chemical Methods*. D.L. Sparks (ed). SSSA Book Series No. 5. Soil Science Society of America, Madison, Wisconsin. pp. 961–1010.

Plunkett, S. 2019. Quality Assurance Project Plan, Evaluation of the impact of biochar amendment on soil and sediment gastrointestinal Pb bioavailability. (SHC Project 3.63, Task 2, Subtask 5), National Health and Environmental Effects Research Laboratory, Western Ecology Division, U.S. Environmental Protection Agency, Corvallis, Oregon. DCN: E-WED-0031954-QP-1-0.

Ramboll. 2016. Addendum No. 1 to the 2014 Residential Soil Study Quality Assurance Project Plan (SRC Inc. 2014). Prepared by Ramboll Environ, Seattle, Washington, for Teck American Incorporated. July.

Ramboll. 2017a. Final work plan for the Soil Amendment Technology Evaluation Study Phase I: test plot characterization and initial amendment alternatives evaluation. Prepared by Ramboll Environ, Seattle, Washington, for Teck American Incorporated. July.

Ramboll. 2017b. Addendum—Soil Amendment Technology Evaluation Study (SATES) final work plan for the Soil Amendment Technology Evaluation Study, Phase I: test plot characterization and initial amendment alternatives evaluation. Prepared by Ramboll Environ, Seattle, Washington, for Teck American Incorporated. September 29.

Ramboll. 2019a. Final Soil Amendment Technology Evaluation Study Phase IA Test Plot Selection and Characterization Data Summary Report. Prepared by Ramboll, Seattle, Washington, for Teck American Incorporated. February.

Ramboll. 2019b. Final work plan for the Soil Amendment Technology Evaluation Study Phase II: bench-scale treatability study. Prepared by Ramboll, Seattle, Washington, for Teck American Incorporated. May.

Saaty, R.W., 1987. The analytic hierarchy process—what it is and how it is used. *Math. Mod.*, 9(3-5):161-176.

SRC. 2014. Quality Assurance Project Plan Upper Columbia River Residential Soil Study Washington State. Prepared by SRC, Inc. for the U.S. Environmental Protection Agency, Region 10.

Thomas, G.W. 1996. Soil pH and soil acidity. pp. 475–490. In: *Methods of Soil Analysis. Part 3.* D.L. Sparks (ed). SSSA Book Series No. 5. Soil Science Society of America, Madison, Wisconsin.

USEPA. 1992. Guide to Management of Investigation-Derived Wastes. OSWER 9345.3-03FS. Office of Superfund Remediation and Technology Innovation, Washington, DC.

USEPA. 2007a. Method 6010C. Inductively coupled plasma-atomic emission spectrometry. In: SW-846. U.S. Environmental Protection Agency, Washington, DC. USEPA Method 6010.

USEPA. 2007b. Method 1312. Synthetic precipitation leaching procedure. In: SW-846. U.S. Environmental Protection Agency, Washington, DC. USEPA Method 1312.

USEPA. 2013. Method 1340. In vitro bioaccessibility assay for lead in soil. In: SW–846. U.S. Environmental Protection Agency, Washington, DC.

USEPA. 2016. Letter from L. Buelow, EPA Project Coordinator, to K. McCaig, TAI Project Coordinator, dated June 21, 2016, regarding soil treatability testing to determine if soil amendment technologies can be developed as an alternative to soil removal and replacement. Letter included the UCR Soil Amendment Technologies Evaluation Study data quality objectives as an attachment.

USEPA. 2017. National functional guidelines for inorganic superfund methods data review. OSWER 9355.0-135. Office of Superfund Remediation and Technology Innovation, Washington, DC.

USGS. 2004. National Uranium Resource Evaluation (NURE) Hydrogeochemical and Stream Sediment Reconnaissance data: U.S. Geological Survey, Denver, CO.

Waring, S.A. and J.M. Bremner. 1964. Ammonium production in soil under waterlogged conditions as an index of nitrogen availability. *Nature* (London) 201:951–952.

FIGURES

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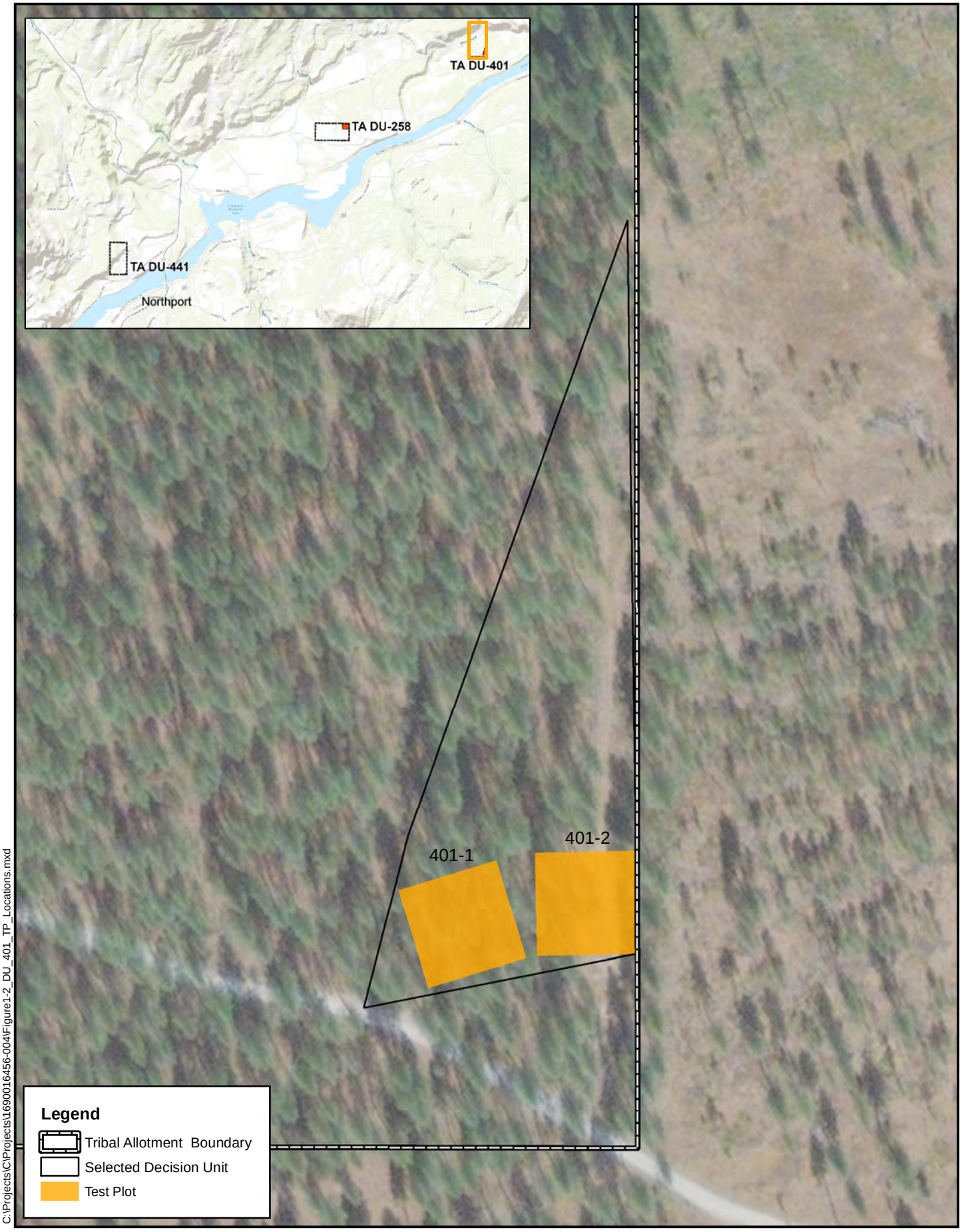
FINAL

RAMBOLL

Figure 1-1
Location of Decision Units with SATES Test Plots
Upper Columbia River SATES Program



RAMBOLL

Figure 1-2
Test Plot Locations - Decision Unit 401
Upper Columbia River SATES Program

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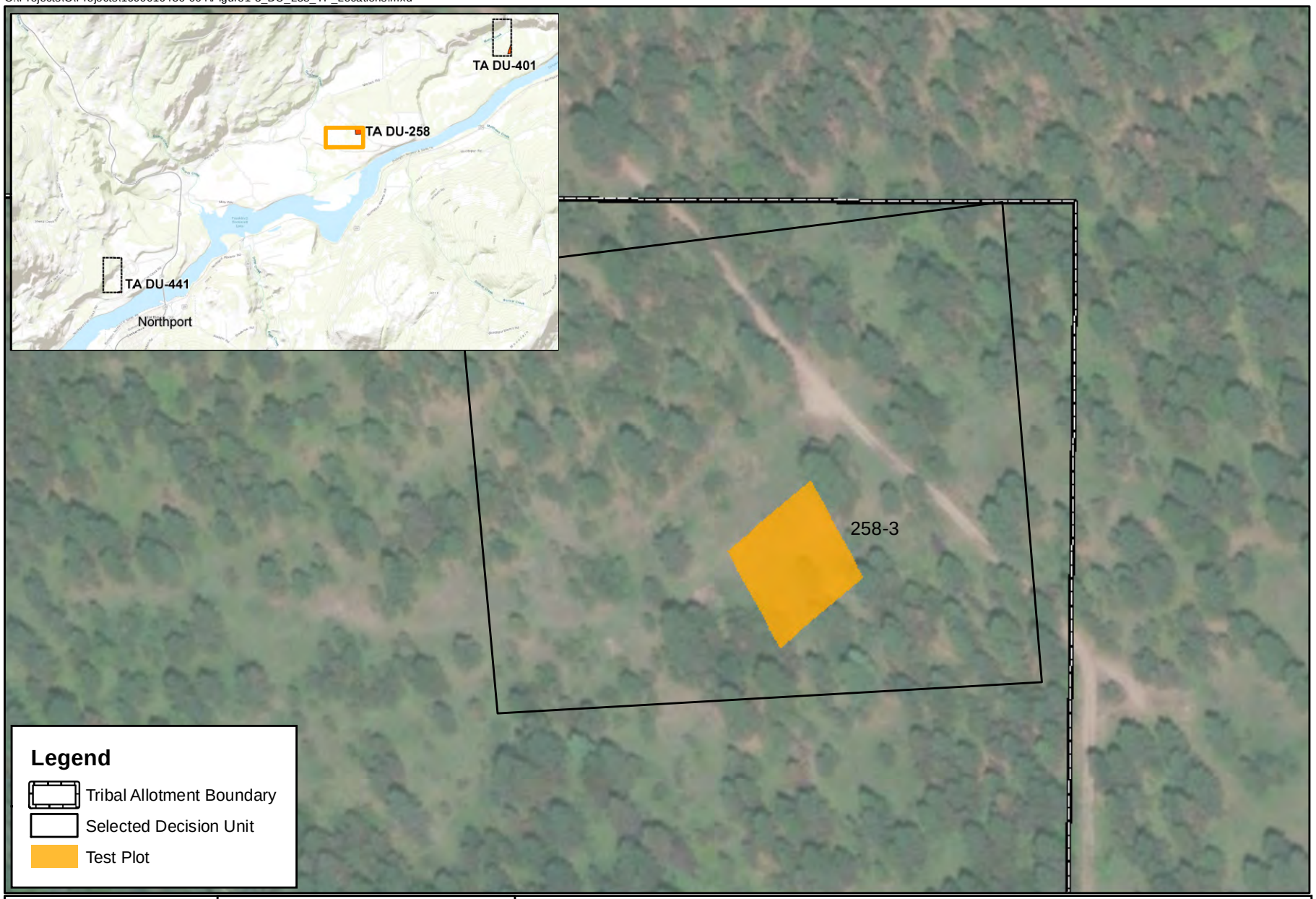

RAMBOLL

Figure 1-3
Test Plot Location - Decision Unit 258
Upper Columbia River SATES Program

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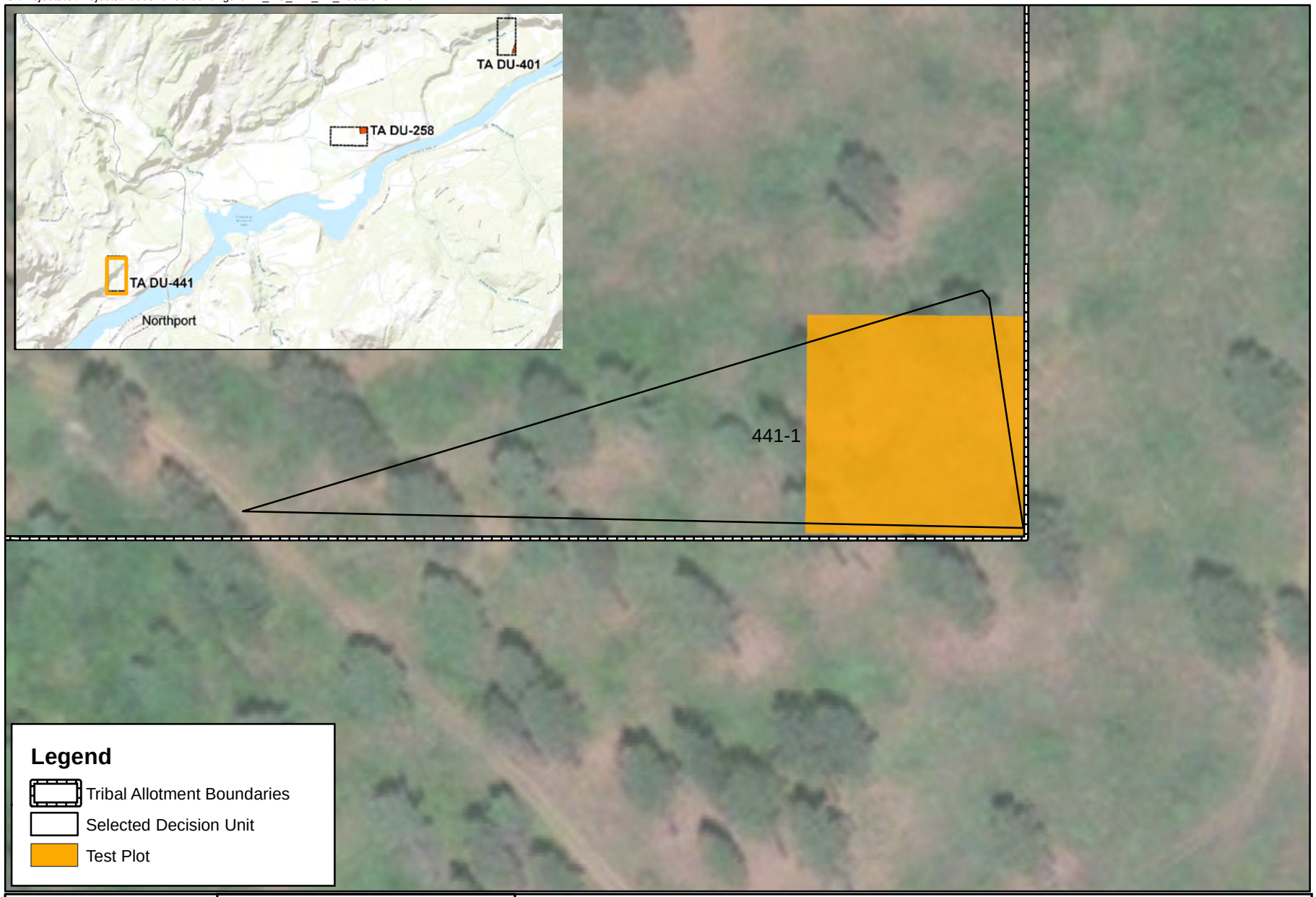
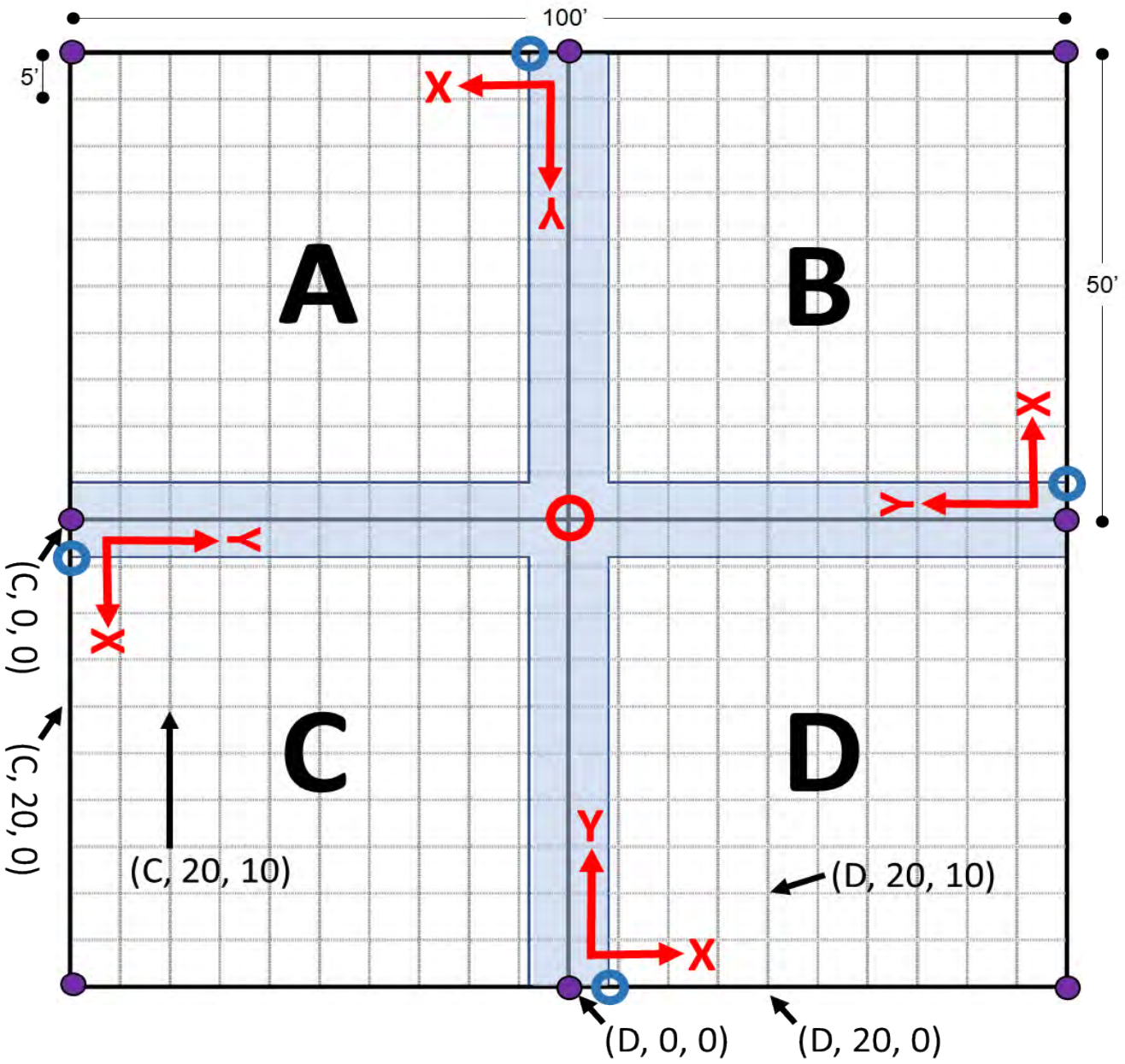


RAMBOLL

Figure 1-4
Test Plot Location - Decision Unit 441
Upper Columbia River SATES Program



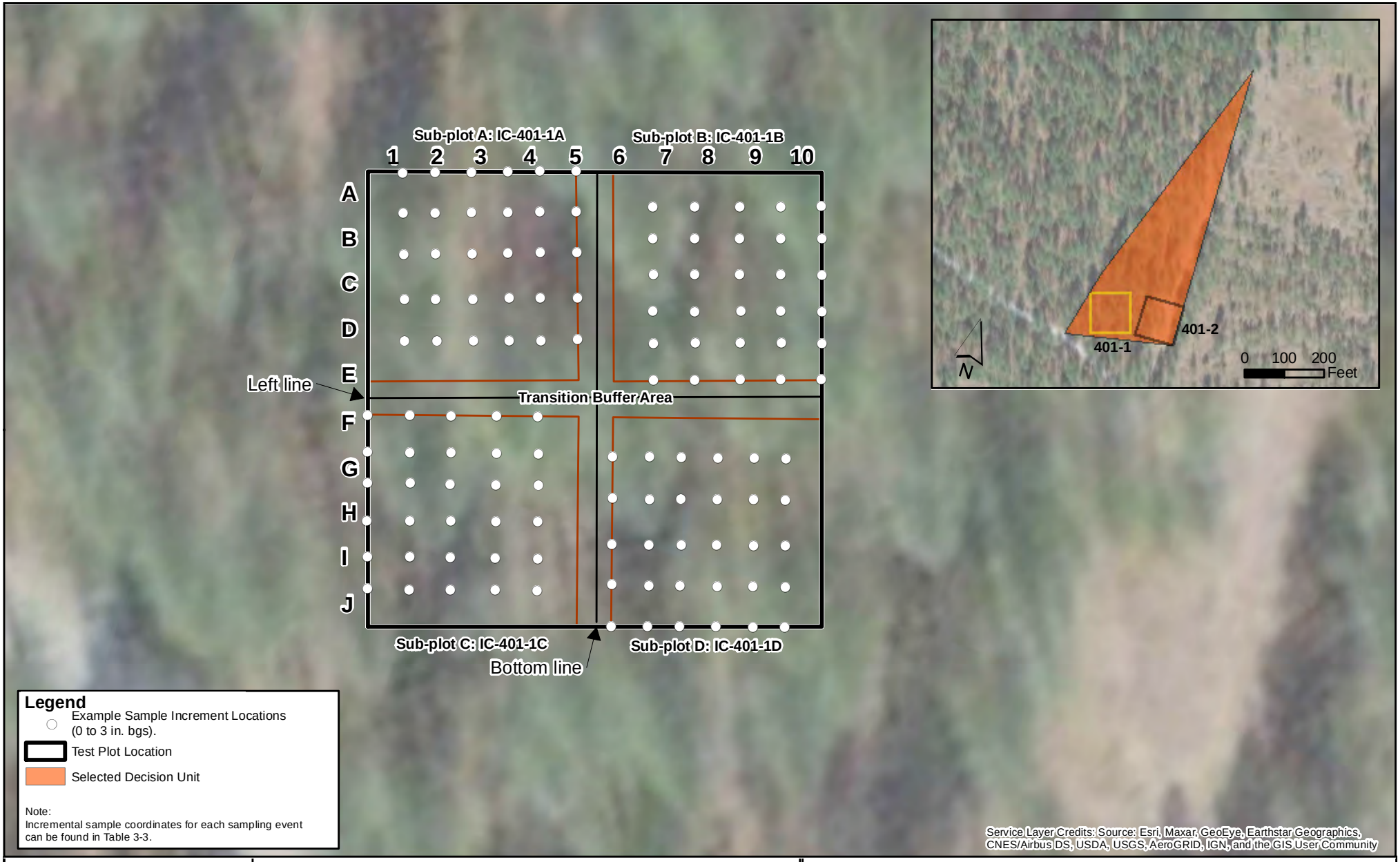
Note: The x and y axis orientation for each subplot rotates counterclockwise around the center of the test plot, starting with Subplot D, where the x axis is horizontal and the y axis is vertical. Moving counterclockwise, on he first rotation from Subplot D to Subplot B, the x and y axes rotate 90 degrees and so on for the second and third rotation around the center point.

RAMBOLL

Legend

- Test plot center
- Test plot corner and subplot corner marking stakes
- Soil sampling starting node for each subplot (4,0)

Figure 3-1
Test Plot and Subplot Layout for Field-Scale Pilot Testing
Upper Columbia River SATES Program



RAMBOLL

DRAFTED BY: JKing | Date: 8/6/2020

0 12.5 25 Meters

0 50 100 Feet

N

Figure 3-2
Test Plot 401-1: Example of Soil Increment Sample Location Array
Upper Columbia River SATES Program

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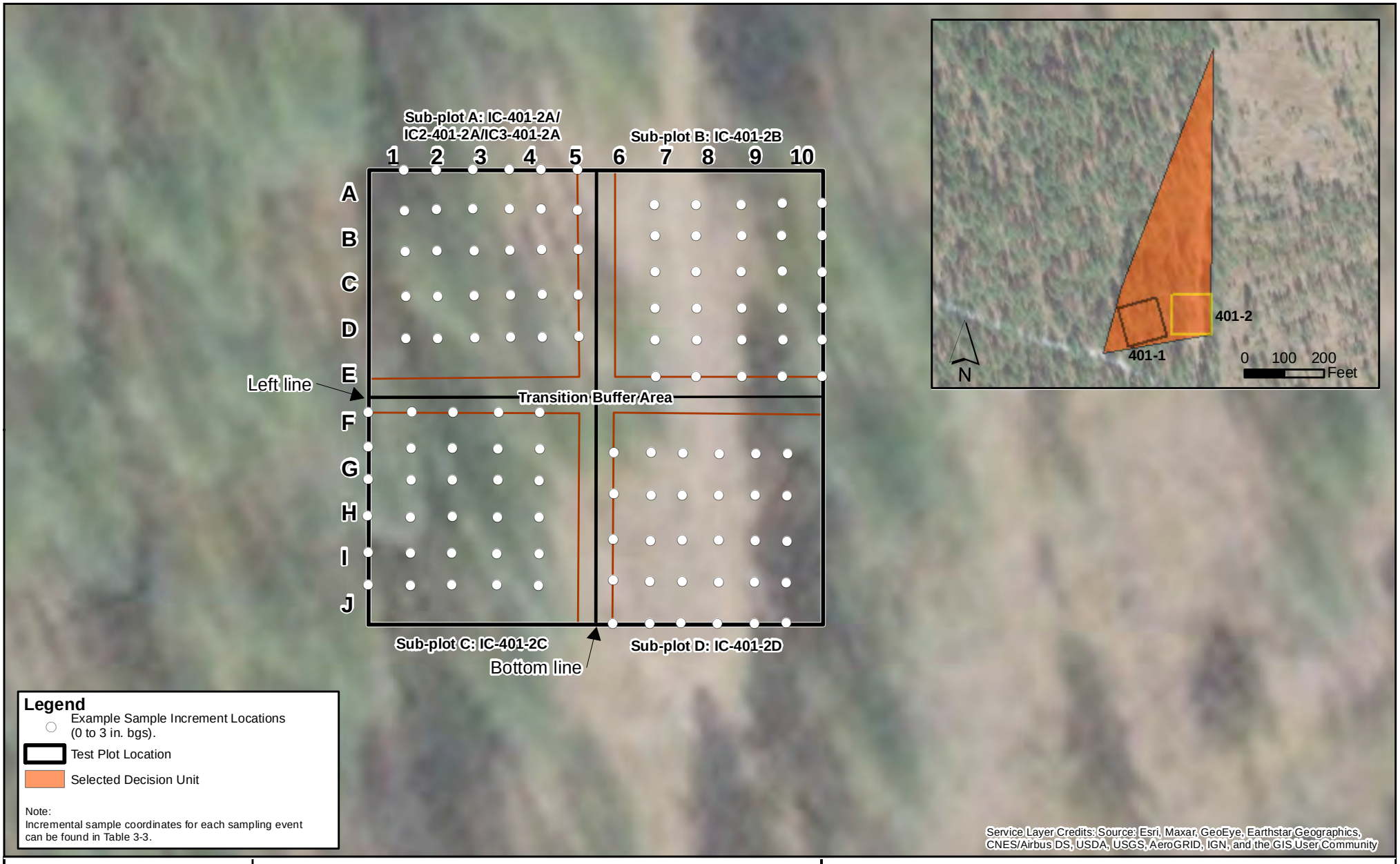
FINAL



RAMBOLL

0 12.5 25
Meters

0 50 100
Feet

N

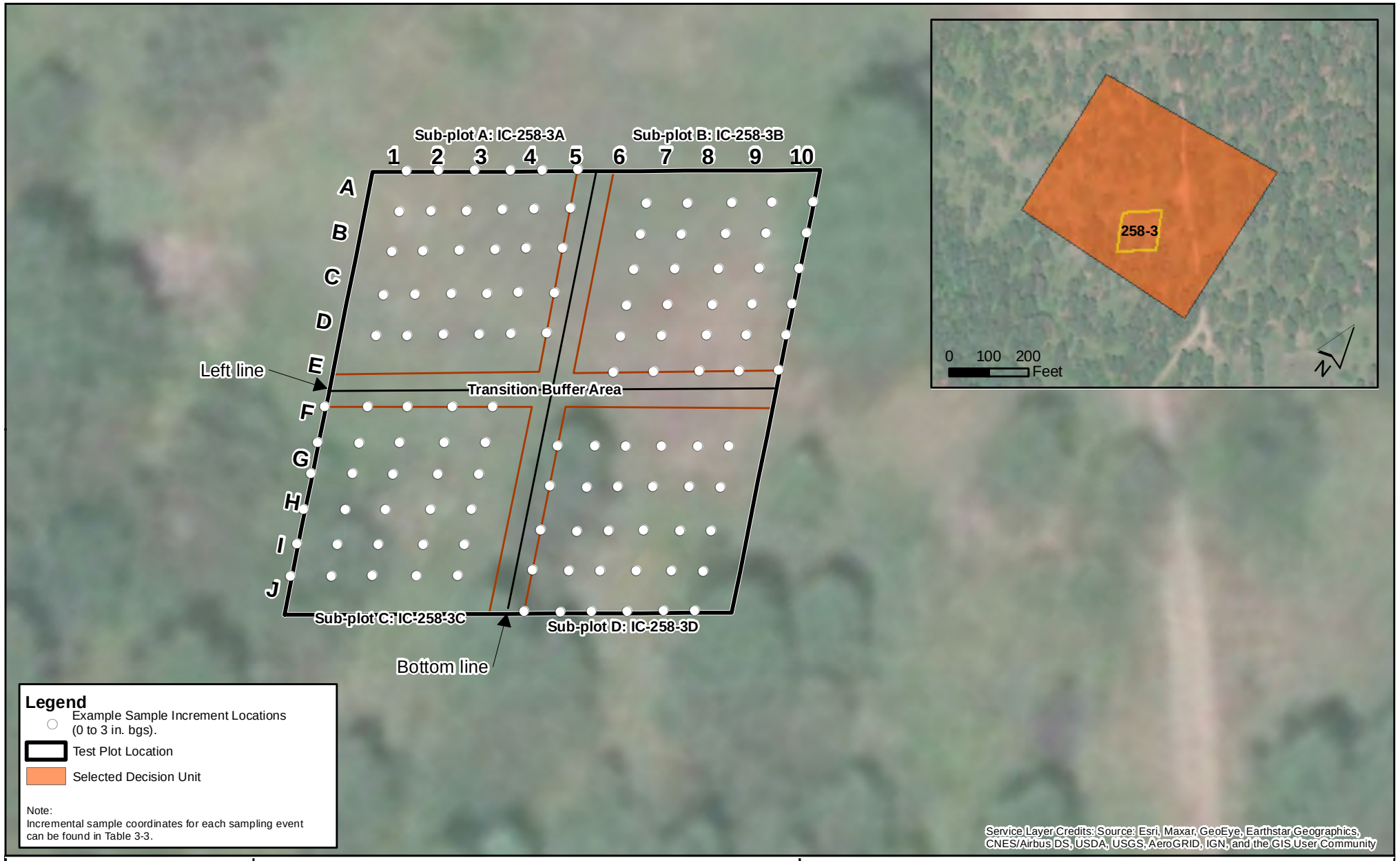
DRAFTED BY: JKing

Date: 8/6/2020

Figure 3-3
Test Plot 401-2: Example of
Soil Increment Sample Location Array
Upper Columbia River SATES Program

C:\Projects\C\Projects\1690016456-004\Figure3-4_DU258.3_Adj_TP_Incremental_Characterization.mxd

FINAL



RAMBOLL

0 12.5 25 Meters

0 50 100 Feet

DRAFTED BY: JKing

Date: 8/6/2020

Figure 3-4
Test Plot 258-3: Example of Soil Increment Sample Location Array
Upper Columbia River SATES Program

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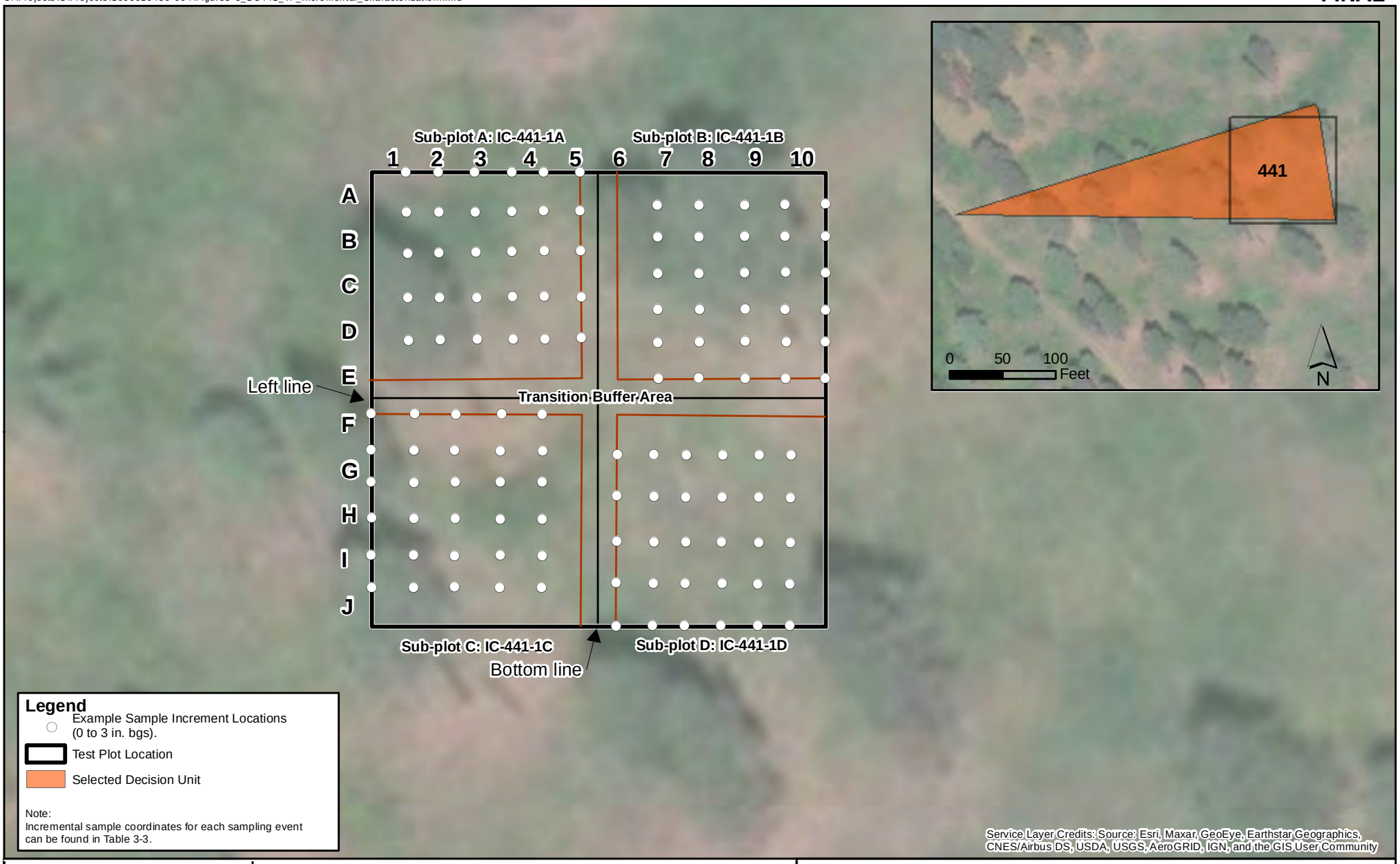
FINAL



RAMBOLL

0 12.5 25 Meters

0 50 100 Feet

N

DRAFTED BY: JKing

Date: 8/6/2020

Figure 3-5
Test Plot 441-1: Example of Soil Increment Sample Location Array
Upper Columbia River SATES Program

TABLES

Table 2-1. Amendment Application Rates for Field-Scale Soil Treatability Testing

Treatment Number	Soil Amendment	Treatment Rate Per Acre	Rate Rationale	Amendment Treatment Rate Per Subplot (lbs)[a]	Application Subplots
Individual Amendments					
1	Soluble phosphate	High rate of phosphate mixed with potash (5.6255 TSP ton/A + 0.375 KCl ton/A)[b]	Approximately 15 times the P/Pb molar ratio + 2 times the Cl/Pb molar ratio for pyromorphite formation. Has produced reductions in lead bioaccessibility in previous studies but not so much that long-term increases in salinity will result.	643 (TSP) 43 (KCl)	401-1-B, 401-2-D, 258-3-C, 441-1-B
2	Compost	Low rate of compost: 1/4-inch-thick layer (estimated to be 22 ton/A)	A 1/4-inch-thick layer of compost decreased lead %IVBA in the laboratory bench-scale study, compost is locally available, this rate is practical to apply over large areas, and the application rate should minimize disturbance to existing vegetation.	2,525	401-1-C, 401-2-A, 258-3-A, 441-1-A
3	Soluble phosphate and biochar	High rate of phosphate plus potash (5.6255 TSP ton/A + 0.375 KCl ton/A) Low rate of biochar: 0.36-inch-thick layer (5.001 ton/A or 1% by weight of top 3 inches of soil)	Soluble phosphate: Approximately 15 times the P/Pb molar ratio + 2 times the Cl/Pb molar ratio for pyromorphite formation. Has produced reductions in lead bioaccessibility in previous studies but not so much that long-term increases in salinity will result. Biochar: A 1% application of biochar decreased lead %IVBA in the laboratory bench-scale study, biochar is locally available, this application rate is practical to apply over large areas, and the application rate should minimize disturbance to existing vegetation.	645 (TSP) 43 (KCl) 574 (biochar)	401-1-A, 401-2-B, 258-3-D, 441-1-D
0	Control	NA	NA	NA	401-1-D, 401-2-C, 258-3-B, 441-1-C

Notes:

[a]1,800 gallons of water will be added to each subplot either in the application of amendments or alone for a balanced experiment. Water alone or the TSP solution will be applied prior to compost and biochar.

[b]TSP and KCl will be mixed in solution with water prior to application

Cl/Pb = chloride-to-lead molar ratio

KCl = potassium (i.e., potash) fertilizer (0-0-60)

NA = not applicable

P/Pb = phosphate-to-lead molar ratio

ton/A = dry U.S. tons per acre

TSP = triple super phosphate (0-45-0)

%IVBA = *in vitro* bioaccessibility

Table 2-2. SATES Field-Scale Monitoring and Analysis Plan

Analysis	Sample Preparation Method Reference	Sample Preparation Procedure	Sample Analysis Method Reference	Sample Analysis Procedure	Sample Sources	Sample Time Points	Soil Grain Size Fraction	Required Mass or Volume Per Sample (grams or ml)	Total Number of Original Samples
Phase III Analyses									
Semivolatile organic compounds	EPA 3510	Separatory Funnel Liquid - Liquid Extraction	EPA 8270	GC/MS	Biochar and compost	Prior to Field Application	NA	120	2
Total TAL metals (except mercury)	EPA 3051A	Acid digestion	EPA 6010	ICP-AES	All amendment materials	Prior to Field Application	NA	0.5	3
Mercury	EPA 7471B	Acid/Permanganate digestion	EPA 7471B	CVAA	All amendment materials	Prior to Field Application	NA	15	3
Mercury	EPA 7470A	Acid/Permanganate digestion	EPA 7470A	CVAA	Water from tanks	Prior to Field Application	NA	125 ml	5
Temperature	NA	NA	EPA 170.1	Thermometer	Water from tanks	Prior to Field Application	NA	Determined in field	5
Electrical conductivity (salinity)	NA	NA	SM 2510B	Electrode	Water from tanks	Prior to Field Application	NA	Determined in field	5
pH	NA	NA	Thomas 1996	Electrode	Water from tanks	Prior to Field Application	NA	Determined in field	5
Total TAL metals (except mercury)	EPA 3010	Acid digestion	EPA 6010	ICP-AES	Water from tanks	Prior to Field Application	NA	5 ml	5
Phase IV Analyses									
Bioaccessible arsenic and lead	EPA 1340	Glycine extraction (Extract at pH 1.5)	EPA 6010B	ICP-AES	Treated and control subplots	Each Phase IV Monitoring Event	<150 micrometer	1	20 per monitoring event
Bioaccessible arsenic and lead	EPA 1340	Glycine extraction (Extract at pH 2.5)	EPA 6010B	ICP-AES	Treated and control subplots	Each Phase IV Monitoring Event	<150 micrometer	1	20 per monitoring event
Electrical conductivity (salinity)	NA	NA	SM 2510B	Electrode	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	5	20 per monitoring event
Mehlich III extractable lead and phosphorus	Mehlich 1984	Acetic and nitric acid; ammonium fluoride and ammonium nitrate; EDTA	EPA 6010	ICP-AES	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	1	20 per monitoring event
Total TAL metals (except mercury)	EPA 3051A	Acid digestion	EPA 6010	ICP-AES	Treated and control subplots	Monitoring Event 1	<2 millimeter	0.5	20 per monitoring event
Mineralizable nitrogen	Waring and Bremner 1964	Short-term (7-day) anaerobic incubation for mineralizable N from organic matter	Waring and Bremner 1964	Lachat	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	5	20 per monitoring event
Oxalate extraction	McKeague and Day 1966	0.2 molar acid ammonium oxalate solution (pH 3.0)	EPA 6010	ICP-AES	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	0.25	20 per monitoring event
pH	NA	NA	Thomas 1996	Electrode	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	5	20 per monitoring event
Soil moisture	NA	NA	Direct measurement	Gravimetric	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	0	20 per monitoring event
SPLP TAL metals (except mercury) and phosphorus	EPA 1312	SPLP	EPA 6010	ICP-AES	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	1.5	20 per monitoring event
Total arsenic and lead	EPA 3051A	Acid digestion	EPA 6010	ICP-AES	Treated and control subplots	Each Phase IV Monitoring Event	<150 micrometer	0.5	20 per monitoring event
Total carbon and nitrogen	NA	NA	Bremner and Mulvaney 1982, Nelson and Sommers 1996	Dry combustion at 900°Celsius	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	10	20 per monitoring event
Total organic carbon	NA	NA	Heanes 1984	Dichromate oxidation	Treated and control subplots	Each Phase IV Monitoring Event	<2 millimeter	0.5	20 per monitoring event
Lead/arsenic and general soil mineralogy	NRMRL QMP L18735 ~500 mg of <250-micrometer freeze-dried soil	~100 mg of soil blended with 10 mg of PVP binder, pressed into a 7-millimeter pellet and encased in Kapton tape	NRMRL QMP L18735 Athena software data analysis	Synchrotron x-rays	Treated and control subplots	Individual samples selected at the end of the study[a]	<2 millimeter	20	≥4[a]

Notes:

[a]Based on analytical results and the discretion of the project technical team

EDTA = ethylenediaminetetraacetic acid
EPA = United States Environmental Protection Agency
CVAA = cold vapor atomic absorption
ICP-AES = inductively coupled plasma - atomic emission spectroscopy
GC/MS = gas chromatography/mass spectroscopy
NA = not applicable
NRMRL QMP = National Risk Management Research Laboratory Quality Management Plan
PVP = polyvinylpyrrolidone
SPLP = synthetic precipitation leaching procedure
TAL = target analyte list
mg = milligram(s)
µm = micrometer(s)
mm = millimeter(s)
mL = milliliter(s)

Table 3-1. Data Requirements for Field-Scale Pilot Testing

Analysis	Rationale	Laboratory
Bioaccessible arsenic and lead pH 1.5	Characterize bioaccessibility of arsenic and lead in soil	OSU
Bioaccessible arsenic and lead pH 2.5	Evaluate treatment effect on bioaccessible arsenic and lead	OSU
Electrical conductivity (Salinity)	Evaluate for potential for amendment applications to affect plant growth	NA - field measured
Mehlich III extractable lead and phosphorous	Evaluate treatment effect on available lead and phosphorus	OSU
Mercury	Pre-screening of amendments and water that will be used during application to evaluate potential changes from amendment application	ALS
Mineralizable nitrogen	Evaluate potentially available nitrogen	OSU
Oxalate extraction	Estimate concentrations of Al and Fe in soils in both non-crystalline and crystalline forms to evaluate how much is available to bind to arsenic	OSU
pH	Affects bioavailability of metals and plant nutrients	NA - field measured
Semi-volatile organic compounds (biochar and compost only)	Pre-screening of amendments	ALS
Soil moisture	Affects chemical reactions in soil	ALS
SPLP TAL metals (except mercury)	Monitor changes in leachability of metals	ALS
Temperature	Necessary for field electrical conductivity measurement	NA - field measured
Total arsenic and lead (<150 µm soil fraction)	Necessary for denominator for %IVBA calculation	OSU
Total carbon and nitrogen	Evaluate treatment effect on nutrient balance	OSU
Total organic carbon	Evaluate treatment effect on soil quality and nutrient balance	ALS
Total TAL metals (except mercury; <2mm soil fraction)	Pre-screening of amendments and water, and evaluate potential changes due to treatment application	ALS
Lead/arsenic and general soil mineralogy, synchrotron x-rays	Evaluate treatment effect on changes in lead and arsenic mineralogy	EPA

Notes:

EPA = U.S. Environmental Protection Agency

NA = not applicable

OSU = The Ohio State University

SPLP = synthetic precipitation leaching procedure

TAL = target analyte list

Table 3-2. Incremental Composite Soil Sampling Location Coordinates for Each Monitoring Event

Location	X	Y
Sub-Plot Datum[a]	0	0
Sample Collection Area Boundary		
Sampling Field Corner 1	4	0
Sampling Field Corner 2	4	50
Sampling Field Corner 3	50	46
Sampling Field Corner 4	46	4

	Baseline Coordinates (ft)		Monitoring 1[b] (ft)		Monitoring 2 (ft)		Monitoring 3 (ft)		Monitoring 4 (ft)		Monitoring 5 (ft)		Monitoring 6 (ft)		Monitoring 7 (ft)		Monitoring 8 (ft)		Monitoring 9 (ft)	
Increment Sampling Points	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
Increment Sampling Point 1	4	0	4	2	4	4	4	6	6	0	6	2	6	4	6	6	8	0	8	2
Increment Sampling Point 2	4	9	4	11	4	13	4	15	6	9	6	11	6	13	6	15	8	9	8	11
Increment Sampling Point 3	4	18	4	20	4	22	4	24	6	18	6	20	6	22	6	24	8	18	8	20
Increment Sampling Point 4	4	28	4	30	4	32	4	34	6	28	6	30	6	32	6	34	8	28	8	30
Increment Sampling Point 5	4	37	4	39	4	41	4	43	6	37	6	39	6	41	6	43	8	37	8	39
Increment Sampling Point 6	12	0	12	2	12	4	12	6	14	0	14	2	14	4	14	6	16	0	16	2
Increment Sampling Point 7	12	9	12	11	12	13	12	15	14	9	14	11	14	13	14	15	16	9	16	11
Increment Sampling Point 8	12	18	12	20	12	22	12	24	14	18	14	20	14	22	14	24	16	18	16	20
Increment Sampling Point 9	12	28	12	30	12	32	12	34	14	28	14	30	14	32	14	34	16	28	16	30
Increment Sampling Point 10	12	37	12	39	12	41	12	43	14	37	14	39	14	41	14	43	16	37	16	39
Increment Sampling Point 11	19	0	19	2	19	4	19	6	21	0	21	2	21	4	21	6	23	0	23	2
Increment Sampling Point 12	19	9	19	11	19	13	19	15	21	9	21	11	21	13	21	15	23	9	23	11
Increment Sampling Point 13	19	18	19	20	19	22	19	24	21	18	21	20	21	22	21	24	23	18	23	20
Increment Sampling Point 14	19	28	19	30	19	32	19	34	21	28	21	30	21	32	21	34	23	28	23	30
Increment Sampling Point 15	19	37	19	39	19	41	19	43	21	37	21	39	21	41	21	43	23	37	23	39
Increment Sampling Point 16	27	0	27	2	27	4	27	6	29	0	29	2	29	4	29	6	31	0	31	2
Increment Sampling Point 17	27	9	27	11	27	13	27	15	29	9	29	11	29	13	29	15	31	9	31	11
Increment Sampling Point 18	27	18	27	20	27	22	27	24	29	18	29	20	29	22	29	24	31	18	31	20
Increment Sampling Point 19	27	28	27	30	27	32	27	34	29	28	29	30	29	32	29	34	31	28	31	30
Increment Sampling Point 20	27	37	27	39	27	41	27	43	29	37	29	39	29	41	29	43	31	37	31	39
Increment Sampling Point 21	35	0	35	2	35	4	35	6	37	0	37	2	37	4	37	6	39	0	39	2
Increment Sampling Point 22	35	9	35	11	35	13	35	15	37	9	37	11	37	13	37	15	39	9	39	11
Increment Sampling Point 23	35	18	35	20	35	22	35	24	37	18	37	20	37	22	37	24	39	18	39	20
Increment Sampling Point 24	35	28	35	30	35	32	35	34	37	28	37	30	37	32	37	34	39	28	39	30
Increment Sampling Point 25	35	37	35	39	35	41	35	43	37	37	37	39	37	41	37	43	39	37	39	39
Increment Sampling Point 26	42	0	42	2	42	4	42	6	44	0	44	2	44	4	44	6	46	0	46	2
Increment Sampling Point 27	42	9	42	11	42	13	42	15	44	9	44	11	44	13	44	15	46	9	46	11
Increment Sampling Point 28	42	18	42	20	42	22	42	24	44	18	44	20	44	22	44	24	46	18	46	20
Increment Sampling Point 29	42	28	42	30	42	32	42	34	44	28	44	30	44	32	44	34	46	28	46	30
Increment Sampling Point 30	42	37	42	39	42	41	42	43	44	37	44	39	44	41	44	43	46	37	46	39

Notes:

[a]See Figure 10 for datum location relative to each sub-plot.

[b]Eaching monitoring heading indicates the monitoring event.

Table 3-3a. Analytical Parameters, Methods, and Target Laboratory Reporting Limits

Analyte	CAS Number	Sample Medium	Units	Laboratory MDL	Laboratory RL	Preservation	Holding Time (days)
TAL Metals (6010)							
Aluminum	7429-90-5	Solid	mg/kg	30	30	None	180
		Aqueous	µg/L	0.2	4	Nitric acid to pH 2, cool to 4°C±2°C	
Antimony	7440-36-0	Solid	mg/kg	2	4	None	
		Aqueous	µg/L	0.02	0.05	Nitric acid to pH 2, cool to 4°C±2°C	
Arsenic	7440-38-2	Solid	mg/kg	2	4	None	
		Aqueous	µg/L	0.09	0.5	Nitric acid to pH 2, cool to 4°C±2°C	
Barium	7440-39-3	Solid	mg/kg	0.3	0.8	None	
		Aqueous	µg/L	0.002	0.05	Nitric acid to pH 2, cool to 4°C±2°C	
Beryllium	7440-41-7	Solid	mg/kg	0.08	0.2	None	
		Aqueous	µg/L	0.005	0.02	Nitric acid to pH 2, cool to 4°C±2°C	
Cadmium	7440-43-9	Solid	mg/kg	0.09	0.2	None	
		Aqueous	µg/L	0.008	0.02	Nitric acid to pH 2, cool to 4°C±2°C	
Calcium	7440-70-2	Solid	mg/kg	1	100	None	
		Aqueous	mg/L	0.9	20	Nitric acid to pH 2, cool to 4°C±2°C	
Chromium	7440-47-3	Solid	mg/kg	0.3	0.8	None	
		Aqueous	mg/L	0.9	4	Nitric acid to pH 2, cool to 4°C±2°C	
Cobalt	7440-48-4	Solid	mg/kg	0.2	0.4	None	
		Aqueous	mg/L	1	2	Nitric acid to pH 2, cool to 4°C±2°C	
Copper	7440-50-8	Solid	mg/kg	0.4	0.8	None	
		Aqueous	mg/L	1	2	Nitric acid to pH 2, cool to 4°C±2°C	
Iron	7439-89-6	Solid	mg/kg	2	40	None	
		Aqueous	mg/L	3	20	Nitric acid to pH 2, cool to 4°C±2°C	
Lead	7439-92-1	Solid	mg/kg	0.7	2	None	
		Aqueous	mg/L	5	10	Nitric acid to pH 2, cool to 4°C±2°C	
Magnesium	7439-95-4	Solid	mg/kg	0.2	100	None	
		Aqueous	µg/L	0.3	5	Nitric acid to pH 2, cool to 4°C±2°C	
Manganese	7439-96-5	Solid	mg/kg	0.04	1.0	None	
		Aqueous	µg/L	0.3	1	Nitric acid to pH 2, cool to 4°C±2°C	
Nickel	7440-02-0	Solid	mg/kg	0.2	0.8	None	
		Aqueous	µg/L	0.6	4	Nitric acid to pH 2, cool to 4°C±2°C	
Potassium	7440-09-7	Solid	mg/kg	10	100	None	
		Aqueous	µg/L	60	200	Nitric acid to pH 2, cool to 4°C±2°C	
Selenium	7782-49-2	Solid	mg/kg	2	5	None	
		Aqueous	µg/L	9	20	Nitric acid to pH 2, cool to 4°C±2°C	
Silver	7440-22-4	Solid	mg/kg	0.3	0.8	None	
		Aqueous	µg/L	2	4	Nitric acid to pH 2, cool to 4°C±2°C	
Sodium	7440-23-5	Solid	mg/kg	5	100	None	
		Aqueous	µg/L	20	200	Nitric acid to pH 2, cool to 4°C±2°C	

Table 3-3a. Analytical Parameters, Methods, and Target Laboratory Reporting Limits

Analyte	CAS Number	Sample Medium	Units	Laboratory MDL	Laboratory RL	Preservation	Holding Time (days)
TAL Metals (6010) (*continued*)							
Thallium	7440-28-0	Solid	mg/kg	1	2	None	180
		Aqueous	µg/L	4	10	Nitric acid to pH 2, cool to 4°C±2°C	
Vanadium	7440-62-2	Solid	mg/kg	0.3	2	None	
		Aqueous	µg/L	1	4	Nitric acid to pH 2, cool to 4°C±2°C	
Zinc	7440-66-6	Solid	mg/kg	0.2	5	None	
		Aqueous	µg/L	0.6	4	Nitric acid to pH 2, cool to 4°C±2°C	
Other Analyses							
SPLP TAL metals (except mercury) and phosphorus	NA	Solid	µg/L	Varies	Varies	None	180
Semivolatile Organic Compounds	See Table 3-3b	Solid	mg/kg	See Table 3-3b	See Table 3-3b	Cool to 4°C±2°C	14
Electrical Conductivity	NA	Solid	dS/m	NA	NA	Cool to 4°C±2°C	28
		Aqueous				None	In field
Temperature	NA	Aqueous	°C	NA	NS	None	In field
Bioaccessible arsenic and lead (at pH 1.5 and pH 2.5)	NA	Solid	%	NA	NA	None	180
pH	NA	Solid	unitless	NA	NA	Cool to 4°C±2°C	In field
		Aqueous				None	In field
Mehlich III extractable lead and phosphorus	NA	Solid	mg/kg	NA	NA	None	180
Total carbon and nitrogen	NA	Solid	%	Equal to RL	Varies	None	60
Mineralizable nitrogen	NA	Solid	mg/kg	Equal to RL	Varies	None	60
Mercury	7439-97-6	Solid	mg/kg	0.002	0.02	None	28
		Aqueous	µg/L	0.002	0.2	Nitric acid to pH 2, cool to 4°C±2°C	28
Total organic carbon	NA	Solid	%	1	1	None	60
Soil moisture	NA	Solid	%	NA	NA	None	60
Lead/arsenic and general soil mineralogy	NA	Solid	NA	NA	NA	None	180

Notes:

RLs for carbon (C) and nitrogen (N) can vary depending on the amount of soil used in combustion. For example, for a 100-mg sample, typical RLs w

MDL and RL concentrations are reported in milligrams per kilogram dry weight, unless otherwise noted.

The laboratory supplied the lowest method achievable MDLs and RLs to meet the soil standards listed in this table.

% = percent

CAS = Chemical Abstracts Service

MDL = method detection limit

mg/kg = milligrams per kilogram

µg/L = micrograms per liter

NA = not applicable

RL = reporting limit

SPLP = synthetic precipitation leaching procedure

TAL = target analyte list

dS/m = decisiemens per meter

Table 3-3b. Analytical Parameters, Methods, and Target Laboratory Reporting Limits, Semivolatile Organic Compounds Analysis

Analyte	Units	CAS Number	Laboratory MDL	Laboratory RL	Preservation	Holding Time (days)
SVOCs (8270)						
1,2,4-Trichlorobenzene	mg/kg	120-82-1	0.011	0.33	Cool to 4°C ± 2°C	14 days to extraction, subsequently 40 days to analysis
1,2-Dichlorobenzene		95-50-1	0.018	0.33		
1,2-Diphenylhydrazine		122-66-7	0.014	0.33		
1,3-Dichlorobenzene		541-73-1	0.018	0.33		
1,4-Dichlorobenzene		106-46-7	0.018	0.33		
2,4,5-Trichlorophenol		95-95-4	0.018	0.33		
2,4,6-Trichlorophenol		88-06-2	0.014	0.33		
2,4-Dichlorophenol		120-83-2	0.016	0.33		
2,4-Dimethylphenol		105-67-9	0.015	0.33		
2,4-Dinitrophenol		51-28-5	0.11	2		
2,4-Dinitrotoluene		121-14-2	0.015	0.33		
2,6-Dinitrotoluene		606-20-2	0.016	0.33		
2-Chloronaphthalene		91-58-7	0.01	0.33		
2-Chlorophenol		95-57-8	0.0099	0.33		
2-Methyl-4,6-dinitrophenol		534-52-1	0.14	2		
2-Methylnaphthalene		91-57-6	0.011	0.33		
2-Methylphenol		95-48-7	0.017	0.33		
2-Nitroaniline		88-74-4	0.017	0.33		
2-Nitrophenol		88-75-5	0.014	0.33		
3,3'-Dichlorobenzidine		91-94-1	0.027	0.33		
3-Nitroaniline		99-09-2	0.018	0.33		
4-Chloro-3-methylphenol		59-50-7	0.017	0.33		
4-Chloroaniline		106-47-8	0.014	0.33		
4-Chlorophenyl Phenyl Ether		7005-72-3	0.016	0.33		
4-Methylphenol		106-44-5	0.017	0.33		
4-Nitroaniline		100-01-6	0.18	2		
4-Nitrophenol		100-02-7	0.15	2		
Acenaphthene		83-32-9	0.013	0.33		
Acenaphthylene		208-96-8	0.016	0.33		
Aniline		62-53-3	0.022	1		
Anthracene		120-12-7	0.014	0.33		
Atrazine*		1912-24-9	0.017	0.33		
Azobenzene		103-33-3	0.014	0.33		
Benz(a)anthracene		56-55-3	0.012	0.33		
Benzo(a)pyrene		50-32-8	0.02	0.33		
Benzo(b)fluoranthene		205-99-2	0.017	0.33		
Benzo(g,h,i)perylene		191-24-2	0.02	0.33		
Benzo(k)fluoranthene		207-08-9	0.019	0.33		
Benzoic Acid		65-85-0	0.14	2		
Benzyl Alcohol		100-51-6	0.017	0.33		
Biphenyl*		92-52-4	0.009	0.33		
Bis(2-chloroethoxy)methane		111-91-1	0.011	0.33		
Bis(2-chloroethyl) Ether		111-44-4	0.012	0.33		
2,2'-Oxybis(1-chloropropane)		108-60-1	0.014	0.33		
Bis(2-ethylhexyl) Phthalate		117-81-7	0.019	0.33		
Butyl Benzyl Phthalate		85-68-7	0.016	0.33		
Caprolactam*		105-60-2	0.15	0.33		
Chrysene		218-01-9	0.012	0.33		
Dibenz(a,h)anthracene		53-70-3	0.027	0.33		
Dibenzofuran		132-64-9	0.012	0.33		
Diethyl Phthalate		84-66-2	0.014	0.33		
Dimethyl Phthalate		131-11-3	0.016	0.33		
Di-n-butyl Phthalate		84-74-2	0.012	0.33		
Di-n-octyl Phthalate		117-84-0	0.024	0.33		

Table 3-3b. Analytical Parameters, Methods, and Target Laboratory Reporting Limits, Semivolatile Organic Compounds Analysis

Analyte	Units	CAS Number	Laboratory MDL	Laboratory RL	Preservation	Holding Time (days)
Fluoranthene		206-44-0	0.011	0.33		
Fluorene		86-73-7	0.013	0.33		
Hexachlorobenzene		118-74-1	0.015	0.33		
Hexachlorobutadiene		87-68-3	0.014	0.33		
Hexachlorocyclopentadiene		77-47-4	0.012	0.33		
Hexachloroethane		67-72-1	0.022	0.33		
Indeno(1,2,3-cd)pyrene		193-39-5	0.039	0.33		
Isophorone		78-59-1	0.014	0.33		
Naphthalene		91-20-3	0.014	0.33		
Nitrobenzene		98-95-3	0.026	0.33		
N-Nitrosodimethylamine		62-75-9	0.025	2		
N-Nitrosodiphenylamine		86-30-6	0.018	0.33		
N-Nitrosodi-n-propylamine		621-64-7	0.019	0.33	Cool to 4°C ± 2°C	14 days to extraction, subsequently 40 days to analysis
Pentachlorophenol		87-86-5	0.13	2		
Phenanthrene		85-01-8	0.01	0.33		
Phenol		108-95-2	0.019	0.33		
Pyrene		129-00-0	0.014	0.33		
Pyridine*		110-86-1	0.02	0.33		
2,4,6-Tribromophenol (surr)		118-79-6				
2-Fluorobiphenyl (surr)		321-60-8				
2-Fluorophenol (surr)	%	367-12-4	NA	NA		
Nitrobenzene-d5 (surr)		4165-60-0				
Phenol-d6 (surr)		13127-88-3				
Terphenyl-d14 (surr)		1718-51-0				

Notes:
MDL and RL concentrations are reported in milligrams per kilogram dry weight, unless otherwise noted
The laboratory supplied the lowest method achievable MDLs and RLs to meet the soil standards listed in this table.
The laboratory notes that, during the analysis for SVOCs, the phosphorus in fertizilier may cause low surrogate and matrix spike recoveries. Dilutions may be performed or RLs may be elevated.
* These compounds are outside of the standard SVOC list and must be requested specifically on the chain of custody form submitted to ALS Environmental with the samples.

% = percent
CAS = Chemical Abstracts Service
MDL = method detection limit
mg/kg = milligrams per kilogram
N/A = not applicable
RL = reporting limit
SVOC(s) = semivolatile organic compound(s)

APPENDICES

APPENDIX A

CULTURAL RESOURCE COORDINATION PLAN

CONTENTS

LIST OF FIGURES

ACRONYMS AND ABBREVIATIONS

ACHP	Advisory Council on Historic Preservation
APE	area of potential effects
ARPA	Archaeological Resources Protection Act of 1979
bgs	below ground surface
CCT	Confederated Tribes of the Colville Reservation
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFR	Code of Federal Regulations
CRCP	cultural resources coordination plan
DAHP	Washington State Department of Archaeology & Historic Preservation
EPA	U.S. Environmental Protection Agency
FOIA	Freedom of Information Act
IC	incremental composite
in.	inch(es)
Lake Roosevelt	Franklin D. Roosevelt Lake
MOA	Memorandum of Agreement
NAGPRA	Native American Graves Protection and Repatriation Act
National Register	National Register of Historic Places
NEPA	National Environmental Policy Act
NHPA	National Historic Preservation Act
NPS	National Park Service
RCW	Revised Code of Washington
RI/FS	remedial investigation and feasibility study
RM	river mile
SATES	Soil Amendment Technology Evaluation Study

SHPO	State Historic Preservation Officer
Site	Upper Columbia River site
STI	Spokane Tribe of Indians
TAI	Teck American Incorporated
THPO	Tribal Historic Preservation Officer
UCR	Upper Columbia River
USBR	U.S. Bureau of Reclamation
WAC	Washington Administrative Code

1 INTRODUCTION

This document presents the cultural resources coordination plan (CRCP) for the Upper Columbia River (UCR) site (herein the 'Site') remedial investigation and feasibility study (RI/FS). Emphasis is placed on sampling field activities associated with the Soil Amendment Technology Evaluation Study (SATES) that will be conducted starting in September 2020 and continuing through approximately November 2023 within the UCR Study Area, as defined by the *Work Plan for the Soil Amendment Technology Evaluation Study, Phase III & Phase IV: Test Plot Field-scale Implementation & Test Plot Monitoring* (hereinafter 'Phase III and Phase IV Work Plan') (Ramboll 2020). These activities include applying selected soil treatment amendments to the soil surface with minimal perturbation and collecting multiple sets of surficial soil samples from within the top 3 in. of soil. In or around late 2023, an additional soil sampling event will be conducted that will involve collecting soil samples from the surface to a depth of 12 in. or more in the upper part of the soil profile. The sampling design and procedures for discrete soil sample collection will be developed later during the field study. The SATES Phase III and Phase IV field activities will be conducted entirely on Colville Tribal tribal allotments.

1.1 BACKGROUND

As specified in the Statement of Work associated with the June 2, 2006 Settlement Agreement (USEPA 2006), "For all RI/FS activities at the Site involving sediment collection or ground penetration/disturbance, the Company shall work with the potentially affected parties to assess the effects of the planned work and seek ways to avoid, minimize or mitigate any adverse effects on historic properties." The purpose of this CRCP is to describe known or likely physical impacts of proposed field-scale soil treatment testing and soil sampling, provide relevant background information, define measures for protecting resources, and define procedures for consulting with the appropriate state, federal, and tribal parties with interests in the cultural resources of the Site.

The Site is located wholly within the state of Washington and includes approximately 150 river miles of the Columbia River extending from the U.S.-Canada border to the Grand Coulee Dam and those areas in proximity to such contamination necessary for implementation of the response actions described in the 2006 Settlement Agreement. The Colville Indian Reservation borders the UCR from approximately river mile (RM) 690 to the Grand Coulee Dam. The Spokane Indian Reservation borders the UCR to the east from approximately RM 650 to RM 640. Franklin D. Roosevelt Lake (Lake Roosevelt) and associated lands are administered by the U.S. Bureau of Reclamation (USBR) and the National Park Service (NPS) of the U.S. Department of the Interior.

The U.S. Environmental Protection Agency (EPA) has responsibilities under the National Historic Preservation Act (NHPA) to consider how its undertakings would affect historic properties. As defined in the NHPA, "historic properties" include archaeological resources, historic-period buildings and structures, and traditional cultural places listed in or determined eligible for listing in the National Register of Historic Places (National Register). To meet the NHPA requirements, EPA must ensure that sampling and other activities would avoid, minimize, or mitigate any adverse effects on any historic properties.

The CRCP is organized into six sections, as follows: 1) this introductory section, which includes summary information on the archaeology, prehistory, Native peoples, and Euroamerican historical development of the project area; 2) an overview of the relevant federal, state, and tribal laws and regulations, and other appropriate procedures and requirements; 3) a description of the proposed sampling program; 4) a plan for coordination and consultation with all affected parties to address known and likely impacts on cultural resources in implementing the proposed work; 5) a list of references; and 6) a glossary of terms.

1.2 CULTURAL SETTING

The broader context of the cultural development of the upper Columbia region provides the critical framework for understanding the importance of cultural resources in the area. Archaeological and historical resources reflect broad patterns of cultural use and development, just as ongoing traditional use of areas and natural resources represents cultural continuity that can be important to individual and social identities. This section of the CRCP serves as a brief introduction to the cultural history of the upper Columbia region. The primary source of information on the prehistory of the area is Goodal et al. (2004); for Native peoples, the source is Kennedy and Bouchard (1998); and for Euroamerican history, McKay and Renk (2002).

Archaeological research contributes significantly to our understanding of the prehistoric past. In the upper Columbia region, systematic archaeological research began in the late 1930s and has continued to the present. Almost 500 archaeological resources have been recorded in and along Lake Roosevelt, representing prehistoric, protohistoric, ethnohistoric, and historic-period human use and occupation. Research at some of these resources has provided the outlines of prehistoric cultural development in the upper Columbia region. Human presence in the region extends back at least 11,000 years. These first humans lived in small groups and were mobile foragers, hunting and gathering plants. The presence of the Columbia River led to an early focus on the abundance of riverine sources. Beginning about 8,000 years ago, populations appear to have increased and led to

a gradual trend to less mobility and more permanent settlements. The growing population also led to use of a greater diversity of resources and increasing reliance on fish.

Permanent settlements increased in size and became concentrated in the river valleys beginning about 6,000 years ago, probably in response to continued population growth. Use of resources in upland areas expanded to meet the needs of the burgeoning populations and settlements. These trends continued until about 1,000 years ago, when there is evidence for a decline in population size. There were fewer settlements, villages were smaller, and there was less use of upland areas.

Cultural patterns of the late prehistoric period were reflected in the lives of the Native peoples at the time of Euroamerican contact. At the time of contact, the UCR was the homeland of the Lakes, Colville, Spokane, and Sanpoil peoples. The Lakes people occupied the Columbia River valley from the vicinity of modern Northport, Washington, north into the Arrow Lakes area of modern British Columbia. The Colville lived along the river downstream of the Lakes as far as around the mouth of the Spokane River. Downriver of the Colville were the Spokane, in the Spokane River drainage, and the Sanpoil, who lived along the Columbia River from around the mouth of the Spokane River to near the modern location of the Grand Coulee Dam.

All of these groups spoke Interior Salish languages and shared many cultural features. Their cultural differences largely reflected differences in the local environments in which they lived. The social, political, and economic foundation of these groups was historically the winter village. The villages were concentrated in the river valleys, and each village was politically independent. Residents of the villages relied on provisions gathered, dried, and stored during the summer to survive through the winter. With the coming of spring, families began moving out of the winter village and shifting among the warm-season camps near resource locations. Gathering of plants and hunting game in upland areas were important subsistence activities during this season, but salmon constituted the most important food staple. Kettle Falls was a major aboriginal fishery, attracting people from throughout the region.

Native life began to change with the introduction of elements of Euroamerican culture. Horses reached the region in the 1700s and significantly changed Native travel and transportation. European diseases such as smallpox appeared in the late 1700s and had disastrous consequences for Native groups. Populations may have declined as much as 80 percent between the 1780s and 1840s. Direct contact with Euroamericans came in the early 1800s, when fur-trade posts were established on the Spokane River and at Kettle Falls.

When American settlement began in the 1840s, it bypassed the upper Columbia region. The discovery of gold in the region in the 1850s led to a major influx of Americans and

growing conflict between the new settlers and Indian groups. A series of treaties with Indian groups were signed in 1855 but did not include the peoples of the upper Columbia region. As American settlement continued, the federal government responded by Presidential Executive Order creating the Colville Reservation in 1872 for the Colville, Spokane, Methow, Okanogan, Sanpoil, Lakes, Calispel, Coeur d'Alene, and scattering bands. Separate reservations were later set aside for the Spokane, Calispel, and Coeur d'Alene Tribes. Both the Colville and Spokane reservations have subsequently lost lands to the allotment process in the late 1800s and early 1900s and inundation from the waters of Lake Roosevelt. The Colville Reservation is now home to the 12 tribes that comprise the Confederated Tribes of the Colville Reservation (CCT); the Spokane Reservation is the home of the Spokane Tribe of Indians (STI).

As already noted, the direct Euroamerican presence in the upper Columbia region began with the establishment of fur-trade posts on the Spokane River and at Kettle Falls. These posts were constructed between 1810 and 1825. The fur traders were followed by Christian missionaries in the 1830s and 1840s. A more substantial Euroamerican presence in the region developed in the 1850s, with the discovery of gold near Fort Colville. Conflicts between miners and Indians led to a military campaign in the Spokane River valley in 1858 and the establishment of an army post (Fort Colville) near Kettle Falls in 1859.

American settlement in the UCR drainage accelerated in the 1860s, initially spurred by mining. Farmers eventually followed the miners, but agricultural activity was limited until the construction of the Spokane Falls and Northern Railway through the region in 1890. With improved access to markets, farming—especially orchard crops—developed as one of the economic mainstays of the area, although mining has continued to play an important role.

The growing demands for agriculture led to plans to construct a dam at Grand Coulee. The dam would provide water for irrigation and inexpensive hydroelectric power. Construction of the dam began in 1934 and was completed in 1942. More than 82,000 acres above the dam was flooded, resulting in the relocation of 11 towns and about 3,000 residents. Since its creation, Lake Roosevelt has provided a growing number of recreational and tourist activities, which have become increasingly important to local economies.

2 OVERVIEW OF LAWS AND REGULATIONS

Implementation of the SATES Phase III and Phase IV work plan will require activities on three CCT tribal allotments. This overview therefore includes a brief description of relevant federal and state law, executive orders, and tribal laws and regulations.

2.1 FEDERAL LEGISLATION AND REGULATIONS

An overview of federal legislation and regulations is provided below. There are three key laws relevant to Site RI/FS activities. The NHPA guides all federal agency actions that could affect cultural resources. Implementation of the RI/FS constitutes an "undertaking" as defined in the NHPA; therefore, complying with the NHPA requirements is the responsibility of EPA. The Archaeological Resources Protection Act (ARPA) of 1979 and the Native American Graves Protection and Repatriation Act (NAGPRA) apply to activities that could affect archaeological resources and Indian burials on federal and tribal lands. These laws and their implementing regulations would therefore apply to RI/FS activities conducted on federal and tribal lands.

2.1.1 National Historic Preservation Act of 1966, as Amended through 1992 (16 USC 470-470w)

The NHPA is the centerpiece of federal legislation protecting cultural resources. In the Act, Congress states that the federal government will "provide leadership in the preservation of the prehistoric and historic resources of the U.S.," including resources that are federally owned, administered, or controlled. For federal agencies, Sections 106 and 110 of the Act provide the foundation for how federal agencies are to manage cultural resources, but other sections provide further guidance. The implementing regulations for the NHPA are in 36 Code of Federal Regulations (CFR) Part 800. These regulations are summarized below.

Section 106

Similar to the National Environmental Policy Act of 1969 (NEPA), Section 106 of the NHPA requires federal agencies to take into account the effects of their actions or programs, specifically on historic and archaeological properties, prior to implementation. This is accomplished through consultation with the State Historic Preservation Officer (SHPO) and/or the Advisory Council on Historic Preservation (ACHP). On lands held by a tribe with a Tribal Historic Preservation Officer (THPO), the THPO has the same duties and responsibilities as the SHPO. If an undertaking on federal lands may affect properties having historic value to a federally recognized Indian tribe, such tribe shall be afforded the opportunity to participate as interested persons during the consultation process defined in

36 CFR 800. Compliance can also be accomplished using agreed-upon streamlined methods and agreement documents such as programmatic agreements.

The Section 106 process is designed to identify possible conflicts between historic preservation objectives and the proposed activity, and to resolve those conflicts in the public's interest through consultation. Neither the NHPA nor the ACHP's regulations require that all historic properties be preserved. Rather, they only require the agency proposing the undertaking to consider the effects of the proposed undertaking prior to implementation.

Failure to take into account the effects of an undertaking on historic or cultural properties can result in formal notification from the ACHP to the head of the federal agency of foreclosure of the ACHP's opportunity to comment on the undertaking pursuant to NHPA. A notice of foreclosure can be used by litigants against the federal agency in a manner that can halt or delay critical activities or programs.

The process for compliance with Section 106 consists of the following steps:

1. **Identification of Historic Properties**—Identification of historic properties located within the area of potential effects (APE) is accomplished through review of existing documentation and/or field surveys.
2. **Property Evaluation**—Evaluation of the identified historic properties using National Register criteria (36 CFR Part 63) in consultation with the SHPO and, if necessary, the ACHP. Properties that meet the criteria will be considered "Eligible" for listing in the National Register and will be subject to further review under Section 106. Properties that do not meet the criteria will be considered "Not Eligible" for listing in the National Register and will not be subject to further Section 106 review.
3. **Determination of Effect**—An assessment is made of the effects of the proposed project on properties that were determined to meet the National Register criteria, in consultation with the SHPO and, if necessary, the ACHP. One of the following effect findings will be made:
    - No Historic Properties Affected—If no historic properties are found or no effects on historic properties are found, the agency official provides appropriate documentation to the SHPO/THPO and notifies consulting parties. However, the federal agency must proceed to the assessment of adverse effects when it finds that historic properties may be affected or the SHPO/THPO or Council objects to a "No Historic Properties Affected" finding. The agency must notify all consulting parties and invite their views.

- No Historic Properties Adversely Affected—When the Criteria of Adverse Effect are applied (36 CFR 800.5(a)), and it is found that historic properties will not be adversely affected by the undertaking, the agency may make a finding of "No Historic Properties Adversely Affected." This finding is submitted to the SHPO for concurrence. Typically, the Council will not review "No Adverse Effect" determinations. However, the Council will intervene and review "No Historic Properties Adversely Affected" determinations if it deems it appropriate, or if the SHPO/THPO or another consulting party and the federal agency disagree on the finding and the agency cannot resolve the disagreement. If Indian tribes disagree with the finding, they can request the Council's review directly, but this must be done within the 30-day review period. Agencies must retain records of their findings of "No Historic Properties Adversely Affected" and make them available to the public. The public should be given access to the information when they so request, subject to Freedom of Information Act (FOIA) and other statutory limits on disclosure, including the confidentiality provisions in Section 304 of the NHPA. Failure of the agency to carry out the undertaking in accordance with the finding requires the agency official to reopen the Section 106 process and determine whether the altered course of action constitutes an adverse effect.
- Historic Properties Adversely Affected—Adverse effects occur when an undertaking may directly or indirectly alter characteristics of a historic property that qualify it for inclusion in the National Register. Reasonably foreseeable effects caused by the undertaking that may occur later in time, be farther removed in distance, or be cumulative also need to be considered. The finding of "Historic Properties Adversely Affected" is submitted to the SHPO for concurrence. The SHPO/THPO may suggest changes in a project or impose conditions so that adverse effects can be avoided and thus result in a "No Historic Properties Adversely Affected" determination.

4. **Resolution of Adverse Effects/Mitigation**—When adverse effects are found, the consultation must continue among the federal agency, SHPO/THPO, and consulting parties to attempt to resolve them. The agency official must notify the Council when adverse effects are found and should invite the Council to participate in the consultation when circumstances as outlined within 36 CFR 15 800.6(a)(1)(i)(A)-(C) exist. A consulting party may also request the Council to join the consultation.

   When resolving adverse effects without the Council, the agency official consults with the SHPO/THPO and other consulting parties to develop a Memorandum of

Agreement (MOA). The MOA will outline the steps or actions to be taken prior to implementation of the project, in order to mitigate the adverse effects on the historic property. Stipulations included in an MOA may include (but are not limited to) documentation, modification of the project to lessen the adverse effects on the property, efforts to sell or relocate the resource, or step-by-step consultation with interested parties throughout the process to ensure it is carried out according to plan.

The MOA is executed between the agency official and the SHPO/THPO and filed with required documentation with the Council. This filing is the formal conclusion of the Section 106 process and must occur before the undertaking is approved.

In some cases, streamlining of the Section 106 process can be accomplished through the use of programmatic agreements. The ACHP and the agency official may negotiate a programmatic agreement to govern the implementation of a particular program or the resolution of effects from complex projects or multiple undertakings. Programmatic agreements are particularly useful when programs or projects affecting historic properties are similar and repetitive, and have known effects, such as routine maintenance or a series of similar rehabilitation projects.

Section 101(d)(2)

This section of the NHPA provides for the assumption by federally recognized Indian tribes of all or any part of the functions of a SHPO with respect to tribal lands (e.g., all lands within the exterior boundaries of any Indian reservation and all dependent Indian communities). Section 101(d)(2) requires federal agencies, in carrying out their Section 106 responsibilities, to consult with federally recognized Indian tribes that attach religious or cultural significance to a historic property. The agency will consult with federally recognized Indian tribes in the Section 106 process to identify, evaluate, and treat historic properties that have religious or cultural importance to those groups.

Section 110

Section 110 of the NHPA is intended to ensure that historic preservation is integrated into the ongoing programs of federal agencies. This section of the Act requires agencies to identify, evaluate, and nominate for listing in the National Register, historic properties owned or controlled by the agency; use historic properties to the maximum extent feasible; ensure documentation of historic properties that are to be altered or damaged; carry out programs and projects that further the purpose of the Act; and undertake such planning and actions as may be necessary to minimize harm to any formally designated National Historic Landmark properties.

Section 111

Section 111 of the NHPA requires agency officials, to the extent practicable, to establish and implement alternatives for historic properties, including adaptive use, that are not needed for current or projected agency uses or requirements. Further, Section 111 allows the proceeds from any lease to be retained by the agency to defray the cost of administration, maintenance, repair, and related expenses of historic properties.

Section 112

Section 112 of the NHPA requires that agency officials who are responsible for protection of historic properties pursuant to the NHPA ensure that all actions taken by employees or contractors meet professional historic preservation standards established by the Secretary of the Interior (Professional Qualifications Standards of the Secretary of the Interior's Standards and Guidelines in Archaeology and Historic Preservation [NPS 1983]).

Section 304

Section 304 of the NHPA requires that information about the location, character, or ownership of a historic property be withheld from public disclosure when the federal agency head or other public official determines that disclosure may cause a significant invasion of privacy, risk and/or harm to the historic property, or impede the use of a traditional religious site by practitioners.

Comprehensive Environmental Response, Compensation and Liability Act and the National Historic Preservation Act

EPA's Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) Compliance with Other Laws Manual: Part II. Clean Air Act and Other Environmental Statutes and State Requirements (USEPA 1989) outlines how "substantive compliance" with the NHPA is to be achieved in CERCLA actions.[1] The initial step is determining if cultural resources are known or are likely to be present "in or near the area under study in the RI." This step may require conducting a survey of both the location of the proposed remedial action and any associated actions that would occur off-site. The CERCLA manual referenced above defines three stages of a survey: Stage IA, literature search and sensitivity study; Stage IB, field investigation; and Stage II, site definition and evaluation. All studies should include Stage IA but implementation of Stage IB is contingent on the results of Stage IA, and the need for Stage II is contingent on the results

[1] As stated in the June 2, 2006 Settlement Agreement (USEPA 2006), "The Parties intend that this RI/FS, while not being carried out under an administrative order or judicial order issued pursuant to the provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), will be consistent with the National Contingency Plan ('NCP'), 40 CFR Part 300."

of Stage IB. If results of the survey identify significant cultural resources (i.e., resources listed or considered eligible for listing on the National Register), effects of the proposed remedial action and associated actions to the significant resources must be evaluated. Adverse effects on significant resources must be either avoided or mitigated. Any proposed mitigation measures must be incorporated into the remedial design process.

2.1.2 Archaeological Resources Protection Act of 1979 (16 USC 470aa-470ll)

ARPA is essentially an update to the 1906 Antiquities Act. It expands and strengthens the activities prohibited under the Antiquities Act, increases the criminal penalties for violation, establishes civil penalties, and provides further guidelines for the issuance of permits. This Act continues to apply only to federal and Indian lands (the definition of "Indian lands" in ARPA differs very slightly from the definition of "tribal lands" in the NHPA). Most archaeological excavations and collection of artifacts on these lands are allowed only with an ARPA permit. Trafficking in illegally obtained archaeological resources from federal and Indian lands is also prohibited. Individuals convicted of violating the Act are liable for the value of the archaeological resource itself, and the cost of restoration or repair of the damage caused by illegal excavation or collection.

The implementing regulations are 43 CFR Part 7 (Department of the Interior), which applies to federal lands that are not within military reservations or national forests. The regulations include detailed definitions of "archaeological resource" and "Indian lands" (lands held in trust by the United States on behalf of a federally recognized tribe or individual members of a federally recognized tribe).

2.1.3 Native American Graves Protection and Repatriation Act (25 USC 3001-3013)

NAGPRA establishes that Native American human remains and associated funerary objects found on federal or tribal lands belong to the lineal descendants of the Native American. When the lineal descendants cannot be determined, the remains belong to the tribe on whose land the remains were found (when found on tribal lands), or to the Indian tribe with the "closest cultural affiliation." This latter rule also applies to unassociated funerary objects, sacred objects, and objects of cultural patrimony (all defined in the Act); NAGPRA applies to both human remains intentionally excavated (which would require an ARPA permit) and those accidentally discovered.

NAGPRA also requires all federal agencies and museums to inventory their holdings of Native American human remains and funerary objects. Once the inventories are completed, the agencies and museums are to notify the appropriate tribes of the remains and other

objects in their collections. The remains and associated funerary objects are to be returned (repatriated) at the request of the lineal descendant(s) or tribe. The same requirement applies to unassociated funerary objects, sacred objects, and objects of cultural patrimony for which a cultural affiliation can be demonstrated. Exceptions to the repatriation requirement are objects that are "indispensable for completion of a specific scientific study, the outcome of which would be of major benefit to the U.S."

The implementing regulations are 43 CFR Part 10, which largely expand on the elements of the statute. The regulations detail: 1) the process of consultation with Indian tribes to address either intentional excavation of human remains or inadvertent discovery of human remains; 2) how agencies and museums are to inventory their collections; and 3) the repatriation process. When human remains, funerary objects, sacred objects, and objects of cultural patrimony are inadvertently discovered on federal lands, the following steps are to be followed: 1) ongoing activity in the area of the find must cease and a reasonable effort made to protect the find; and 2) the federal land agency (i.e., the federal agency on whose lands the remains or objects have been found) must be immediately notified by telephone, with written confirmation. The federal land agency must then notify the appropriate tribe(s) and further secure and protect the discovery. The activity may be halted for up to days while an appropriate response to the find is negotiated by the federal agency and the appropriate tribe(s).

2.1.4 American Indian Religious Freedom Act (42 USC 1996)

This Act states that it is the policy of the United States to protect and preserve the rights of American Indians to practice traditional religions. That policy includes rights of access to sacred sites and to the use and possession of sacred objects. There are no implementing regulations.

2.2 PRESIDENTIAL EXECUTIVE ORDERS

Presidential executive orders define policies and procedures for federal agencies to facilitate their execution of laws passed by the Congress or clarify how specific laws are to be implemented. Presidential executive orders can be considered instructions or directives from the President to federal agencies on how to carry out specific laws. The executive orders listed below are either directly related to cultural resources or define relationships between federal agencies and tribes.

2.2.1 Executive Order 11593. Protection and Enhancement of the Cultural Environment

Issued in 1971, Executive Order 11593 states that the federal government would provide leadership in "preserving, restoring, and maintaining the historic and cultural environment of the Nation." Federal agencies were directed to inventory cultural resources under their jurisdiction and nominate National Register-eligible properties to the National Register. Properties that have been determined eligible are not to be transferred, sold, demolished, or altered without providing the ACHP on Historic Preservation with an opportunity to comment. Properties to be demolished or substantially altered were to be documented prior to demolition or alteration. National Register properties or National Register-eligible properties under federal control were to be maintained following standards set by the Secretary of the Interior. Executive Order 11593 also assigns specific responsibilities to the Secretary of the Interior, including managing the National Register and assisting and advising other federal agencies in the management of cultural resources.

2.2.2 Executive Order 13007. Indian Sacred Sites

Issued in 1996, Executive Order 13007 directs federal agencies to provide access and ceremonial use of Indian sacred sites, where practicable, legal, and not inconsistent with essential agency functions. Agencies are also directed to avoid adversely affecting sacred sites and maintain the confidentiality of such sites. A "sacred site" as defined by this executive order is a specific location that is sacred because of its religious significance to or ceremonial use in an Indian religion.

2.2.3 Executive Order 13175. Consultation and Coordination with Indian Tribal Governments

Issued in 2000, Executive Order 13175 directs federal agencies to consult with tribal officials in the development of policies and regulations that have "tribal implications" or that preempt tribal law. Executive Order 13175 also emphasizes the importance of government-to-government relationships between the United States government and tribes. Agencies must designate an official responsible for implementing the executive order and must document tribal consultation in the development of the relevant policies and regulations.

2.3 TRIBAL LEGISLATION AND REGULATIONS

Tribal laws and regulations addressing cultural resources would apply to lands on the reservations and off-reservation trust lands. The SATES program field activities are being carried out entirely on Colville Tribal allotment lands, therefore the CCT is the tribe whose laws and regulations would be potentially applicable to the Site. The legal code of the CCT

addresses cultural resources, as summarized below. This code applies to both on-reservation actions and off-reservation actions by federal agencies that could affect cultural resources. The CCT has a THPO that has the same authority and responsibilities as the SHPO.

2.3.1 Confederated Tribes of the Colville Reservation. Colville Tribal Law and Order Code Chapter 4-4, Cultural Resources Protection

This Colville Tribal Code establishes the Colville Cultural Resources Board, which has the responsibility of developing policies and procedures to protect cultural resources of interest and concern to the Colville Tribes, both on and off the Colville Reservation. The Board reviews proposed federal agency actions off the reservation and is responsible for reviewing all proposed on-reservation actions that could affect significant cultural resources. The code also establishes a Colville Register of Historic and Archaeological Properties for listing of historic properties on the Colville Reservation.

This code defines the roles and responsibilities of the Colville History and Archaeology Department, which include identifying significant cultural resources on the reservation, nominating properties to the National Register and the Colville Register, and promoting efforts to protect cultural resources on the reservation.

Chapter 4-4 of Colville Tribal Code prohibits the excavation, disturbance, or other adverse effects to archaeological resources and historic properties on the reservation without a permit issued by the History and Archaeology Department. The code defines the procedure for the issuance of permits and the duties of permittees.

2.4 STATE LEGISLATION AND REGULATIONS

Washington state laws and regulations regarding archaeological and historical resources, as well as the law protecting Indian graves, are not applicable on federal lands or on tribal trust lands. These laws would apply, however, to any RI/FS-related activities that would affect private lands, non-federal lands, or non-tribal public lands.

2.4.1 Revised Code of Washington (RCW) Chapter 27.44, Indian Graves and Records

This legislation prohibits the removal or other disturbance of Indian burials, cairns, and "glyptic or painted records." "Burials" and "graves" are not defined in the statute. Excavation or removal of burials is permitted only under provisions of a permit issued by the Washington Department of Archaeology and Historic Preservation. Procedures for obtaining permits are defined in Washington Administrative Code (WAC) Chapter 25-48.

2.4.2 RCW Chapter 27.53, Archaeological Sites and Resources

This legislation prohibits the excavation or disturbance of archaeological sites on public and private lands in Washington except under provisions of a permit issued by the Washington Department of Archaeology and Historic Preservation. Procedures for obtaining permits are defined in WAC Chapter 25-48.

2.4.3 RCW Chapter 68.60, Abandoned and Historic Cemeteries and Historic Graves

This legislation prohibits the destruction, alteration, or other disturbance of historical land, abandoned cemeteries, and historic graves (Indian graves and burials are protected in RCW Chapter 27.44). A historic cemetery is defined in the statute as one established before November 1889. A historic grave is a grave or graves outside of a cemetery placed prior to June 1990.

2.4.4 RCW Chapter 43.21C, State Environmental Policy Act

This legislation directs state and local agencies in Washington to address environmental impacts of proposed projects. The implementing rules (WAC Chapter 197-11) require that impacts on historic and cultural resources are to be addressed in the State Environmental Policy Act process.

3 PROPOSED SAMPLING PROGRAM

Figure A -1 shows the locations of the Colville Tribal allotments where the field-scale testing will be performed, and Figures A-2 through A-4 show the test plot locations where the work described in the Phase III and Phase IV Work Plan will be carried out. A detailed description of sampling techniques is provided in the Phase III and Phase IV Work Plan. As indicated in the Work Plan, the soil treatment amendments selected for field-scale testing will be applied to the soil surface within each of the four test plots that were previously selected for field testing portion of the SATES program. To monitor the effects of the amendments applied to the soil, soil sampling will occur two to three times yearly and will involve collecting samples from the top 3 in. of surficial soil on the four test plots, located on the tribal allotments using decontaminated sampling tools. The same test plots will be sampled during each Phase IV monitoring event, although the sample locations will be shifted a few inches to avoid resampling a location that was previously sampled.

Most of the soil samples will be collected from within the test plot boundaries using the incremental composite (IC) sampling method within a predefined sampling grid. IC sampling entails the collection of multiple individual volumes of soil (increments) from a target area, which for the purpose of this sampling method is defined as a decision unit. The IC soil sampling will be conducted in accordance with guidance developed by the Interstate Technology and Regulatory Council (ITRC 2012). The increments collected from the test plots will be composited and subsampled by the analytical laboratory according to a detailed standard operating procedure prior to laboratory analysis. IC sampling is planned for all sampling events planned to occur starting in 2020 and ending in late 2023. One round of discrete core sample collection will be conducted at each of the test plots from the upper part of the soil profile toward the end of the field study, likely in late 2023. The discrete sampling plan and specifications will be prepared in advance of that work.

For the IC sampling method, all of the soil increments will be collected using a 2- to 3-in.-diameter cylindrical sampling instrument, to collect a small core from the top 0 to 3 in. of soil. Each increment should contain a proportionate amount of soil particles over the sampled depth, with an equal volume of soil particles contained in the top and bottom portions of the sample. A total of 30 increments will be collected to comprise one IC sample. Each increment will undergo a visual inspection by the cultural monitor. If no cultural resources are identified, it will be placed in a sample container with the other increments collected for an IC sample.

4 COORDINATION PLAN

The objective of the CRCP is to ensure that implementation of the SATES field activities does not adversely affect any cultural resources. The plan therefore defines a general process and more specific procedures to meet this objective.

Few of the surveys conducted prior to about 1975 are likely to have met current regulatory and professional standards. In addition, many of the previous surveys focused on archaeological resources to the exclusion of other types of cultural resources (and older archaeological surveys documented only evidence of prehistoric use or occupation). Finally, it is likely that there are some locations previously surveyed at which burials or buried archaeological resources are present but not evident and therefore not recorded at the time of the survey (many surveys both in the past and in the present rely entirely or primarily on surface evidence of archaeological resources or burials).

This plan therefore defines procedures that address sampling at known locations of cultural resources and locations where no cultural resources are currently recorded. EPA is the lead federal agency for cultural resources coordination for the Site. The SATES field work will be conducted entirely on Colville Tribal allotments. Therefore, any issues or concerns related to cultural resources during the planning or implementation of Site work shall be brought to the attention of EPA for consultation with the CCT, as appropriate.

4.1 GENERAL CONSULTATION FRAMEWORK

Successful implementation of the SATES program and of this CRCP, given the issues defined above, will require ongoing consultation and coordination with the CCT. Other consulting parties (STI and the Washington State Department of Archeology and Historic Preservation [DAHP]) may be recognized in the future whose participation would be important for general consultation or coordination in the SATES process or for specific sampling locations. For the purposes of cultural resources coordination activities, the "consulting parties" referred to in this plan are distinguished from other "participating parties" to the SATES and RI/FS processes.

4.2 CULTURAL RESOURCE PROCEDURES IN THE SAMPLING PROCESS

This section defines general procedures to be followed in the sampling process to minimize the potential for inadvertent disturbance of cultural resources. More specific protocols to respond to discoveries are defined in the following sections.

As each of the SATES test plots are on Colville Tribal allotments, a tribal cultural resources (archeological) monitor and tribal representative will be present on site to monitor sampling. The protocol for this monitoring is defined below.

4.2.1 Archaeological Monitoring

To ensure compliance with the NHPA and the applicable requirements, procedures, and standards of the CCT, the following procedures have been developed to address potential discoveries, including inadvertent discoveries, of cultural materials and deposits (including sacred objects, funerary objects, and objects of cultural patrimony as defined in NAGPRA) and Indian burials and human remains (as defined in NAGPRA) during sediment and soil sampling and associated activity that could result in ground disturbance.

Archaeologist and/or Tribal Representative Cultural Monitor On Site

An archaeological monitor and/or tribal representative will be present on site when ground-disturbing sampling or sampling-related activity occurs. The archaeological monitor will visually examine all samples to determine if evident or likely artifacts are present or if other deposits are present that are likely to be cultural in origin. The archaeological monitor will not make physical contact with the sample unless artifacts or other cultural deposits are present. If artifacts or likely archaeological deposits are present, the archaeologist or tribal representative will record the location of the materials and photograph the materials in place in such a manner to provide information on provenience. The artifacts and other archaeological materials will then be re-deposited at their original location.

The archaeological monitor and/or tribal representative will document their observations on a daily basis, including field notes and photographs that record the location and character of the sampling or other ground-disturbing activity, any archaeological discoveries made, and any decisions made within the provisions of this plan by the archaeological monitor and tribal representative in response to any archaeological discoveries. A standardized archaeological monitoring form may be substituted for the field notes referenced above.

All archaeological monitors and tribal representatives present on site will be required to have read the applicable health and safety plan and to have complete understanding of the archaeological monitoring provisions of this plan. The archaeological monitors and tribal representatives will also be required to meet requirements for personal protective equipment. In addition, all on-site personnel are subject to the directions of the task field supervisor at all times.

Discoveries—Archaeological Monitors Present

At the discretion of the archaeological monitor or tribal representative, ground-disturbing sampling or other associated activity may be slowed or halted at any time that a suspected archaeological object or archaeological resource is encountered. The objective of slowing or halting of ground-disturbing activity is to allow the archaeologist or tribal representative to confirm and/or make a preliminary assessment of the discovery. At the discretion of the archaeological monitor or tribal representative, a specific sample may be relocated from the location of the discovery but at the sampling location. Such relocation will be coordinated with the on-site task field supervisor.

At the request of the archaeological monitor or tribal representative, sampling personnel will either:

- Assist in securing access to the location of the discovery and take appropriate measures to protect the location of the discovery from rain, storm water, and other possible disturbances, or
- Assist in moving the artifacts to a protected and secure area of the site away from the immediate sampling area. Removal of artifacts from the discovery location will be undertaken only if leaving the artifacts in place would jeopardize their integrity due to erosion or collection by unauthorized individuals.

The archaeological monitor, tribal representative, or a member of the Teck American Incorporated (TAI) field sampling team will remain at the site to ensure the security of the find until more extensive efforts can be made to secure the site from further disturbance or a more extensive evaluation and documentation of the discovery can be made.

Notification of any archaeological discoveries must be provided to EPA for further coordination with consulting parties within 24 hours of the discovery. EPA contact information is provided in Attachment D1. All telephone notification of discoveries must be promptly followed by notification in writing (via email or conventional mail).

Discovery of Human Remains

Native peoples in the UCR Study Area consider the graves of their ancestors to be important in both their cultural identity and in defining their relationship with the land. These graves are therefore considered sacred and should be left undisturbed. Should inadvertent disturbance occur, the remains and associated materials ("funerary objects") must be treated with respect and honor. All appropriate federal, tribal, and state laws, regulations, and procedures regarding burials should be rigorously enforced. If likely or confirmed human remains are encountered, all further sampling or other ground-disturbing activity will cease immediately.

Upon such discovery, the TAI task field supervisor team and/or CCT cultural monitor will notify EPA for further coordination with consulting parties (consisting minimally of the STI, and the DAHP). Additionally, the field sampling team will assist the archaeological monitor and tribal representative in securing the location of the discovery.

If no archaeological monitor or tribal representative is present, the TAI field sampling team will secure the location of the discovery in such a manner that both maintains the physical integrity of the remains and any associated objects and precludes further disturbance, or a member of the TAI field sampling team will remain on-site until an archaeologist or tribal representative can arrive to assess the find.

Other conditions for responses to discoveries of archaeological materials may be defined in the permit(s) issued for the sampling program. Responses to any discoveries of burials must comply with provisions of NAGPRA and its implementing regulations (in addition to those referenced above), as well as the existing protocols of the CCT. These protocols are provided in Attachment D2.

4.2.2 Curation

Artifacts and other cultural materials that may be recovered during the sampling program (with the exception of human remains and associated items subject to NAGPRA) will be curated at a facility that meets the standards of 36 CFR 79. The appropriate tribe will designate the curation facility for cultural materials recovered from tribal lands.

4.2.3 Reporting

Within 150 days of completion of each sampling activity that is covered under the Phase III and Phase IV Work Plan, the CCT archaeologist will prepare a confidential written report (refer to Section 4.3, Confidentiality) that presents the results of the archaeological monitoring and responses to any discoveries of archaeological resources or burials. This report will include: 1) copies of field notes, descriptions, and maps of all locations at which sampling-related archaeological monitoring was conducted; 2) descriptions of any discoveries made during such monitoring and the outcome of the discoveries (including the rationale for the decisions for the disposition of any finds); 3) descriptions and maps of all non-monitored locations at which inadvertent discoveries were made and the outcome of those discoveries; and 4) recommendations for any changes in the monitoring protocol or coordination plan that may be appropriate to address results of the monitoring or how well existing coordination procedures worked.

The draft report will be provided to EPA for review.

4.3 CONFIDENTIALITY

TAI shall make its best efforts, in accordance with state and federal law, to ensure that its employees and contractors keep the discovery of any found or suspected human remains, other cultural items, and potential historic properties confidential. Pertinent TAI employees and contractors will be required to read and sign a confidentiality statement that specifies procedures to be followed in response to media and public contacts regarding archaeological and other cultural resources. To the extent permitted by law, prior to any release of information, EPA, TAI, and the other consulting parties shall concur on the amount of information, if any, to be released to the public, any third party, and the media and the procedures for such a release.

5 REFERENCES

Goodal, N.B., W.C. Prentiss, and I. Krujit. 2004. "Cultural complexity: a new chronology of the Upper Columbia drainage." In: *Complex Hunter-Gatherers: Evolution and Organization of Prehistoric Communities on the Plateau of Northwestern North America*, edited by William C. Prentiss and Ian Krujit. Pp. 36-48. University of Utah

ITRC. 2012. Technical and regulatory guidance: incremental sampling methodology. Prepared by the Interstate Technology and Regulatory Council, Washington, DC. 475 pp. Available at: http://www.itrcweb.org/gd.asp.

Kennedy, D.I.D., and R.T. Bouchard. 1998. "1998 Northern Okanagan, Lakes and Colville." In: *Handbook of North American Indians*, Vol. 12, W.C. Sturtevant, general editor. Smithsonian Institution, Washington, DC.

McKay, K.L., and N.F. Renk. 2002. Currents and under currents: an administrative history of Lake Roosevelt National Recreation Area.

NPS. 1983 (with updates). Archeology and historic preservation: secretary of the interior's standards and guidelines (as amended and annotated). National Park Service, U.S. Department of Interior. Available at: http://www.nps.gov/history/local-law/arch_stnds_9.htm.

Ramboll. 2020. Work Plan for the Soil Amendment Technology Evaluation Study, Phase III & Phase IV Work Plan: Test Plot Field-scale Implementation & Test Plot Monitoring. Prepared for Teck American Incorporated. Draft August 2020.

USEPA. 1989. CERCLA compliance with other laws manual: Part II. Clean Air Act and other environmental statutes and state requirements. U.S. Environmental Protection Agency, Region 10, Seattle, WA.

USEPA. 2006. Settlement agreement for implementation of remedial investigation and feasibility study at the Upper Columbia River Site. June 2, 2006. U.S. Environmental Protection Agency, Region 10, Seattle, WA.

6 GLOSSARY OF TERMS

Burial—A burial is defined in NAGPRA as "[a]ny natural or prepared physical location, whether originally below, on, or above the surface of the earth, into which as part of the death rite or ceremony of a culture, individual human remains are deposited."

Curation—Long-term storage and preservation of archaeological collections. Archaeological collections from federal lands must be curated at facilities that meet the standards of 36 CFR 79.

Ethnohistoric—Information on Native peoples gathered from historical accounts.

Historic, historic-period, historical—The NHPA uses the term "historic" to refer to properties that are listed or have been determined eligible for listing on the National Register of Historic Places. To avoid confusion with this definition of "historic," "historic-period" or "historical" are used to reference resources, places, events, and people associated with the period since the appearance of Euroamericans and the beginning of written accounts (ca. 1780–1810 in the Pacific Northwest).

Protohistoric—The period of time transitional from prehistory to history. In the Pacific Northwest, the protohistoric can be generally defined as from the late 1600s until late 1700s.

FIGURES

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Figure A-1
Location of Decision Units with SATES Test Plots
Upper Columbia River SATES Program

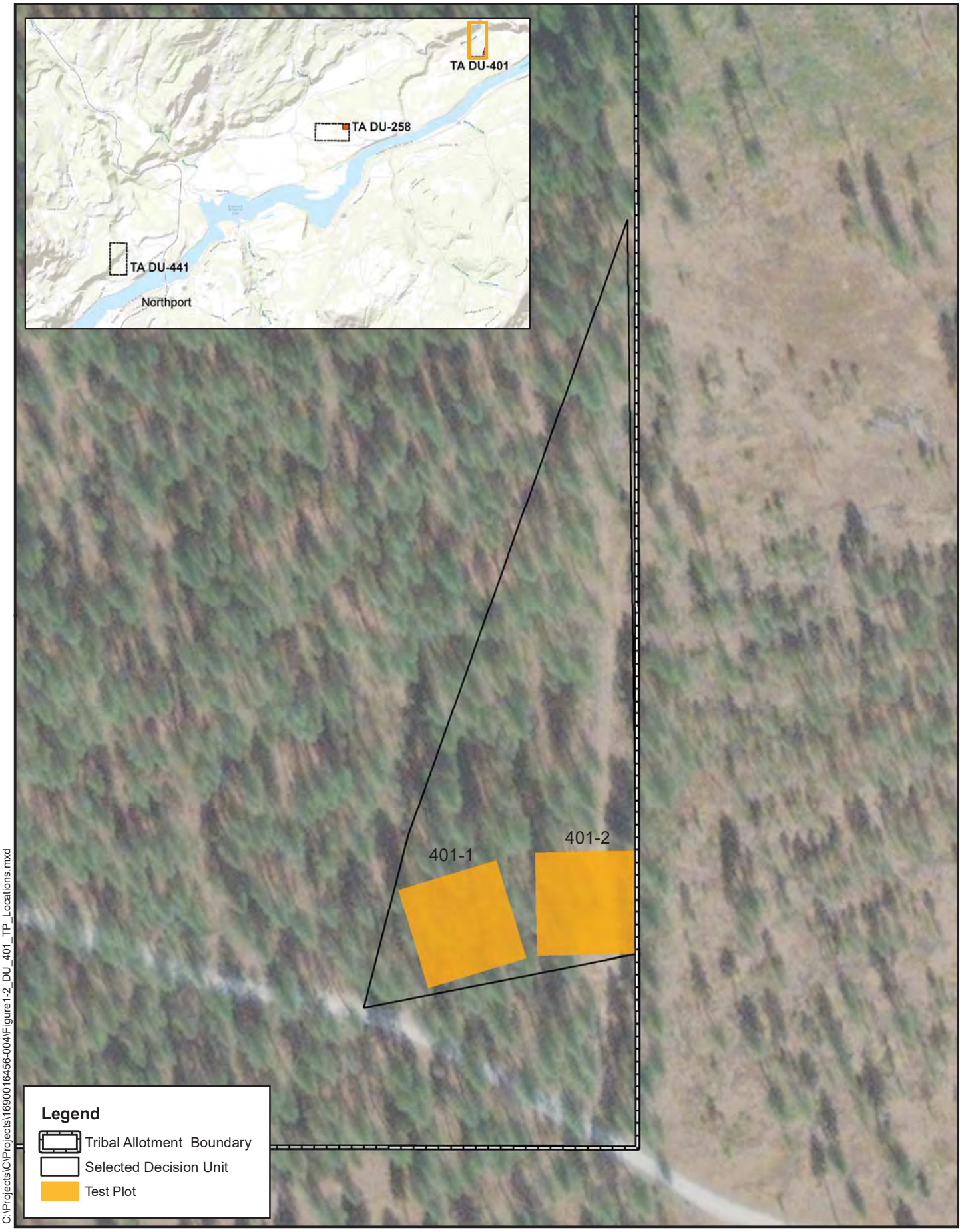

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Figure A-2
Test Plot Locations - Decision Unit 401
Upper Columbia River SATES Program

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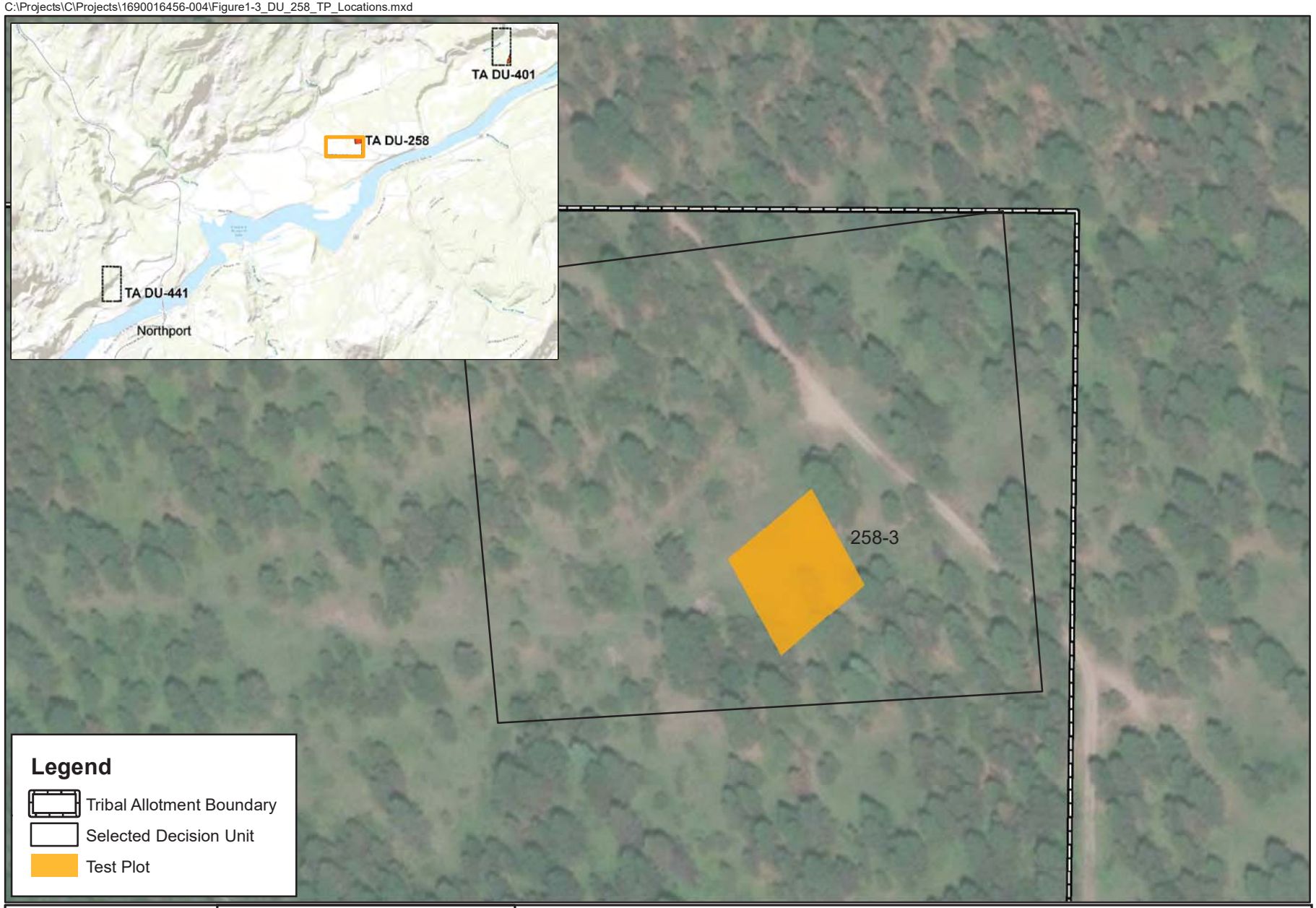

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Figure A-3
Test Plot Location - Decision Unit 258
Upper Columbia River SATES Program

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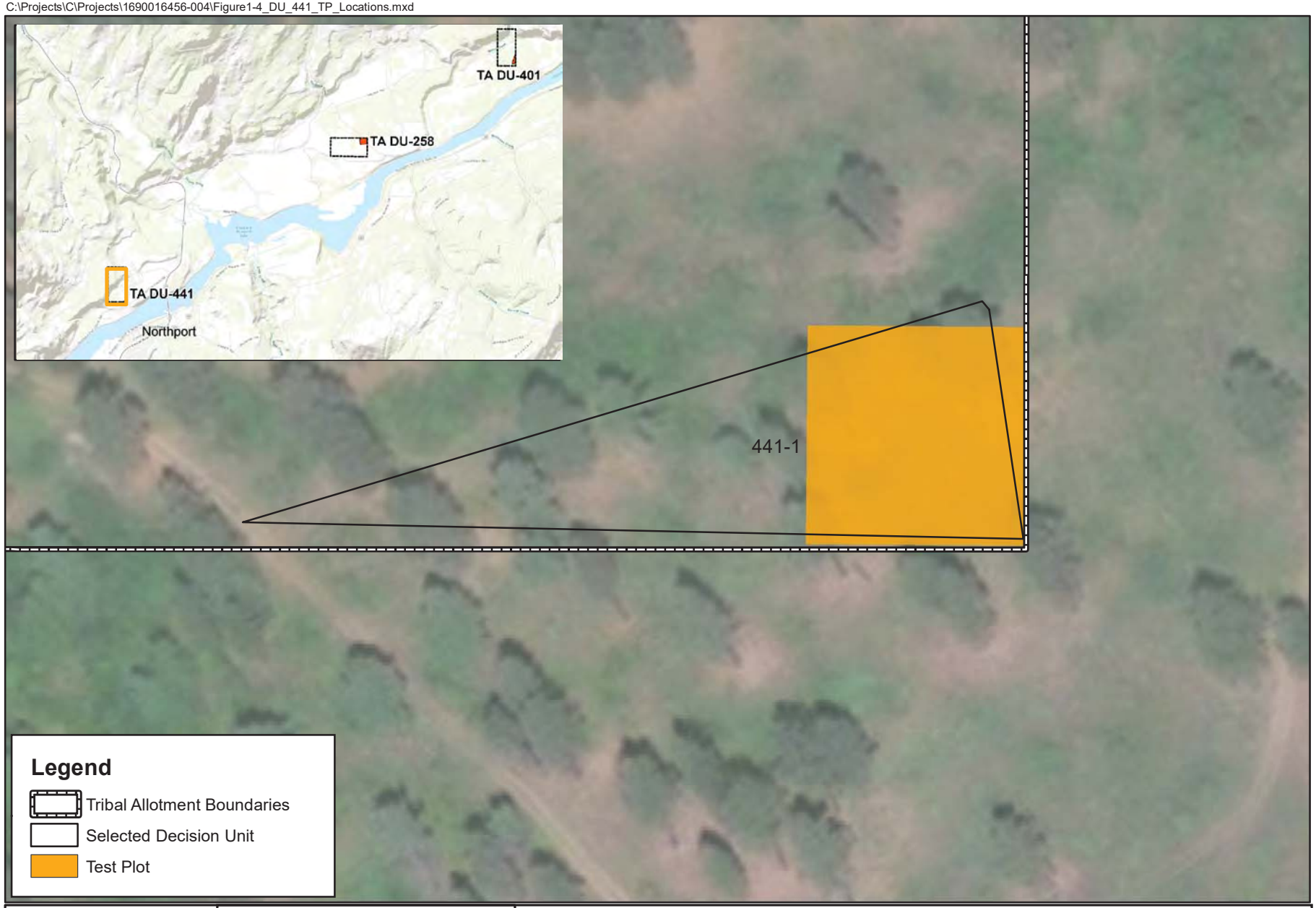

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Figure A-4
Test Plot Location - Decision Unit 441
Upper Columbia River SATES Program

ATTACHMENT A1

EPA CONTACT INFORMATION

EPA CONTACT INFORMATION

Robert Tan is the primary contact for the EPA for implementation of the Cultural Resource Coordination Plan. Mr. Tan's telephone number is (206) 553-2580 (office) and his email address is Tan.Robert@epa.gov. Mr. Tan will have a cell phone number that will be provided to the SATES Phase III implementation and Phase IV field sampling team(s), tribes, and state of Washington, before each Phase III and Phase IV field event begin.

If Mr. Tan cannot be reached, the Kathryn Cerise is the alternate EPA contact. Ms. Cerise's phone number is (206) 553-2589 (office), and email can be sent to cerise.kathryn@epa.gov.

If Mr. Tan or Ms. Cerise cannot be reached, then Kira Lynch is the alternate EPA contact at (206) 553-2144 (office) and at lynch.kira@epa.gov.

ATTACHMENT A2

PROTOCOLS FOR INADVERTENT DISCOVERIES

Federal Columbia River Power System (FCRPS)
Grand Coulee Dam Project
and Lake Roosevelt National Recreation Area
Inadvertent Discovery of Human Remains Protocol

Treatment of Human Remains Found on Federal or Tribal Lands

This protocol covers human remains and/or other cultural objects that are subject to the Native American Graves Protection and Repatriation Act (NAGPRA) that are discovered inadvertently on Federal or tribal lands after November 16, 1990. In this document, Federal lands are defined as: within the boundaries of lands managed by the National Park Service (NPS), Bureau of Reclamation (Reclamation), the Confederated Tribes of the Colville Reservation (CCT), or the Spokane Tribe of Indians (STI). If remains that are potentially human or other NAGPRA items are encountered, any activity in the vicinity of the discovery will cease. All reasonable efforts will be made to protect the remains and any associated cultural items.

1. Secure the area and take protective measures to assure that the remains are not in danger of further depredation or disturbance. The burial or location will not be disturbed. All human remains and associated artifacts will be treated in a respectful manner.
2. In cases where a potential crime scene exists, *personnel except those necessary to protect the location will leave the immediate vicinity in order to prevent unintentional destruction of crime scene information.* The appropriate law enforcement office (Tribal within the boundaries of the Reservation Zone, NPS within the boundaries of the Recreation Zone, and Reclamation within the boundaries of the Reclamation Zone) will be immediately notified, however, site specific information should not be included in radio transmissions to maintain site security.
3. The Tribal Historic Preservation Officer (THPO) (CCT or STI), if applicable, and the archaeologists working for the appropriate tribe or agency will also be contacted immediately after law enforcement (contact phone numbers are provided below). For NAGPRA discoveries associated with the Lake Roosevelt shoreline, Reclamation's Grand Coulee Power Office (GCPO) Archaeologist will be notified. For inadvertent discoveries in the Reservation Zone, the NPS archaeologist does not need to be contacted. Live phone contact is required; backup staff is identified if the primary contacts are unavailable. Phone contact will be followed up by written confirmation, e-mail is acceptable. E-mail should not include detailed (site specific information) for security reasons.

4. Law enforcement, in consultation with a professional archaeologist (if needed), trained in human osteology, will determine if the remains are human, whether it is of recent origin, and if it is part of a crime scene. These initial investigations conducted by law enforcement will be conducted carefully and with a mind toward minimizing damage to potential human remains and burial features
5. A professional archaeologist will also assist law enforcement in determining if the human remains are archaeological in origin and if they should be classified as NAGPRA items. If they are determined to be NAGPRA items yet there is an ARPA-related crime scene (i.e., there is evidence for intentional disturbance or looting of archaeological materials), the archaeologist will assist law enforcement as needed in the collection of archeological data to support the ARPA case. In order to document the crime scene, law enforcement officers and assisting archaeologists may take photographs of human remains and collect other relevant evidence.
6. If law enforcement determines that the find is human and not of law enforcement concern, they will release the site to the appropriate federal or tribal archaeologist. It is then the responsibility of that archaeologist to contact the appropriate Tribal representatives and the Reclamation archaeologist if contact has yet to be made about the Inadvertent Discovery. Live phone contact is required; backup staff are identified if the primary contacts are unavailable. Phone contact will be followed up by written confirmation.
7. As soon as the remains have been determined to be human, then efforts will be made in the field to determine whether they are Native American. The basis of this determination will be documented in writing. If the items are determined to be Native American, go to Item 10. All NAGPRA procedures and protocols for Inadvertent Discoveries on Federal Lands After November 16, 1990 will be followed.
8. If the remains are determined **not** to be Native American, then Washington State burial laws apply and will be followed (Title 68, Chapter 68.50 RCW HUMAN REMAINS).
9. If the NAGPRA items' affiliation cannot be determined in the field, further non-destructive analysis of human NAGPRA items and/or associated cultural materials may be required. The CCT or the STI, the NPS, and Reclamation will coordinate regarding the types of non-destructive analysis to be conducted.
10. On lands managed by the Tribes, NPS, or Reclamation, it will be assumed that the human remains fall under the coverage of ARPA. No further investigations by non-agency or non-tribal personnel will be conducted until an ARPA permit is in place. For the purposes of advancing the process, and out of caution and respect for the concerns of local tribes, it will be assumed that the remains are

Native American and affiliated with the local tribes. A Written Plan of Action will be prepared in consultation with the affected tribe. Provenience information will be collected as specified by the Written Plan of Action and ARPA permit, if applicable. The Reclamation contract language for burials recovered in the shoreline of the National Recreation Area will also apply and should agree with the Written Plan of Action and these protocols.

11. Recording of provenience may include any or all of the following: documenting the location of the burial or scattered NAGPRA items and general site conditions on a site form or on an addendum to an existing form; describing the surface-visible NAGPRA items to the degree that can be accomplished without causing additional disturbance to the grave; documenting the location of the burial on a USGS 7.5' topographic sheet and with a GPS unit (following the methods shown in Appendix C).
12. If it is possible to rebury or cap the NAGPRA items in place, then that decision will be documented in the Written Plan of Action in agreement with the Tribes.
13. If NAGPRA items must be excavated or removed, procedures will be specified by the Written Plan of Action. The Reclamation contract language for burials recovered in the shoreline of the NRA will also apply and will agree with the Written Plan of Action and these protocols. If NAGPRA items are to be excavated or removed by personnel other than those employed by the CCT, the STI, or the US government, an ARPA permit will be required from the NPS or Reclamation. The Written Plans of Action for individual discoveries will detail exact procedures for further implementation of NAGPRA.
14. NAGPRA items will be removed using standard professional archaeological practices in compliance with the ARPA permit issued for the removal, if applicable, and in a culturally sensitive manner at the direction of a Tribal representative. Because each burial is unique and recoveries need to be suited to different situations (e.g., position of the burial on the landform, weather, fluctuating reservoir levels). If work is contracted beyond the reservoir group, the Contractor will brief the appropriate federal and/or tribal archaeologist about their plan for the recovery and seek their concurrence. Because of the sensitivity of the local tribes regarding photographs of human remains, no such photographs will be taken. The only possible exception would be a photograph used for initial identification of remains as human versus non-human. Instead, those removing the remains will create a sketch showing the position of the human remains in the burial feature. After excavations have been completed, a photograph will be taken showing the stratigraphic position of the burial feature so that its association to other potential cultural features is documented.

15. Inadvertent discoveries that result from activities requiring easements or other non-ARPA permits (such as access, construction, etc.) will be dealt with by the permitting agencies, which may be Reclamation or the NPS. This protocol document will be included with documents issued to permittees.

16. Inadvertent discoveries have to be protected. This is primarily the job of the enforcement officers with jurisdiction with the various Lake Roosevelt zones. Additional assistance may be provided as follows: if the find occurred on the Mainstem then the CCT will assist to maintain a presence at the location of the discovery as needed until all contacts have been made and appropriate treatment of the NAGPRA items has been conducted. If the find occurs on the Spokane Arm, the STI will fill this role (see below for the STI contact).

17. Contact Information

    a. Guy Moura, CCT THPO and Program Manager of the CCT History/Archaeology Program, is the primary contact for the CCT. Mr. Moura's phone number is (509) 634-2695, FAX (509) 634-2694, and the internet address is guy.moura@colvilletribes.com. After work hours, Mr. Moura can generally be reached at (509) 633-8361 (home) or (509) 631-1705 (cell). If Mr. Moura cannot be reached, then Brent Martinez is the alternate contact: phone (509) 634-2648 (work) or (509) 631-1177 (cell); email brent.martinez@colvilletribes.com . Additional contacts include Brenda Covington 634-2699 and Jackie Cook 634-2635.

    b. Randy Abrahamson, STI THPO, is the primary contact for the STI. Mr. Abrahamson's phone number at the Department is (509) 258-4315, FAX (509) 258-6965, and his e-mail address is randya@spokanetribe.com. After work hours, Mr. Abrahamson can generally be reached at (509) 951-0524 (cell). If Mr. Abrahamson cannot be reached, Mr. John Matt shall be contacted at (509) 258-4060 (work), (509) 258-8945 (home), or (509) 993-1921 (cell).

    c. Justin Eichelberger, Park Archeologist for the Lake Roosevelt National Recreation Area, is the primary contact for the NPS. Mr. Justin Eichelberger's phone number is (509) 738-6266, ext. 114, FAX (509) 633-3862, and internet address is justin_eichelberger@nps.gov." The NPS will issue an ARPA permit for burial recoveries in the Recreation Zone. If Mr. Eichelberger cannot be contacted in person, the District Ranger can be contacted at (509) 738-6266, ext. 109.

    d. Derek Beery, Grand Coulee Power Office Archaeologist, is Reclamation's primary contact for NAGPRA on Lake Roosevelt. His phone number is (509) 633-9233, and internet address is dbeery@usbr.gov. His work cell phone is (509) 237-4477 and his home phone is (360) 477-5058. If Mr. Beery is not available, then Dr. Sean Hess, Regional Archaeologist, is Reclamation's

alternate contact. His phone number is (208) 378-5316, Cell (509) 631-0581, and internet address is "shess@pn.usbr.gov." In the event that neither Mr. Beery nor Dr. Hess is available, Reclamation's Contracting Officer will be contacted directly at (208) 378-5364.

e. Gregory Anderson, FCRPS Cultural Resource Project Manager/Archaeologist, is the primary contact for Bonneville Power Administration. Mr. Anderson's phone number is are: (503) 230-4721, gmanderson@bpa.gov.

Upon completion of the above steps, the appropriate land manager, or its consultant, will prepare a written report of the discovery. The report will include a description of the contents of the discovery, a summary of consultation, and a description of the treatment or mitigation measures. The DAHP and THPO will have 30 days to review and submit comments on the report. The appropriate land manager will then revise the document and file final copies with the appropriate THPO and DAHP if the find occurred outside either reservation.

Treatment of Human Remains Found on Private or State Lands under Washington Law

In the event that human remains are encountered during construction, maintenance, or operation of the Project on private or state lands, the following procedures are to be followed to ensure compliance with RCW 68.60: *Abandoned and Historic Cemeteries and Historic Graves*, and RCW 27.44: *Indian Graves and Records*.

1. Pursuant to RCW 68.60.(050), if a member of the project work force or an archaeologist believes that he/she has encountered human skeletal remains, he/she must immediately stop work and inform the Construction Supervisor or site manager, if applicable. The Construction Supervisor will be responsible for stopping all excavation work adjacent to the discovery in an area large enough to provide for the security and integrity of the remains. The Construction Supervisor will be responsible for taking appropriate steps to protect the remains by installing a physical barrier (i.e., exclusionary fencing) and prohibiting machinery, other vehicles, and unauthorized individuals from coming within at least 100 ft (30 meters) of the discovery site.
2. The Construction Supervisor or other project staff will promptly contact the appropriate local law enforcement, County Coroner, and the landowner. The remains should not be touched, moved, or further disturbed, and will remain secured until law enforcement arrives. They will also notify law enforcement that the treatment of all Native American human remains and associated objects should be respectful and confidential, until the origin of the remains can be determined.

3. The County Coroner will assume jurisdiction over the human skeletal remains and make a determination of whether the remains are forensic or non-forensic. If the Coroner determines the remains are non-forensic, he/she will report that determination to the DAHP who will then take jurisdiction over the remains and report the discovery to the appropriate County cemeteries and affected Indian tribes. The State Physical Anthropologist will determine whether the remains are Native American or non-Native American and will report that finding to the appropriate parties. The State Physical Anthropologist will also establish an appropriate buffer zone around the discovery site within which no work may proceed while investigations proceed. The DAHP will then handle all consultation with the appropriate Indian tribes and parties as to the preservation, excavation, and disposition of the remains.
4. If the human remains are Indian, all subsequent proceedings, including any visits to the discovery site by affected tribes that have been authorized by the DAHP, will be conducted with dignity and respect by all employees and contractors. The State Physical Anthropologist will assess whether a buffer zone larger than 100 ft (30 meters) is needed to accommodate any excavation work, tribal visits or ceremonies, etc.
5. Construction activities will not resume within the established buffer zone of the discovery site until authorized disposition of the human remains has been completed and permission from the appropriate authority to resume work in the buffer zone has been received. In the case of Indian human remains, written permission to resume work must be obtained from the DAHP.

APPENDIX B

STANDARD OPERATING PROCEDURES FOR FIELD OPERATIONS

STANDARD OPERATING PROCEDURE SOP-1

AMENDMENT PLACEMENT AND VERIFICATION

Scope and Applicability

This standard operating procedure (SOP) presents the general information used for amendment placement on the subplots designated for field-scale soil treatability testing.

Equipment and Materials

- Amendment materials
- Equipment for applying and spreading amendment on subplots
- Equipment or materials necessary to prevent spread of amendment into non-target subplots
- Equipment for measuring accuracy and evenness of amendment spread
- High-precision handheld GPS unit (e.g., Trimble GeoXH)
- 50-ft or longer tape measures
- Digital camera
- Field logbook and other record-keeping materials

Selected Amendments

The soil treatment amendments that will be used in the field-scale pilot testing phase of SATES (Phases III [application of amendments to test subplots] and IV [monitoring changes in soil chemistry and vegetation on test subplots]) are:

- Soluble phosphate with added potash
- Compost
- Mixture of soluble phosphate and biochar.

Application Locations

Four test plots have been selected for SATES Phase III application (401-1, 401-2, 258-3, 441-1; Figures B-1 through B-4). Each plot has been subdivided into four different subplots (A, B, C, D), with a 4-foot buffer around each interior side of each subplot (Figures B-5 through B-9). Each subplot has been randomly assigned to an amendment or control plot (Table B-1).

The application contractor is required to implement the controls necessary to ensure amendments are placed only on their designated subplots and do not spill onto other subplots within the same test plot area. To ensure even placement over the full area of the targeted subplot, some spill into the buffer area is acceptable.

Application rate

The application rate for each amendment can be found in Table B-1 and also as organized by subplot in Table B-1. Additionally, each subplot will receive the same amount of water, 1,800 gallons (gal). Water must be applied at a rate that will minimize disturbance of the surface soil, prevent erosion, and avoid the potential to harm plants growing on the test plots. Water will be applied to all of the subplots being treated for testing and the control subplots as follows:

- **Soluble phosphate with added potash:** Apply a 1% aqueous solution requiring the amounts specified in Table B-1 to be mixed with 1,600 gal of water prior to application. An additional 200 gal of water will be applied after the aqueous solution has been applied to assist infiltration of the solution into the surficial soil layer and, because some of the phosphate material used may not dissolve, this final water-only application will help to integrate remaining undissolved phosphate solids into the soil.
- **Soluble phosphate and biochar:** Soluble phosphate with added potash should be applied first, in the same manner as the soluble phosphate-only treatment, followed by the biochar application. If both the biochar and soluble phosphate will be applied using water, the total amount of water used should equal that applied to the other subplots (1,800 gal.).
- **Compost subplots:** Water will be added prior to applying the compost to prevent flushing the compost to another location on the subplot and causing uneven distribution of the compost. If the ground becomes overly muddy (i.e., soft enough that plants are uprooted easily or pushed into the soil due to walking around) after water is applied, the applicator should wait 24 hours or more before applying the compost to minimize soil disturbance.
- **Control subplots:** Only water will be applied.

Application contractor responsibilities

The contractor responsible for amendment placement will prepare an Application Quality Management Plan to ensure even and accurate placement of the amendments to each subplot designated for treatment in the field-scale testing phase of the study. This plan will detail the amendment application methods and safeguards that will be employed to

ensure amendment placement on the targeted subplots. A draft plan will be provided to the U.S. Environmental Protection Agency in advance of the field implementation for review and approval.

STANDARD OPERATING PROCEDURE SOP-2

CULTURAL RESOURCES COORDINATION AND REPORTING

Scope and Applicability

The procedures described herein are to be followed by all Teck American Incorporated (TAI) technical team field personnel, including subcontractors, should potential discoveries of cultural materials and deposits, and/or Indian burials and human remains occur during execution ground-disturbing sampling or other activities that will occur during implementation of the Soil Amendment Technology Evaluation Study (SATES) field-scale testing, near Northport, Washington. This field work will take place entirely on Colville tribal allotments. Cultural materials and deposits (including sacred objects, funerary objects, and objects of cultural patrimony) as well as Indian burials and human remains are defined in the Native American Graves Protection and Repatriation Act (NAGPRA).

The U.S. Environmental Protection Agency (EPA) has responsibilities under the National Historic Preservation Act (NHPA) to consider how its undertakings would affect historic properties. To meet the NHPA requirements, EPA must ensure that sampling and other activities will avoid, minimize, or mitigate any adverse effects on any historic properties. The procedures detailed below were developed to assure compliance with the NHPA and the applicable requirements, procedures, and standards of the National Park Service (NPS), the U.S. Bureau of Reclamation (USBR), the Confederated Tribes of the Colville Reservation (CCT), and the Spokane Tribe of Indians (STI).

Archaeological and Cultural Resources Monitoring in the Sampling Program

Each of the decision units (DUs) where soil treatment testing and related soil sampling activities are being performed as part of the SATES program are located on CCT tribal allotments. Therefore, an archaeological monitor and tribal representative will be present at all times during ground disturbance activities. The archaeological monitor will visually examine all samples to determine if cultural resources are present. The archaeological monitor will not make physical contact with the sample unless cultural

deposits are present. If cultural resources are present, the archaeological monitor will record the finding. The cultural resources materials will then be re-deposited at their original location or collected for further analysis at the discretion of the archaeological monitor.

Throughout the course of the project, the archaeological monitor will document their observations on a daily basis in their field notes and photographs. A standardized archaeological monitoring form may be substituted for the field notes referenced above.

The archaeological monitor(s) will be required to have read the Site health and safety plan (SHSP) and have complete understanding of the archaeological monitoring provisions of this plan. The archaeological monitor is required to comply with requirements identified for personal protection and safe work, including the use of personal protective equipment required for on-site personnel. All on-site personnel are subject to the directions of the task field supervisor at all times.

Discoveries When an Archaeological Monitor is Present

At the discretion of the archaeological monitor, ground-disturbing sampling or associated activity may be slowed or halted at any time when a suspected archaeological resource is encountered. The objective of slowing or halting ground-disturbing activity is to allow the archaeological monitor to confirm and/or make a preliminary assessment of the discovery. The discovery and the material in which it is contained may be returned to a location distinct from, but nearby, the original location of discovery. Any such relocation will be coordinated with the task field supervisor.

At the request of the archaeological monitor, sampling personnel will either:

- Assist in securing access to the location of the discovery and take appropriate measures to protect the location of the discovery from rain, stormwater, and other possible disturbances; or
- Assist in moving the artifacts to a protected and secure area away from the immediate sampling area.

Removal of artifacts from the discovery location will be undertaken only if leaving the artifacts in place would jeopardize their integrity due to erosion or collection by unauthorized individuals, or collected for further analysis at the discretion of the archaeological monitor.

The archaeological monitor or a member of the TAI technical team will remain on site to ensure the security of the find until more extensive efforts can be made to secure the site

from further disturbance or a more extensive evaluation and documentation of the discovery can be made.

Notification of any cultural resources that have the potential to delay or halt sampling activities (i.e., human remains or those items covered under NAGPRA) must be provided as soon as possible to EPA for further coordination with the consulting parties.

Discovery of Human Remains

Native peoples in the study area consider the graves of their ancestors to be important in both their cultural identity and in defining their relationship with the land. These graves are therefore considered sacred and should be left undisturbed. If inadvertent disturbance occurs, the remains and associated materials ("funerary objects") must be treated with respect and honor. All appropriate federal, tribal, and state laws, regulations, and procedures regarding burials should be rigorously enforced.

In the event that likely or confirmed human remains are encountered, all further sampling or other ground-disturbing activity will cease immediately. The protocol and notification procedures to be followed for any potential discoveries of human remains are provided in protocols of the NPS, USBR, CCT, and STI (Attachment 1 to the Cultural Resource Coordination Plan [CRCP]). Any discoveries within the boundaries of the Colville or the Spokane reservations, or other tribal lands, must also be reported immediately to the respective Tribe.

TAI's on-site technical team will assist the archaeological monitor in securing the location of the discovery.

Other conditions for responses to discoveries of archaeological materials may be defined in the Archeological Resources Protection Act permit(s) issued for the sampling program. As detailed in the CRCP, responses to any discoveries of burials must also comply with provisions of NAGPRA and its implementing regulations, as well as the existing protocols of the NPS, USBR, CCT, and STI (Attachment 1 to the CRCP).

Discoveries When an Archeological Monitor is Not Present

As previously stated, an archaeological monitor will be present during all sampling activities. In the event, however, that suspected or evident artifacts or other archaeological deposits are encountered when an archaeological monitor is not present, the immediate vicinity of the discovery will be secured. The discovery will be mapped and photographed in place but will be otherwise left as found (other than appropriate measures to secure the find and maintain this security). In consultation with the land-

managing agency or appropriate tribe, as well as other interested parties, TAI will arrange for the location of the discovery to be examined by an archaeologist and/or tribal representative in a timely manner. If the archaeologist confirms the presence cultural resources, the procedures defined above for discoveries made during ground-disturbing activity monitored by an archaeologist will be implemented. The archaeologist will prepare appropriate State of Washington archaeological forms to document the find.

To ensure proper recognition of artifacts and other cultural items or deposits, all TAI field personnel will be provided with training by an archaeologist to recognize these materials prior to the initiation of any sediment and soil sampling.

Curation Artifacts and other cultural materials that may be recovered during the sampling program (with the exception of human remains and associated items subject to NAGPRA) will be curated at a facility that meets the standards of 36 CFR 79. CCT will designate the curation facility for cultural materials recovered from tribal lands.

Reporting

Within 150 days of completion of the field activity that is covered under this plan, an archaeologist will prepare a confidential written monitoring report or letter report (report) that presents the results of the archaeological monitoring and responses to any discoveries of archaeological resources or burials. The report will include: 1) copies of field notes, descriptions, and maps of all locations at which sampling-related archaeological monitoring was conducted; 2) descriptions of any discoveries made during such monitoring and the outcomes of the discoveries (including the rationale for the decisions for the disposition of any finds); 3) descriptions and maps of all non-monitored locations at which inadvertent discoveries were made and the outcome of those discoveries; and 4) recommendations for any changes in the monitoring protocol or coordination plan that may be appropriate to address results of the monitoring or how well existing coordination procedures worked.

The report will be provided to EPA for dissemination to the consulting parties.

Confidentiality

In accordance with state and federal law, all field personnel are required to keep the discovery of any found or suspected human remains, other cultural items, and potential historic properties confidential. Personnel are instructed that they are prohibited from contacting the media or any third party or otherwise sharing information regarding the

discovery with any member of the public, and that they should immediately notify the field supervisor of any inquiry from the media or public. The field supervisor will notify TAI of any such inquiries. To the extent permitted by law, prior to any release of information, TAI in coordination with EPA and other consulting parties shall concur on the amount of information, if any, to be released to the public, any third party, and the media and the procedures for such a release.

STANDARD OPERATING PROCEDURE SOP-3

AMENDMENT AND POTABLE WATER SAMPLE COLLECTION PRIOR TO FIELD APPLICATION

Scope and Applicability

This standard operating procedure (SOP) describes the procedures for collecting the soil treatment amendments and potable water samples that will be applied to the Soil Amendment Technology Evaluation Study (SATES) test plots selected for field-scale pilot testing. This SOP supports the field-scale pilot testing phase of the SATES program, as described in the *Soil Amendment Technology Evaluation Study Phase III and Phase IV Work Plan: Field-Scale Implementation and Test Plot Monitoring* (work plan) (Ramboll 2020). The sampling described will be performed as part of the SATES Phase III field implementation. The chemical analyses to be performed on the amendments and the potable water samples are presented in work plan Table 3-2.

These procedures may be modified in the field by the field supervisor and field personnel, based on field and site conditions, after appropriate annotations have been made in the field logbook.

Equipment and Materials

The following is a list of equipment and materials needed by the sampling team:

- Field logbook
- Field data sheets
- Pens and pencils, including a fine-tipped waterproof marker
- Chain-of-custody records and custody seals
- Water-resistant sample labels
- Laboratory-provided sample containers
- ContainerSEAL stretch tape or an equivalent product
- Plastic sheeting
- Sample preparation work table (for amendment material sampling)
- Disposable food-grade polyethylene or polycarbonate scoops for sampling bulk amendment materials
- Disposable food-grade polyethylene or polycarbonate bowls, for bulk amendment material sample compositing
- Resealable plastic bags large enough to fit sample containers
- Water quality multimeter (pH, electrical conductivity, temperature)

- Field calibration standard fluids for water quality multimeter
- New plastic or glass containers for water quality multimeter samples, if no container is provided with the multimeter
- Coolers
- Water ice or pre-frozen cooling packs
- Packing material (inert, non-water soluble), e.g., bubble wrap disposable nitrile gloves for handling samples
- A copy of the work plan and Site-specific Health and Safety Plan.

Amendment Materials Sampling Procedures

The following describes the general procedures for collecting representative samples of the amendment materials selected for use in the field study. These materials will be sampled for analysis in advance of the field implementation for field testing. At the discretion of the field supervisor, a representative supply of retail stock of the amendment materials may be sampled before they are shipped to the site for use in the field study. These procedures may be modified by the field supervisor based upon confirmation of the means by which the bulk materials will be delivered for the field study.

1. Sampling personnel will randomly select 10 percent of the bulk materials supplied for the soluble phosphorus (i.e., both the triple super phosphate and potash), compost (supplied as G&B Organics Potting Soil), and biochar (Black Owl Supreme) treatment media.

2. All samples will be sent to the laboratory as solids. In the laboratory prior to analysis, the phosphorus amendment (i.e., both the triple super phosphate and potash) will be mixed into a 1% solution using deionized water to mimic the solution that will be applied in the field.

3. For materials delivered in multiple bags on pallets (typically with 40 bags per pallet), collect discrete samples from randomly-selected bags on a single pallet, representing a 10 percent sample frequency, that will be used to prepare one composite sample from an even mixture of the discrete samples. One composite sample will be prepared from one pallet of material. Thus, if a pallet is delivered with 40 bags of material, four discrete samples should be collected, one from each of four bags. Sampling steps for palletized bags are as follows:

    a. The palletized bags will be counted as they are moved to and restacked on a new pallet.

        i. For the purpose of this process and for sampling the materials, the north-facing side of the pallets will be designated as the front of the pallets.

ii. The bags with numbers randomly selected for sampling will be sequentially pulled or segregated from the restacking procedure and placed on a sample preparation table at the work site. For example, a pallet with randomly selected bags identified with numbers 1, 13, 15, and 29, when those number are counted or reached on the first pallet, the bag will be pulled aside for sampling.

iii. The front of the bag will be denoted by the manufacturer's label or branding.

iv. Each bag will be placed with its bottom end firmly on the floor or work surface so that it can be opened at the top for sampling and will not topple when sampling begins.

b. Bag samples will be collected from a cross-section of the contents from the labeled front to back of the bag, oriented from the open bag top.

c. To develop the composite sample, a disposable scoop will be used to obtain a discrete sample from each randomly selected bag and placed into a disposable food-grade polyethylene or polycarbonate bowl; all of the sampled material will be placed into one bowl. The samples should be of equal size to ensure equal proportions are contributed to the composite sample.

d. After a sample has been drawn from each of the selected bags and added to the bowl, the material in the bowl will be stirred to mix well and then a single composite sample will be collected from this mixture.

e. The composite sample will be collected from the mixture in the bowl using a clean disposable scoop and placed directly from the scoop into a labeled laboratory-supplied sample container(s).

f. After sampling the pallet, the disposal scoop and mixing bowl will be discarded.

g. Sampled amendment bags will be resealed using a staple gun or tape.

4. For materials delivered in Super Sacks, collect four individual discrete (grab) samples, one from each quadrant of each Super Sack, that will be used to prepare a single composite sample from an even mixture of the four discrete samples. One composite sample will be prepared from one pallet of material. The steps for collecting Super Sack samples are as follows:

    a. Super Sack quadrants will be numbered according to their position from the front of the pallet, with the upper left quadrant labeled Q1, the upper right quadrant as Q2, the lower left quadrant as Q3, and the lower right quadrant as Q4. For the purpose of the material sampling, the front of the sack will be the north-facing side.

b. To develop the composite sample, a disposable scoop will be used to obtain a discrete sample from each quadrant of the Super Sack at a depth which does not cause sloughing or the flow of overburden (non-sampled) material in adjacent quadrants.

c. Each sample will be transferred directly from the disposable scoop into a disposable food-grade polyethylene or polycarbonate bowl; all four of the Super Sack quadrant samples will be placed into one bowl. The samples should be of equal size to ensure equal proportions are contributed to the composite sample.

d. After a sample has been drawn from all four quadrants of the Super Sack and added to the bowl, the material in the bowl will be stirred to mix well and then a single composite sample will be collected from this mixture.

e. The composite sample will be collected from the mixture in the bowl using a clean disposable scoop and placed directly from the scoop into a labeled laboratory-supplied sample container(s).

f. At the conclusion of the sampling of each Super Sack, the disposal scoop and mixing bowl will be discarded. Super Sacks will be resealed after sampling using the existing cinching system.

5. For each type of amendment material, the composite sample will be placed in the appropriate laboratory-supplied sample container(s), sealed, and labeled with a sample identifier that can be used to trace the sample to the specific palletized bags or Super Sack it was taken from.

6. The composite samples will be labeled consistent with the procedures given in SOP-7. The samples will be identified by product type, container type and number (Super Sack or pallet), and sample type. Samples will be identified by the following general format:

   Product Type - Container -Sample Type – Collection Date

   Product types will be identified in the sample number using the following codes:

   - **PHO** = soluble phosphate
   - **PTS** = potash
   - **CPS** = compost-based potting soil
   - **PBI** = soluble phosphate and biochar combination

   Container: **SS** = Super Sack, **P** = Palletized bags

   Sample Type: **C** = composite

Date sampled: MMDDYY (e.g., for October 31, 2020, the date in the sample ID would be written as "103120")

7. Filled sample containers will be placed inside a sealable plastic bag (e.g., Ziploc or equivalent) and placed in a cooler with ice and cooled to 4 ± 2oC, until ready to ship to the laboratory. Ice will be placed into and sealed inside a resealable plastic bags to reduce leakage (see SOP-9).
8. Sampling personnel will record on field data sheets or in a field logbook the type of amendment materials sampled, how the materials were or will be shipped (e.g., Super Sacks, bags on pallets, etc.), lot number if available, pallet numbers, sample numbers, and other sample identifiers, as needed, to track the source and sample. Refer to documentation procedures provided in SOP-4.
9. The samples will be prepared for transfer to the laboratory and shipped following the procedures provided in SOP-9.

Potable Water Sampling Procedures

Field Water Quality Parameter Testing

1. Calibrate the pH and electrical conductivity meters using the instrument-specific standards prior to use each day. Record the procedures and findings of the calibration process in the field notebook.
2. Water samples for measurement of pH, electrical conductivity, and temperature will be collected from a sample collected in a clean container and measurements taken immediately prior to collecting the water samples for laboratory analysis following the multimeter directions. These water quality parameter measurements will be collected from the same tank of water as the laboratory analysis samples. Five samples will be collected: one sample every 5,700-gals. If multiple storage tanks are filled, samples should be split so that some samples come from the different tanks.
3. If the water will be collected from a nozzle, turn on the water nozzle, allow a small amount of water to flow out of the nozzle onto the ground to flush the nozzle with the supplied water before collecting the sample. After flushing, place the provided sample container(s) or designated glass or plastic container under the nozzle, without touching the container opening to the nozzle, to collect the water sample. Empty the container onto the ground, and then repeat the procedure to collect a volume of water for testing as required by the multimeter directions.
4. Follow the multimeter directions to measure pH, electrical conductivity, and temperature. Record the results in the field logbook or on a field data sheet.

Water Sample Collection

1. Samples of water obtained from a potable water source or other acceptable source will be collected from storage tanks staged at or near to the work location. These samples will be collected before the water is used to mix with amendment material and before applying the water to the test plots.
2. Field personnel will collect one sample every 5,700-gals of water; a total of five water samples should be collected for analysis. If multiple storage tanks are filled, samples should be split so that one or more samples come from each tank..
3. The ALS Environmental laboratory in Kelso, Washington will provide appropriate sealed sample containers for the samples. The laboratory may provide one or more containers per sample, depending on the type and number required for the analyses specified in the work plan.
4. Prior to collection of each laboratory analytical sample, perform the field water quality parameter testing as described below,
5. Water-resistant labels will be filled out and affixed to the side of the sealed jar prior to collecting the sample.
6. The sample number will be written on the lid of the container with permanent marker prior to sample collection.
7. When collecting each water sample, the field personnel should open the sample container and if the water will be collected from a nozzle, turn on the water nozzle, allow a small amount of water to flow out of the nozzle onto the ground to flush the water through the nozzle and outlet from the tank. Place the container under the nozzle to collect the sample without touching the container to the nozzle.
8. Fill the sample completely unless otherwise directed by the laboratory. If the sample container contains a preservative, care must be taken to prevent overfilling the container and to avoid spilling the sample during or after collection.
9. Once full, put the lid back on the container and tighten completely. Dry the edge around the top of the container.
10. Using the ContainerSEAL stretch tape or an equivalent product, tape around the edge of the lid and the top of the container to form a tight seal.

Storage, Packaging, and Shipping of the Samples

1. Place each filled sample container inside a resealable plastic storage bag (Ziploc® or similar), write the assigned sample number on the outside of the bag with permanent

marker, and seal the bag. Then, wrap each sample in one to two layers of bubble wrap to prevent breakage or crushing the samples while they are being shipped. The samples should not be overwrapped as this could insulate the samples from the ice and interfere with chilling them to the specified temperature(4 ± 2°C).

2. Place the packaged amendment and potable water samples inside sample cooler(s) and store on ice at 4 ± 2°C. Samples should be placed in the cooler upright and secured in that position with packing material so they will not fall, collide with one another, or break during handling and shipment.
3. Ship sample-filled cooler(s) to the analytical laboratory with all required documentation following the procedures described in SOP-8 (Sample Custody) and SOP-9 (Sample Storage, Packaging, and Shipping).
4. Prior to shipping, pack the cooler(s) with a sufficient amount of water ice to ensure the samples arrive at the laboratory at a temperature of 4 ± 2°C. (See SOP-9).

Documentation and Record-Keeping

After the amendments and water have been applied to the subplots to initiate the field-scale testing, enter the pH, electrical conductivity, and temperature records into a digital spreadsheet and submit to the designated project analytical chemistry laboratory coordinator (see work plan) along with the other sampling documentation for inclusion in the project records, as summarized in SOP-4.

Reference

Ramboll. 2020. Soil Amendment Technology Evaluation Study Phase III and Phase IV Work Plan: Field-Scale Implementation and Test Plot Monitoring. Prepared for Teck American Incorporated, Spokane, WA, by Ramboll, Seattle, WA. August.

STANDARD OPERATING PROCEDURE SOP-4

FIELD DOCUMENTATION

Scope and Applicability

This standard operating procedure (SOP) presents the general information that should be documented for all soil collection activities performed as part of the Soil Amendment Technology Evaluation Study (SATES). Proper record keeping will be implemented in the field to allow samples to be traced from collection to final disposition. All information pertaining to field operations during sample collection must be properly documented to ensure transparency (and reproducibility) of methods and procedures. Several types of field documents will be used for this purpose by field personnel.

Equipment and Materials

- Field logbook
- Waterproof black-ink pen
- Field forms
- Digital camera

Field Logbooks

During field sampling events, field logbooks are used to record all daily field activities. The purpose of the field logbook is to thoroughly document the sampling event to ensure transparency and reproducibility. The field logbook will contain soil sampling-related information supplemental to the field data sheets. Any deviations from the project-specific field sampling plan that occur during sampling (e.g., personnel, responsibilities, sample station locations) and the reasons for these changes will be documented in the field logbook. Other types of information that may be included in the field logbook include the following:

- Project sampling name/type
- Name of person making entries
- Other field staff
- Onsite visitors, if any
- Observations made during sample collection, including collection complications, visible debris, and other details not entered onto the field form

- Any surface vegetation that may be removed from the sampling location prior to sampling
- A record of site health and safety meetings, updates, and related monitoring
- Presence of construction/maintenance activities or man-made features that may influence soil composition or transport
- The locations of nearby surface water features (e.g., streams, wetlands, oxbows) or anthropogenic influences (e.g., roads, houses, campsite, evidence of firearm discharge)
- Equipment calibration records (e.g., instrument type and serial number, calibration supplies used, calibration methods and calibration results, date, time, and personnel performing the calibration).

The field supervisor will maintain the field logbook and is responsible for ensuring that the field logbook and all field data forms are correct. Requirements for logbook entries will include the following:

- Entries will be made legibly with black (or dark) waterproof ink
- Unbiased, accurate language will be used
- Entries will be made while activities are in progress or as soon afterward as possible (the date and time that the notation is made should be noted, as well as the time of the observation itself)
- Each consecutive day's first entry will be made on a new, blank page
- The field supervisor must sign and date the last page of each daily entry in the field logbook
- When field activity is complete, the logbook will be entered into the Teck technical team project file.

All logbook entries must be completed at the time any observations are made. Logbook corrections will be made by drawing a single line through the original entry, allowing the original entry to be read. The corrected entry will be written alongside the original. Corrections will be initialled and dated and may require a footnote for explanation. When possible at the end of each day of sampling, backup copies of the pages having entries for the current day should be made. These copies should be stored at a secure location (e.g., the hotel room) and not returned to the field.

Upon completion of the field sampling event, the field supervisor will be responsible for submitting all field logbooks to be copied. A discussion of copy distribution is provided below.

Field Data Forms

Field data forms will be used during each sampling event to record the relevant sample information collected during a sampling event. These forms will be filled out completely by the sampling team during collection of each soil sample and will include the following information:

- Project name and date
- Names of all members of the sampling team
- A brief description of the weather
- The time each station had soil collected
- The station number
- Station location details from the GPS: latitude, longitude, positional accuracy, and elevation
- The sample ID and analysis to be performed
- A list of photograph numbers of the site
- Any additional collection comments.

Upon completion of the field sampling event, the field supervisor will be responsible for submitting all field data forms to be copied. A discussion of copy distribution is provided below.

Photographs

In certain instances, digital photographs of sampling stations may be taken using a camera and lens system with a perspective similar to the naked eye. Photographs should include a measured scale in the picture when practical (e.g., ruler, pencil, coin, etc.). Do not take a photograph without a reference. Use a whiteboard with descriptive information, if necessary. Photographs may also be taken of sample characteristics and routine sampling activities. The following items should be recorded in the field logbook for each photograph taken:

1. The photographer's name or initials, the date, the time of the photograph, and the general direction faced (orientation)
2. A brief description of the subject and the field work portrayed in the picture
3. For digital photographs, the sequential number of the photograph, the file name, the file location, and back-up compact disk (CD) number (if applicable).

Upon completion of the field sampling event, the field supervisor will be responsible for submitting all photographic materials to be copied to electronic media. The electronic media will be placed in the project files (at the task manager's location). Photo logs and

any supporting documentation from the field logbooks will be photocopied and placed in the project files with the disks.

Distribution of Copies

Electronic scans of the field logbooks and field data forms will be made after completion of the field sampling event and stored electronically in the project files for use by project staff. The original field logbooks and forms will be placed in a locked file cabinet at the task manager's location.

Set-up of Locking File Cabinet

Each field event will have its own dedicated section in a locking file cabinet. The section label will include the project name and work order number. The following documents may be included in this folder for each field event:

- Original field logbook(s)
- Original field data forms
- Photograph CDs (or other electronic media)
- Original signed COC forms

STANDARD OPERATING PROCEDURE SOP-5

POSITIONING SOIL SAMPLING LOCATIONS

Scope and Applicability

This standard operating procedure (SOP) describes the procedures for locating soil sampling stations on test plots for soil sampling at during the Soil Amendment Technology Evaluation Study (SATES) field-scale testing (SATES Phase IV) at the Upper Columbia River (UCR) Site. During field-scale testing of soil treatments applied to SATES test plot soils, periodic soil sampling and analysis will be conducted for up to three years to monitor changes in soil conditions. Incremental composite (IC) soil samples will be collected during each sampling event following SOP-6.

This procedure for positioning soil sampling locations will be followed during each soil sampling event. Accurate positioning of sampling stations is necessary to ensure the quality and consistency of soil samples collected during the field study and is important to support data analysis. Station positioning must be both relatively accurate in that the position must be repeatable and to avoid repeat sampling at previously sampled locations in the test plots.

Equipment and Materials

The following is a list of equipment and materials needed by the field sampling team:

- A hard copy of Table B-3, specifying spatial (x-y) coordinates for the soil sampling stations identified for soil sample collection at each of the test subplots
- A hard copy of Figures B-5 through B-9, showing correct subplot orientation and lettered subplot designations within each SATES test plot
- Three measuring tapes at least 50 ft in length
- Flagging tape or duct tape
- A hand-held compass with a rotating degree dial
- High-precision handheld GPS unit (e.g., Trimble GeoXH)
- Spare batteries
- Charging unit
- Test plot map and subplot sampling map

Positioning System Verification

A GPS hardware system such as Trimble GeoXH GPS or an equivalent device will be used for locating the corners of each sub-plot, such as a. SATES test plot and sub-plot outlines, along with other applicable geographic information systems data layers (e.g., aerial photos, topography), will be uploaded into the handheld GPS unit(s) prior to the sampling effort. The standard projection method to be used during field activities is the horizontal datum of World Geodetic System of 1984 (Decker 1984[1]).

GPS requires no calibration because signal propagation is controlled by the U.S. government (the Department of Defense for satellite signals, and the U.S. Coast Guard and U.S. Forest Service for differential corrections). Verification of the accuracy of the GPS requires that coordinates be known for one (or more) horizontal control points within the study area. The GPS position reading at any given station can then be compared to the known control point. If possible, GPS accuracy should be verified at the beginning or end of each sampling day.

Station Location Procedures

The starting point will change each sampling event conducted for the SATES field study. Table B-3 lists the pre-selected sample locations for each sampling event. The field sampling personnel will use this table as a guide to correctly position the sampling stations each time. The entire sampling grid and associated sampling stations will be shifted to a new orientation and spatial coordinate position for each sampling event. The purpose for shifting sampling locations is to avoid resampling any one point.

For each sampling event, at each test plot site, the sampling crew will use the hand-held GPS device to locate the corners and permanent corner markers of the SATES test plot. The corners of the test plot (100 ft by 100 ft) and each sub-plot (approximately 50 ft by 50 ft) within the test plots are marked by durable flush-with-ground yellow plastic markers. If desired, the field team can temporarily mark the corners with additional pin flags, flagging tape, or another type of marker to aid in quickly finding the corners. Additional markers, if used, may remain in place during the sampling event but must be removed at the end of the sampling event.

Once the corners have been located, the crew will select the first subplot to be sampled. Two 50-ft or longer tape measures will be laid out along two edges of the subplot (50 ft on each side) as per the diagram in Figure B-5 to delineate the x and y axes. As shown on Figure B-5, the x-y coordinates for each subplot sampling grid rotate counterclockwise around a pivot point centered in the middle of the test plot. With this counterclockwise rotation, the x-y intersect (i.e., x = 0, y = 0) will be positioned at the midpoint of the outer test plot boundary (50 ft from each corner

[1] Decker, B.L., 1986. World geodetic system 1984. Defense Mapping Agency Aerospace Center St Louis Afs Mo.

marker). The x-y coordinates for each subplot sampling grid are to be laid out starting with the following 0,0 (see Figure B-5):

- **Subplot A:** A0,0 (x = 0 and y = 0) is positioned at the test plot midpoint between subplots A and B
- **Subplot B:** B0,0 is positioned at the test plot midpoint between subplots B and D
- **Subplot C:** C0,0 is positioned at the test plot midpoint between subplots A and C
- **Subplot D:** D0,0 is positioned at the test plot midpoint between subplots C and D

Flagging tape or duct tape should be attached to the third tape measure at intervals along the tape to indicate where samples are to be taken. This marked measuring tape will serve as the sampling transect. Field personnel should consult Table B-3 when marking the sampling transect tape measure to make sure each marker on the tape is placed at the appropriate point.

Once the transect tape is assembled, a compass bearing should be taken along the appropriate x or y axis. The compass bearing will be used to ensure that the sampling transect tape remains parallel to the axis measuring tape.

To lay out the sampling stations, marked tape will be laid out along either the x or y axis, depending on the preferred direction of sampling. Using this tape as a guide, samples will be taken every 9 ft along the y axis and every 8 ft along the x axis..

Field personnel are responsible to verify that the sampling positions are generally consistent with the coordinates given in Table B-3 prior to sample collection. At each sampling point check the x and y coordinates and record the coordinates in the Field Logbook (see SOP-4).

Field replicate and field triplicate samples will be collected as described in SOP-6. The space needed to reserve space for these quality control samples should be taken into consideration when setting sampling station positions for each sampling event, to avoid interfering with other sampling locations.

Contingency for Repeat Sampling

If a plugged sampling hole from a previous sampling event, which will be marked with a wooden dowel or saw-cut segment, is found during sampling, the field sampling team should STOP SAMPLING, notify the field manager, and follow the steps outlined below.

1. To determine the source of the error, the sampling team should:
    a. Check Table B-3 and make sure that the points for the correct sampling event, plot, and sub-plot were selected.
    b. Check Figures B-5 through B-9 and use a compass to confirm that the x and y axes are correctly positioned in the sub-plot.

c. Check the orientation of the sample transect measuring tape (for example if measurements were marked for the x axis, but it is lined up along the y axis this may be the error).

d. Check the orientation of any duplicates or triplicates collected.

2. If an error is found early in IC sampling, the error should be documented in the Field Logbook, including a list of the incorrectly sampled locations.

3. The field supervisor must notify the project manager upon discovering the error. Following this notification, the collected soil should be discarded outside of the SATES test plot area and the positioning of sample stations should begin again, taking care to ensure the sample points are positioned in the locations specified in the Work Plan.

4. If no error can be found and an unidentified error from a prior field season is suspected, the location where the repeat sample was collected should be noted in the field logbook, and the new sampling point be moved 6 in. away from the grid cell location, making sure that the sample point stays inside of the plot boundaries.

5. If a large number of the IC sample increments have been collected in a plot before the error is found, the field supervisor should contact the project manager to determine a course of action.

STANDARD OPERATING PROCEDURE SOP-6

INCREMENTAL COMPOSITE SAMPLE SURFACE SOIL SAMPLE COLLECTION AND FIELD pH TESTING

Scope and Applicability

This procedure describes the methods that will be used to collect surface soil samples (i.e., 0 to 3 in. below ground surface) for the Soil Amendment Technology Evaluation Study (SATES) program. This SOP supports SATES field-scale pilot testing phase of the SATES Program, as described in the *Soil Amendment Technology Evaluation Study Phase III and Phase IV Work Plan: Field-Scale Implementation and Test Plot Monitoring* (hereinafter, the "work plan") (Ramboll 2020). The sampling described herein will be performed as part of the field-scale testing monitoring task (SATES Phase IV). The chemical analyses to be performed on the soil samples collected during Phase IV are presented in work plan Table 3-2. These procedures may be modified in the field by the field supervisor and field personnel, based on field and site conditions, after appropriate annotations have been made in the Field Logbook (see SOP-4 – Field Documentation).

Note that the soil pH testing procedure summarized in this SOP assumes use of a test kit that measures pH of a mixture of soil sample and deionized water. If another type of testing kit is used, the Project Manager must review and approve the testing protocol prior to use in the field.

Equipment and Materials

This procedure is designed to allow representative samples to be collected and accurate and precise pH measurement, with due care aby each sample team member. The following is a list of equipment and materials needed by the sampling team:

- Hand-held global positioning system (GPS) device
- Soil probe, preferably a 2-in.-diameter stainless steel soil punch
- Tape measure
- Survey stakes or flags
- Maps of each test plot and subplots showing the sampling grid
- Camera and digital storage card
- Field logbook
- Pens and pencils
- Chain-of-custody records and custody seals
- Field data sheets

- Sample labels
- 5-gallon plastic buckets
- Re-sealable plastic bags (e.g., Ziploc® or similar)
- Cooler(s)
- Water ice or pre-frozen cooling packs
- Canvas or plastic sheet on which to work with collected samples
- Soil pH field testing kit, to include
    - Soil sample collection and preparation containers (glass or plastic)
    - Scale (±0.1 gram accuracy)
    - Laboratory-supplied deionized water
    - Plastic or stainless steel sample spatula
    - pH meter and probe
    - Calibration standards
- Disposable nitrile gloves for handling samples
- Radios (for communication)
- A copy of the work plan and Site-specific Health and Safety Plan.

Procedures for Surface Soil Sample Collection

The steps below detail sample collection procedures for incremental composite (IC) sampling.

1. Prior to beginning the field sampling effort, the field team will review the IC sample locations in Table B-3 and will print the locations to be sampled during the current sampling effort. Hard copies should be printed on waterproof paper.

2. Field personnel will mobilize to the site selected for sampling, with the necessary supplies and sampling equipment.

3. Measurement and documentation procedures to accurately locate all of the sample collection points are described in SOP-5 (Positioning Soil Sample Locations), included in Appendix B of the work plan.

4. Document the vegetation observed and any observed anthropogenic features in the vicinity of the sampling location in the field notebook. Take digital photographs of the increment locations, and record the photo information in the photo log, per SOP-4. Multiple sample locations can be included in a single photograph.

5. A 4-ft-wide buffer area separates the four subplots within each test plot. No soil samples will be collected from within the buffer area.

6. Select a location to collect the soil sample as close as practical to the grid location specified in Table B-3 for the monitoring event being conducted. The actual increment location may be shifted from the specified grid location to target available soil and avoid obstacles such as woody vegetation or rocks that may interfere with successful sample collection. If necessary, field personnel may shift the sample in the direction of the sample that was taken during the previous monitoring event (Table B-3) to avoid disturbing locations designated to be sampled during future SATES Phase IV sampling events. This adjustment should be a minimum distance required to avoid the obstacle and should not exceed 2 feet from the original sample location.
7. Clear vegetation and large surface debris (e.g., woody debris, undecomposed leaves and pine needles, and surficial rocks) and duff from the increment location to expose the soil surface; the freshly exposed surface is considered the 0-in. depth. When clearing vegetation, care should be taken to minimize disturbance to living vegetation. Retain surficial materials to put back at the same location after the sample has been collected.
8. Collect soil sample increment(s) from each increment location (see Table B-3) using a decontaminated soil punch or equivalent sampling device.
    a. Incremental samples will be collected using a 2-in.-diameter soil punch from the 0- to 3-in. depth interval.
    b. At each incremental collection point within in the sampling grid (i.e., the subplot being sampled) the soil sample punch tool will be deployed to ensure that the soil collected contains a proportional volume of soil from the top of the sample to the bottom. This will be achieved by scraping the length of the core using a decontaminated stainless-steel trowel or disposable scoop to remove the sample from the corer into a plastic bag for cultural monitor observation (see 8.e., below). Each increment across each subplot will be collected in this manner.
    c. For locations where multiple increment samples will be collected for replicate and triplicate sample development, as described below for Field Quality Control Samples, all increments collected at an increment location should be collected as close as possible to the GIS coordinate location specified in Table B-3 and in close proximity to one another (within 4 in.).
    d. Place the increment for laboratory analysis into a quart-sized zipper closure plastic bag (e.g., Ziploc® or comparable) dedicated to the IC sample.
    e. Inspect the increment in the quart-sized bag(s) for cultural resources.
        i. If the increment passes the visual cultural resources review, continue sampling.

ii. If the increment does not pass the cultural resources review, STOP SAMPLE COLLECTION. Notify the field supervisor for management-of-change procedures. The field supervisor should refer to SOP-2 for further direction.

9. If the sample passes the cultural resource visual inspection, transfer the increment for laboratory analysis from the quart-sized inspection bag into a large heavy-duty plastic resealable bag (e.g., Ziploc® or similar),containing other increments collected for that IC sample, taking care to ensure equal volume of soil is collected from each increment collection point in the sampling grid.
10. Complete field documentation for this increment location, as described in SOP-4.
11. After collecting the increment, fill sampling hole with a marker, a 2.5-in.-long, wooden dowel, to prevent resampling the same location in future monitoring events. Place previously removed vegetation/plant debris or local soil over top of plug.
12. Dry decontaminate (brush off) sample collection equipment between increment locations within each sub-plot, as described in SOP-10.
13. After all of the soil increments have been collected from a subplot, mix the soil within the IC sample container by gently stirring with a clean stainless steel spoon, being careful not to damage the container.
14. After all of the increments have been collected for a subplot IC sample, decontaminate all reusable sampling equipment following the full decontamination procedures provided in SOP-10, before commencing sampling in another subplot.
15. Discard dedicated sampling equipment such as gloves, quart-sized bags used for cultural resources monitoring, paper towels, and other expendable materials.
16. Collect all pin flags, flagging tape, or other temporary markers that were placed when positioning the soil sample locations (per SOP-5). Do not remove the semi-permanent test plot and subplot corner markers.

Field Quality Control Samples

Field QC samples will include replicate and triplicate samples that will be collected during each soil sampling event as described below.

1. Field personnel will collect **two field replicate samples** (approximately 15 percent of the total number of samples collected in each event) for homogenization and analysis. The first sample should be collected approximately 4 in. (10 cm) from the primary increment location, relative to the x axis of the subplot (Figure B-5), and the second sample approximately 4 in. (10 cm) along the y axis of the subplot, ensuring that all increments

are collected inside the subplot boundaries. (See SOP-5 for information on sample station positioning to orient the x and y axes within the subplot area being sampled.)

2. Collect field replicate IC samples from co-located samples at each of the 30 increment locations in the same manner as described above for IC soil sampling.
3. The co-located increments will be used to develop two separate IC samples that will be assigned different sample identifiers (see SOP-7).
4. Field personnel will collect **one set of triplicate IC samples** (one primary IC sample plus two replicate IC samples), selected randomly, from within a single subplot during each field monitoring event.
5. Triplicate increments will be collected approximately 4 in. (10 cm) from the primary increment location, relative to the x axis and y axis line of the test plot, respectively, while remaining inside the subplot boundaries. Triplicates should not be collected from the same physical location; each replicate of a triplicate increment must be a separate core associated with the primary increment location. All triplicate increments will be collected from the same subplot.
6. Increments for the triplicate IC samples will be collected in the same manner as all other IC sample increments, and used to develop three separate IC samples, and will be submitted to the analytical laboratory as separate IC samples, each labeled as described in SOP-7.
7. Field sampling personnel will place all IC samples as they are collected into sample cooler(s) and stored on ice at 4 ± 2°C.

Field pH Measurement

1. At the beginning of each field day, calibrate the pH meter following the manufacturer's instructions, and record the procedure, result, and time calibration was completed in the field logbook or on a field data sheet (see SOP-7).
2. Remove a small amount of soil from the bag containing the IC sample to prepare for three pH measurements, from different locations in the bag, and place in approximately equal amounts into three clean glass or plastic containers designated for field pH testing. Approximately 20 grams of soil is needed for each measurement. .
3. Wet the soil with a small amount of laboratory-supplied deionized water and mix thoroughly to make a slurry. New, full containers of deionized water should be used to minimize the potential for acidification of the water upon exposure to atmospheric carbon dioxide. The pH probes cannot typically accurately measure pH in deionized water

because of the lack of dissolved ions, so testing the pH of the deionized water prior to sample preparation is not recommended.

4. Set the pH probe in the soil slurry to measure the pH and follow the directions to obtain pH reading for the three subsamples from each IC soil sample. Collect one reading from each of the three containers. Wetted soil from the pH tests should be discarded to the container used to collect water used in decontamination and disposed of after the study as directed in SOP-10 (Decontamination of Soil Sampling Equipment).

6. Record the pH results in field logbook or on the field data sheet, the time measurements were taken, and the IC sample identifier. The three aliquots will be identified using the same sample ID as the IC sample, appended with -1, -2, and -3.

Sample Storage, Packaging, and Shipping

1. Ship sample-filled collection cooler(s) to the analytical laboratory with all required documentation following the procedures described in SOP-8 (Sample Custody) and SOP-9 (Sample Storage, Packaging, and Shipping).

2. Prior to shipping, pack the cooler(s) with a sufficient amount of ice to ensure the samples arrive at the analytical laboratory at a temperature of 4 ± 2°C. (See SOP-9).

Documentation of IC Sample Information

1. After sampling has been completed, the field supervisor will transcribe the pH results and soil sample information into an electronic spreadsheet format.

2. The electronic spreadsheet file and copies of paper documentation (field logbook, field data sheets, etc.) will be transferred to the Project Analytical Chemistry Laboratory Coordinator for the project records, as described in SOP-7.

Reference

Ramboll. 2020. Soil Amendment Technology Evaluation Study Phase III and Phase III Work Plan: Field-Scale Implementation and Test Plot Monitoring. Prepared for Teck American Incorporated, Spokane, WA, by Ramboll, Seattle, WA. August.

STANDARD OPERATING PROCEDURE SOP-7

SAMPLE LABELING

Scope and Applicability

This standard operating procedure (SOP) describes the general procedures for completing sample labels that will be used on the Soil Amendment Technology Evaluation Study (SATES) program. The project-specific work plan or field sampling plan should be consulted for information on how the sampling labeling protocol was established for SATES soil sampling activities.

Equipment and Materials

- Sample labels
- Indelible marker (fine tip)
- Work Plan Section 3.5.1

Sample Identifier Labels

Sample identifiers (IDs) will be established before each field sampling event begins and then assigned to each sample as it is collected. Sample IDs consist of codes designed to fulfill three purposes: 1) to identify related samples (i.e., replicates) to ensure proper data analysis and interpretation; 2) to obscure the relationships between samples so that laboratory analysis will be unbiased by presumptive similarities between samples; and 3) to track individual sample containers to ensure that the laboratory receives all of the material associated with a single sample. Note that sample labels with some data pre-printed onto the labels, such as sampler name and analyses, are acceptable for use. The codes and uses are described below for soil samples collected during the initial screening and characterization efforts.

Soil Samples

Each incremental composite (IC) soil sample collected during subplot monitoring (SATES Phase IV) will be assigned a unique ID based on the type of sample, location, and date collected.

In the test plots, each subplot has been designated with an alphabetical identifier (A, B, C, and D; see Figures 3-2 through 3-5). Starting with the subplot identifier, soil samples will be coded with the following information:

- IC for incremental composite soil sample, WP for potable water
- Test plot number
- Subplot letter
- Six-digit date (MMDDYY)
- Three-letter code for the amendment applied to a treated subplot and for the control, as follows:
  - CTL = control
  - PHO = soluble phosphate
  - CPS = compost-based potting soil
  - PBI = soluble phosphate and biochar combination

For example, an IC soil sample collected on October 21, 2020 from test plot 258-3, subplot A with the soluble phosphorus treatment, would be designated by the identification number "IC-258-3A-102120-PHO". If multiple containers are sent from the laboratory in which to collect one sample (this may occur for water samples), append the following suffixes to the end of the sample code: -1, -2, -3, etc.

Field QA/QC Samples

Triplicate IC samples will be labeled with the prefix "IC1-", "IC2-", "IC3" included in the sample identification number (e.g., **IC1**-258-3A-102120-PHO, **IC2**-258-3A-102120-PHO, **IC3**-258-3A-102120-PHO).

Field replicate IC soil samples will be labeled with the same designator as the original sample and then the suffix "-R" will be added to end of the sample ID (e.g., IC-258-3A-102120-PHO-**R**).

Duplicate potable water samples will be labeled with the parent sample identified with "WP-" used to identify the parent sample and "WP2-" used to identify the duplicate sample.

Other information that will be written on the sample label includes:

- Samplers initials
- Date
- Time

If necessary, corrections will be made on the sample labels by drawing a single line through the error and entering the correct information with an indelible marker. All corrections will be initialed and dated by the person performing the correction (i.e., the individual who made the error).

The sample labels will be affixed to each sample container. Sample packaging is discussed in SOP-7.

STANDARD OPERATING PROCEDURE SOP-8

SAMPLE CUSTODY

Scope and Applicability

This procedure describes the requirements for custody management of environmental samples collected during the Soil Amendment Technology Evaluation Study (SATES). This procedure is to be used in conjunction with SOP-4 (Field Documentation), SOP-7 (Sample Labeling), and SOP-9 (Sample Storage, Packing, and Shipping).

Chain-of-custody (COC) documentation ensures that samples are traceable from the time of collection through processing and analysis until final disposition. A sample is considered to be in a person's custody if any of the following criteria are met:

1. The sample is in the person's possession.
2. The sample is in the person's view after being in possession.
3. The sample is in the person's possession and is being transferred to a designated secure area.
4. The sample has been placed in a locked, secure area to prevent tampering after it was in the person's possession.

At no time is it acceptable for samples to be outside of designated personnel's custody unless the samples have been transferred to a secure area (i.e., locked up and custody sealed) or transferred to the laboratory. If the samples cannot be placed in a secure area, then a field team member must physically remain with the samples (e.g., at meal times, etc.).

Materials and Methods

- COC forms
    - COC forms may be produced in an electronic format using a database program (e.g., FORMS II Lite), in which case field personnel will need to have a computer and printer available when the field work is being performed. Sample field forms are provided in Appendix D and should be referenced should new forms be developed for the planned field work.
- Custody seals

- Shipping air bills.

Chain-of-Custody Forms

The COC form is critical because it documents sample possession from the time of collection through the final disposition of the sample. The form also identifies the sample preparation and analyses the laboratory is required to perform on the samples that are shipped, and other instructions for sample handling or processing, if applicable (e.g., hold for analysis).

The COC form will be completed after each soil sampling event, before the samples are shipped to the laboratory. Project-assigned soil sample identifiers will be recorded on the COC form as described in SOP-7. The COC form will also identify the sample collection date and time, the type of sample, the project, and the sampling personnel. Two COC form copies will be sent to the laboratory along with the sample(s). Copies of the COC form will be placed into a re-sealable plastic bag and secured to the inside top of each cooler. The field supervisor will retain a copy of the COC form for filing in the project files by the task manager upon completion of each sampling event.

Sampling personnel are responsible for the care and custody of the samples from the time they are collected to the time they are shipped to the laboratory. When transferring possession of the samples, the individuals relinquishing and receiving the samples must sign the COC form(s) and record on the form(s) the time and date the transfer occurs.

Procedures

The following guidelines will be followed to ensure the integrity of the samples:

1. Prior to sample shipping or storage, COC entries will be made electronically for all samples on a secure computer. Information on the COCs will be checked against field logbook entries to ensure name of the sampler, sample identifiers, collection date(s) and time(s), analyses requested, and other details are transcribed correctly and match with the sample analysis plan.
2. At the bottom of each COC form is a space for signatures of the persons relinquishing and receiving the samples, and for recording the time and date that the transfer occurred. The time samples were relinquished should match the time they were received by another party. Under no circumstances should there be any time when custody of the samples is undocumented.
3. The COC form should not be signed until the field supervisor has checked the information recorded on it for accuracy, and any inaccuracies or errors have been corrected. All changes must made by drawing a single line through the incorrect

entry and initialing and dating the revision. Revised entries should be made in the available space below the entries. Any blank lines remaining on the COC form after corrections are made should be marked out with single lines, and initialed and dated by the person who completed the form. This procedure will preclude any unauthorized additions to the COC form.

4. If samples are sent by a commercial carrier not affiliated with the laboratory, such as Federal Express (FedEx) or United Parcel Service (UPS), the name of the carrier should be recorded on the COC form. Any tracking numbers supplied by the carrier should be also entered on the COC form. The time of transfer should be as close to the actual drop-off time as possible.
5. After two copies of the COC forms have been signed, they will be placed inside a sealable plastic bag (e.g., a zippered bag) and then taped inside the top of the shipping container (usually an insulated cooler). The field supervisor will retain the third signed copy of the COC form for the project files.
6. If errors are found after the shipment has left the custody of sampling personnel, a corrected version of the forms must be made and sent to all relevant parties, and a copy filed in the project record. Minor errors can be rectified by making the change on a copy of the original with a brief explanation and signature. Errors in the signature block may require a letter of explanation.
7. Upon completion of the field sampling event, the field supervisor will be responsible for submitting all COC forms to be copied.

Custody Seal

As security against unauthorized handling of the samples during shipping, three custody seals (see Appendix D) will be affixed to each sample cooler. The custody seals will be placed across the front and on each side of the cooler prior to shipping. It is the field supervisor's or other field staff's responsibility to verify that the seals are properly affixed to the cooler so they cannot be removed during shipping. Placing additional transparent packaging tape across the seal may be prudent.

Shipping Air Bills

When samples are shipped via a commercial carrier (e.g., Federal Express, UPS), an air bill or receipt is provided by the shipper. Upon completion of the field sampling event, the field supervisor will be responsible for submitting the sender's copy of all shipping air bills to the task manager. The air bill number (or tracking number) should be noted on the applicable COC form before it is sealed inside the cooler.

Acknowledgement of Sample Receipt

In most cases, on the day samples are received by the testing laboratory, the laboratory will confirm receipt with the task analytical chemistry laboratory coordinator. This confirmation may be via e-mail or an official laboratory 'Acknowledgment of Sample Receipt' form that confirms the sample identification numbers and analysis(es) to be performed. If an error is detected by the task analytical chemistry laboratory coordinator, the laboratory will be called immediately. Decisions made during any telephone conversation should be documented in writing and archived in the project file by the task manager. If necessary, corrections should be made to the COC form and the corrected version of the COC form should then be sent by the task analytical chemistry laboratory coordinator to the laboratory (either via e-mail or facsimile) to ensure a complete and accurate record for the associated samples.

STANDARD OPERATING PROCEDURE SOP-9

SAMPLE STORAGE, PACKAGING, AND SHIPPING

Scope and Applicability

This standard operating procedure (SOP) presents the method to be used when packaging samples that will be either hand-delivered or shipped by commercial carrier to the analytical chemistry laboratory. Specific requirements for sample packaging and shipping must be followed to ensure the proper transfer and documentation of environmental samples collected during field operations, and to maintain the integrity of the samples.

Equipment and Supplies

Specific equipment and supplies necessary to properly pack and ship environmental samples include the following:

- Work plan for the Soil Amendment Technology Evaluation Study phases III and IV
- Project-specific field logbook(s)
- Resealable airtight bags (assorted sizes)
- Laboratory-supplied decontaminated buckets for IC sample collection
- Wet ice in doubled, sealable bags or frozen Blue Ice®
- Insulated coolers
- Bubble wrap
- Fiber-reinforced packing tape and duct tape
- Clear plastic packing tape
- Scissors or knife
- Chain-of-custody (COC) forms: these may be produced in an electronic format using a database program (e.g., FORMS II Lite),in which case, a computer and printer will be needed
- COC seals
- Large plastic garbage bags (preferably 3 mil [0.003 in.] thick) to line the inside of coolers
- Paper towels
- Package labels – “Fragile,” “This End Up,” or “Handle With Care”

- Mailing labels
- Airbills for overnight shipments.

Procedure

In some cases, samples may be transferred from the field to a local storage facility where they can be refrigerated. Depending on the logistics of the operation, field personnel may transport samples to the laboratory themselves or utilize a commercial courier or shipping service. If a courier service is used, then field personnel should be aware of potentially limiting factors to timely shipping (e.g., availability of overnight service, whether weekend deliveries can be made, etc.) before shipping the samples.

Sample Storage Prior to Shipment

Samples will be placed in secure storage (i.e., locked room or vehicle) or remain in the possession of sampling personnel before shipment. Sample storage areas will be locked and secured to maintain sample integrity and COC requirements. In the field, samples will be maintained in coolers with wet ice at 4°C ± 2°C until they are packaged for shipping to the offsite analytical laboratory.

Sample Preparation

The following steps should be followed to ensure the proper transfer of samples from the field to the laboratory:

At the sample collection site

1. Appropriately document all samples using the proper logbooks or field forms and required sample container identification (i.e., sample labels with unique identifiers [IDs]) using the sample labeling techniques described in SOP-7.
2. Clean the outside of all dirty sample containers to remove any residual material that may lead to cross-contamination.
3. Store each sample container in an individual sealable plastic bag that allows the sample label to be read.
4. Place a sufficient amount of wet ice in the sample cooler to maintain the required storage temperature inside the cooler (i.e., 4°C ± 2°C) throughout the sampling day.
5. Store all sample containers in coolers on wet ice until ready for shipping.

To prepare samples and coolers for shipping

1. Choose the appropriate size cooler(s) and make sure that the outside and inside of the cooler is clean of gross contamination. If the cooler has an external drain, the drain should be capped and thoroughly taped shut with duct tape to ensure no leakage will occur.

2. Use bubble wrap to line the cooler and place an opened large plastic bag (preferably a bag with a thickness of 3 mil) inside the cooler.

3. Ensure incremental composite sample bags or buckets are placed inside an additional sealable plastic bag. If using buckets, place each bucket inside of a garbage bag, twist the top of the bag to seal and either tie the bag closed or fasten with zip ties or wire ties. Place the wrapped samples into the large plastic bag in the cooler, leaving sufficient room for ice to keep the samples cold (i.e., 4°C ± 2°C). These samples should be packaged in the cooler in a manner that prevents the sample(s) from coming into contact with ice melt water in the cooler during transport to the laboratory.

4. While the samples are being placed in the shipping cooler(s), the field supervisor will fill out COC form with sample IDs and laboratory analyses to be performed (see example blank and filled out COC forms in Appendix D of the work plan).

5. Make sure all applicable laboratory quality control sample designations have been made on the COC forms. Samples that will be archived for possible future analysis should be clearly identified on the COC form and should be also be labeled as "Do Not Analyze: Hold and archive for possible future analysis", as some laboratories interpret "archive" to mean continue holding the residual sample after analysis.

6. Check sample containers against the COC form to ensure all samples intended for shipment are included. Information on the COC shall only include sample information for the samples within the individual cooler.

7. Add enough ice to keep the samples refrigerated during overnight shipping (i.e., 4°C ± 2°C) because the samples have a required storage temperature. Always overestimate the amount of ice that may be required. Place the ice in sealable plastic bags and then place each bag into a second sealable plastic bag to prevent water leakage into the cooler. Avoid separating the samples from the ice with excess bubble wrap because it can insulate the sample containers from the ice. After all samples and ice have been added to the cooler, use bubble wrap (or other available clean packing material) to tightly fill empty space in the cooler to keep the samples from shifting during transport.

8. The field supervisor will sign and date the completed COC form and retain a copy for project files. Place the signed COC form in a resealable clear plastic bag and

tape the bag containing the form to the inside of the cooler lid. Each cooler should contain an individual (or multiple) COC form(s) for the samples contained in that particular cooler only.

8. After the cooler is sufficiently packed to prevent shifting of the containers, close the lid and seal it shut with fiber-reinforced packing tape. The cooler must be taped shut around the opening between the lid and the bottom of the cooler and around the circumference of the cooler at both hinges.

9. Apply one COC seal across the opening of the cooler lid, one on the front of the cooler and one on each side to prevent unauthorized handling of the samples. Place additional clear packing tape across each seal so they are not inadvertently torn or removed during transport.

10. Notify the analytical laboratory coordinator that samples will be shipped and the estimated arrival time. Upon completion of field activities, the field supervisor will provide copies of all COC forms to the task manager and analytical laboratory coordinator.

Sample Shipping

Hand Delivery to the Testing Laboratory

1. The field supervisor will notify the project analytical chemistry laboratory coordinator that samples will be delivered to the laboratory and the estimated arrival time.

2. In most instances, environmental samples that are hand delivered to the testing laboratory will be received by the laboratory on the same day that they were packed in the coolers.

3. Copies of all COC forms will be provided to the task manager and analytical laboratory coordinator.

Shipping by Commercial Carrier to the Laboratory

1. Use a mailing label and label the outside of the cooler with destination and return addresses and add other appropriate stickers, such as "This End Up," "Fragile," "Perishable," and "Handle With Care." If the shipment contains multiple coolers, indicate on the mailing label the number of coolers that the testing laboratory should expect to receive (e.g., 1 of 2; 2 of 2). Place clear tape over the mailing label to firmly affix it to the outside body of the cooler (not the lid) and to protect it from the weather. This is a secondary label in case the airbill is lost during shipment.

2. Fill out the airbill as required and fasten it to handle tags provided by the shipper (or the top of the cooler if handle tags are not available).

3. The field supervisor will notify the laboratory contact and the task analytical chemistry QA/QC coordinator that samples will be shipped and the estimated arrival date and time. Samples are to be shipped overnight for next morning delivery, and packaged with a sufficient amount of ice to maintain a cooler temperature of 4°C ± 2°C. The field supervisor will provide copies of all COC forms to the task manager the analytical chemistry laboratory coordinator upon completion of each field sampling event.

STANDARD OPERATING PROCEDURE SOP-10

DECONTAMINATION OF SOIL SAMPLING EQUIPMENT

Scope and Applicability

This standard operating procedure (SOP) describes procedures for decontaminating sampling and processing equipment contaminated by inorganic materials. This SOP supports SATES field-scale pilot testing phase of the Soil Amendment Technology Evaluation Study (SATES) program, described in the Phase III and IV work plan. Surficial soil samples (0 to 3 in. in depth below ground surface) will be collected for most of the Phase IV monitoring portion of the field-scale test using the incremental composite sampling methodology, and one round of depth-discrete soil samples will be collected near the end of the field test. This SOP applies to both sample collection methods, but may be reviewed and updated, if necessary, prior to commencing the discrete sample collection event later in the study.

To prevent potential cross-contamination of samples, all reusable soil sampling and processing equipment will be decontaminated before each use. Reusable sampling equipment includes the stainless-steel trowels, soil sample punches, bowls, spoons, etc. Decontaminated equipment will be stored away from areas that may cause recontamination. When handling decontamination chemicals, field personnel will follow all relevant procedures and will wear protective clothing as stipulated in the site-specific health and safety plan. Two general types of decontamination will be used during the field program – dry decontamination and full decontamination, depending on the nature of the samples collected.

Equipment and Materials

Equipment and materials needed for decontamination are:

- Plastic bucket(s) (e.g., 5-gallon buckets)
- Potable water (e.g., tap water)
- Properly labeled squirt bottles (or large spray bottles if needed)
- Funnels
- Alconox®, Liqui-Nox®, or equivalent industrial non-phosphate detergent
- Long handled, rigid natural or synthetic fiber (non-metallic) bristle brushes

- Plastic sheeting, garbage bags, and aluminum foil
- Paper towels
- Polyethylene or polypropylene tub (to collect rinsate)
- Disposable nitrile gloves
- Eye protection such as safety glasses with side shields or goggles.

Dry Decontamination

Dry decontamination procedures will be used only between soil increments collected for a single sample increment during incremental composite (IC) sampling. Full decontamination procedures will be used between samples submitted for analysis under separate sample identifiers. The specific procedures for dry decontamination of soil sampling and processing equipment used to collect soil samples are as follows:

1. If needed, use a brush with rigid natural or synthetic fiber bristles (a non-metallic brush) to remove larger soil particles adhered to the equipment.
2. Wipe visible soil and residue from the equipment using a clean cloth or paper towel.
3. After decontaminating the sampling equipment, solid wastes, including soil residue removed from the equipment and used gloves and cloths/paper towels will be placed in garbage bags for disposal in a solid waste landfill.

Full Decontamination

Full decontamination will be completed on reusable equipment prior to collection between separate IC samples and before collecting any discrete soil samples. Always follow the procedures listed in the Site-specific Health and Safety Plan (TCAI 2009) when decontaminating sampling equipment (i.e., wear appropriate gloves and safety glasses or goggles). Containerize all decontamination fluids for proper disposal following procedures listed in this SOP.

Procedures for full decontamination of soil sampling equipment are as follows:

1. Rinse the equipment thoroughly with potable water to remove visible soil. This step should be performed on all equipment while on site. After removing visible solids, sampling equipment that will not be used again that day may be set aside and thoroughly cleaned in the field laboratory at the end of the day.
2. Pour a small amount (1 to 2 tablespoons) of concentrated Alconox®, Liqui-Nox®, or other phosphate-free laboratory detergent into a bucket and fill the bucket

halfway with potable water. If the detergent is in crystal form, the mixture should be gently stirred to make sure all crystals have dissolved completely prior to use.

3. Scrub the equipment in the detergent solution using a long-handled brush with rigid natural or synthetic fiber bristles.
4. Rinse the equipment with potable water twice and set on a clean, stable surface to drain. Do not allow any cleaned surface that will come into contact with a soil sample to touch any potentially-contaminated surface. Equipment does not need to be dried completely before the next use.
5. When sampling equipment is cleaned at the field laboratory and then transported to the sampling site, the clean equipment will be wrapped in aluminum foil with the dull side facing the cleaned surface(s) and stored and transported in a clean plastic bag (e.g., a trash bag) to the sampling location. This equipment should be stored in the bag until ready for use.
6. When the decontaminated sampling equipment will not be used immediately or again on the same day, small stainless-steel items will be wrapped in aluminum foil with the dull side facing the cleaned surface(s), and stored in the foil until it can be cleaned at the end of the day in the field laboratory.
7. After all the reusable sampling equipment has been decontaminated, all disposable gloves and used foil will be placed in garbage bags for disposal in a solid waste landfill. Water generated during equipment decontamination will be containerized, temporarily stored at a designated staging area in 55-gallon drums or portable tanks and disposed appropriately after the field sampling event has been completed based on analytical results.

Reference

TCAI. 2009. Upper Columbia River general site health and safety plan for the remedial investigation and feasibility study. Prepared for Teck American Incorporated. Integral Consulting Inc., Mercer Island, Washington, and Parametrix, Bellevue, WA.

STANDARD OPERATING PROCEDURE SOP-11

ELECTRONIC DATA DELIVERABLE SPECIFICATIONS

Laboratory analytical data generated as part of the Soil Amendment Technology Evaluation Study (SATES) program will be reported in an electronic data deliverable (EDD) format that is consistent with the EDD format used universally for the Upper Columbia River remedial investigation and feasibility study project. This procedure describes the EDD requirements for the UCR project that will be applied to the SATES laboratory data reporting.

The database manager uses several different databases to manage environmental data, including a custom-developed database that can accommodate most types of laboratory quality control (QC) data. This document describes the target format for laboratory EDDs that are to be loaded into the database. The target EDD format includes up to 12 data tables that may be completed and provided by the laboratory. These tables describe laboratory samples and analytical methods and contain the results of analyses of environmental samples as well as blanks, spikes, laboratory control samples (LCSs), and surrogates. Depending on the needs of the project, as indicated in the work order issued to the laboratory, 4 to 12 tables may be relevant for each data package or sample delivery group.

The 12 different tables that form an EDD contain the following different types of information:

- A description of each laboratory data package or set of samples that is analyzed and reported together
- The correspondence between laboratory sample identifiers and client sample identifiers
- Analytical results for each client sample, by laboratory sample identifier
- Details of the preparation, extraction, digestion, and analytical methods used
- The dates of sample extraction and analysis, and the mass or volume of sample analyzed, for each analysis conducted
- Instrument calibration dates
- Laboratory QC “batches” (which may, but need not, be unique for each data package)
- Laboratory quality control sample descriptions

- Analytical results for spikes and matrix spikes
- Analytical results for method blanks
- Analytical results for LCSs
- Analytical results for surrogates.

The first four of these are the minimum that is required for any project. If laboratory quality control data are also to be reported in electronic format, then some or all the other tables may also be required (per the work order). A list of required tables can be found in Table B-4.

EDDs should be provided in Microsoft® Access database files, in which each of the EDD tables corresponds to a separate database table. The name of the Access file should correspond to the data package. Excel spreadsheets can also be used but must contain all of the data necessary to transfer the data to the approved Access Database. The delivery format should be specified in the laboratory work order. Each set of EDD data tables must be accompanied by an electronic version of a transmittal document (or case narrative) that names the data package(s) and the data file(s) that are being transmitted. If an EDD is resubmitted, the transmittal document must also identify specifically which elements (tables and/or laboratory samples) of the previous transmittal are to be replaced.

The fields, or columns, making up each of the EDD tables are described in Table B-4. Information such as sample material descriptions, analyte names, and measurement basis codes should be represented by a consistent set of names or codes, both within and across tables. An explicit list of valid values for analyte names and other similar information has been developed for this project and will be provided to the laboratory. If the laboratory encounters any questions or difficulties while populating the EDD tables, the database manager should be contacted to discuss and resolve the problem.

The laboratory should also submit a Laboratory Report and additional documentation necessary for data validation.

FIGURES

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Figure B-1
Location of Decision Units with SATES Test Plots
Upper Columbia River SATES Program

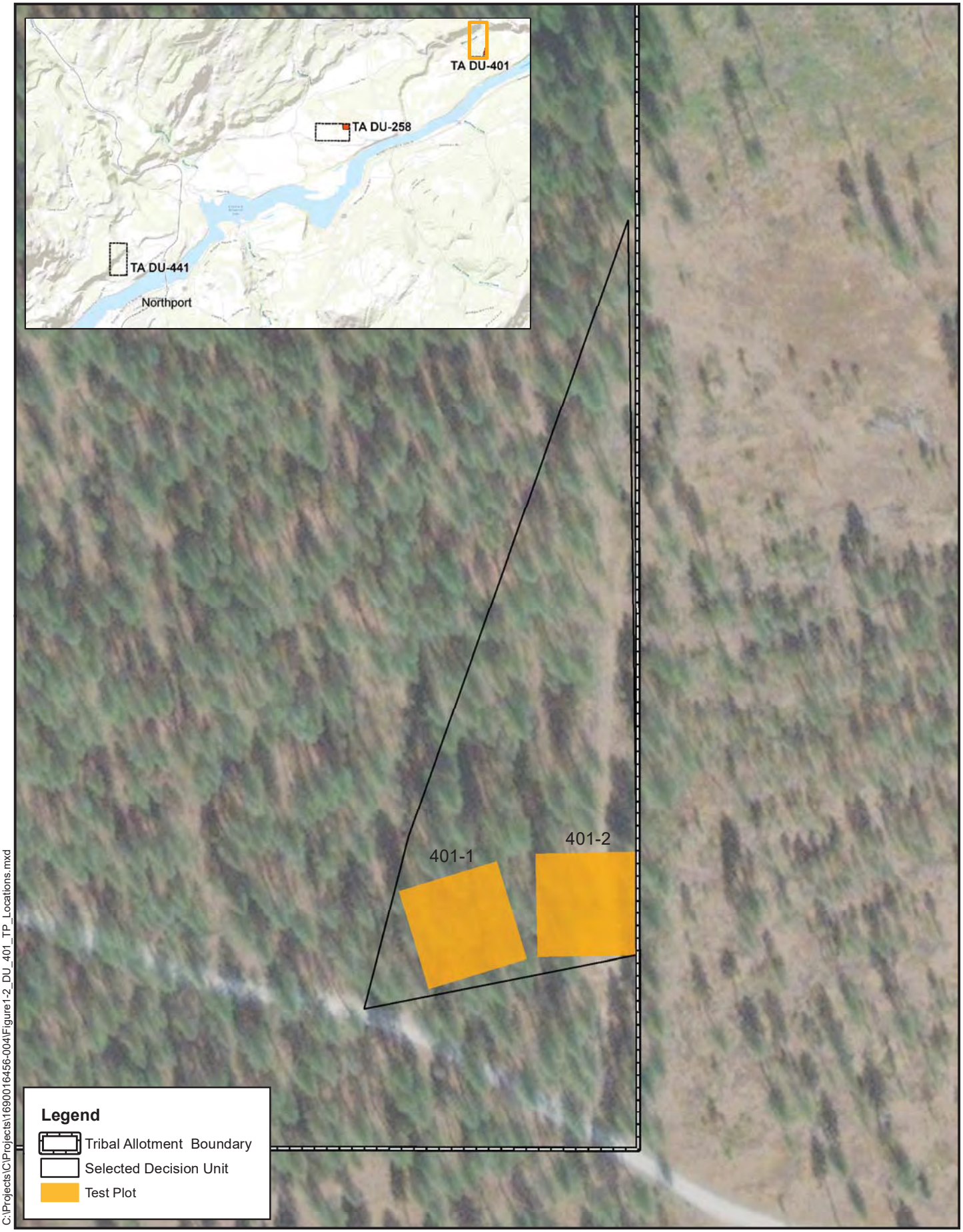

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Figure B-2
Test Plot Locations - Decision Unit 401
Upper Columbia River SATES Program

C:\Projects\C\Projects\1690016456-004\Figure1-3_DU_258_TP_Locations.mxd

FINAL

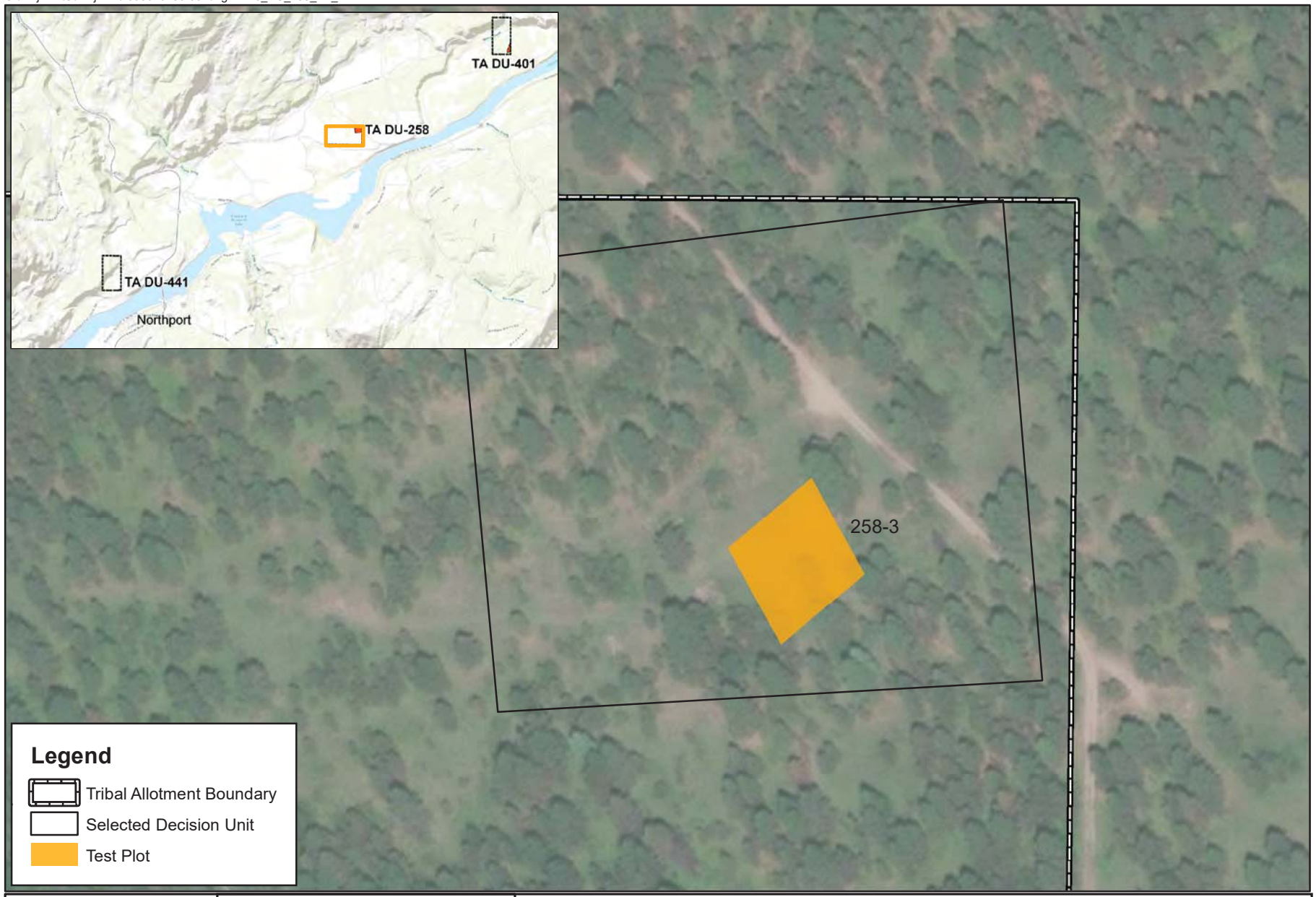

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Figure B-3
Test Plot Location - Decision Unit 258
Upper Columbia River SATES Program

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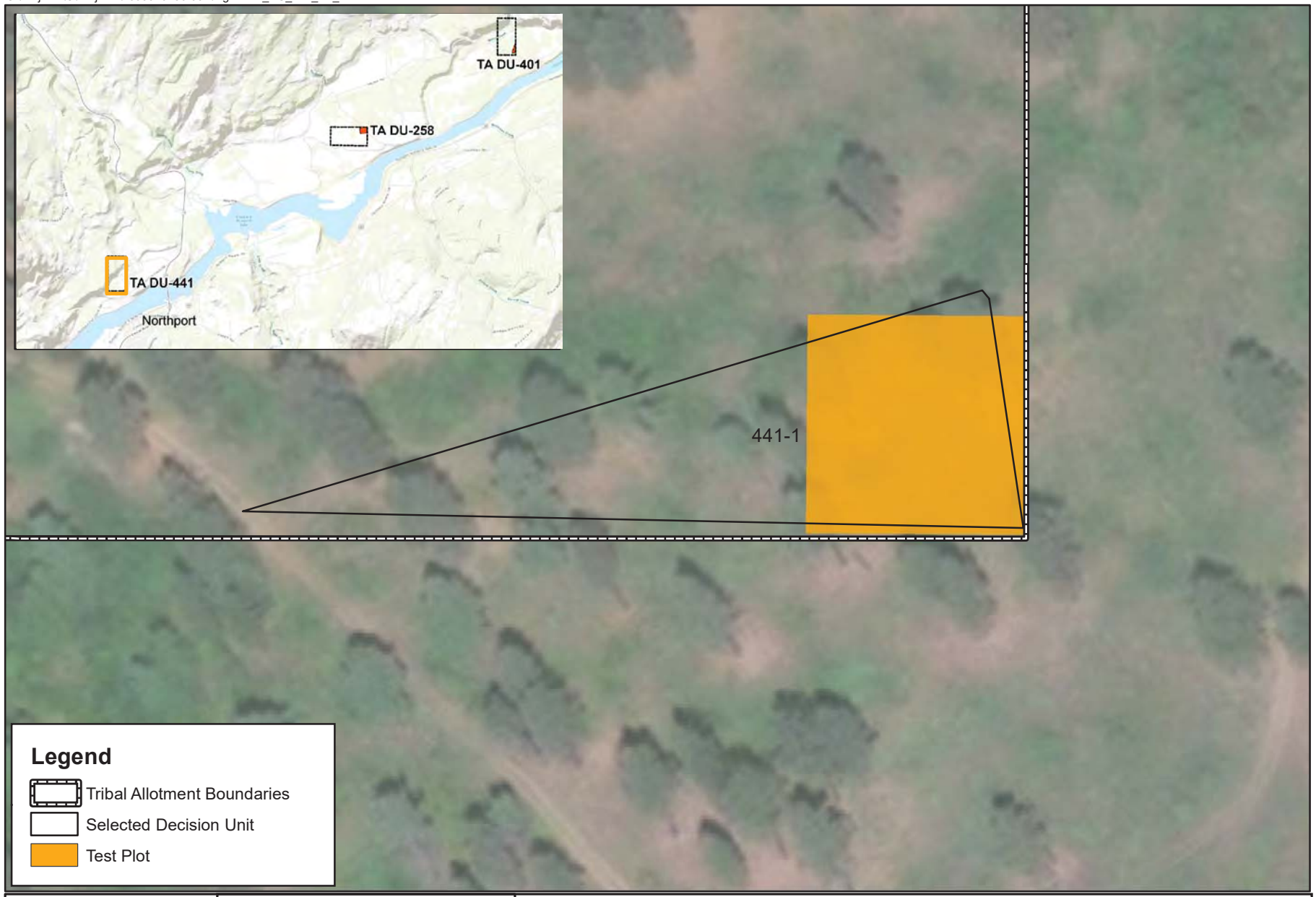

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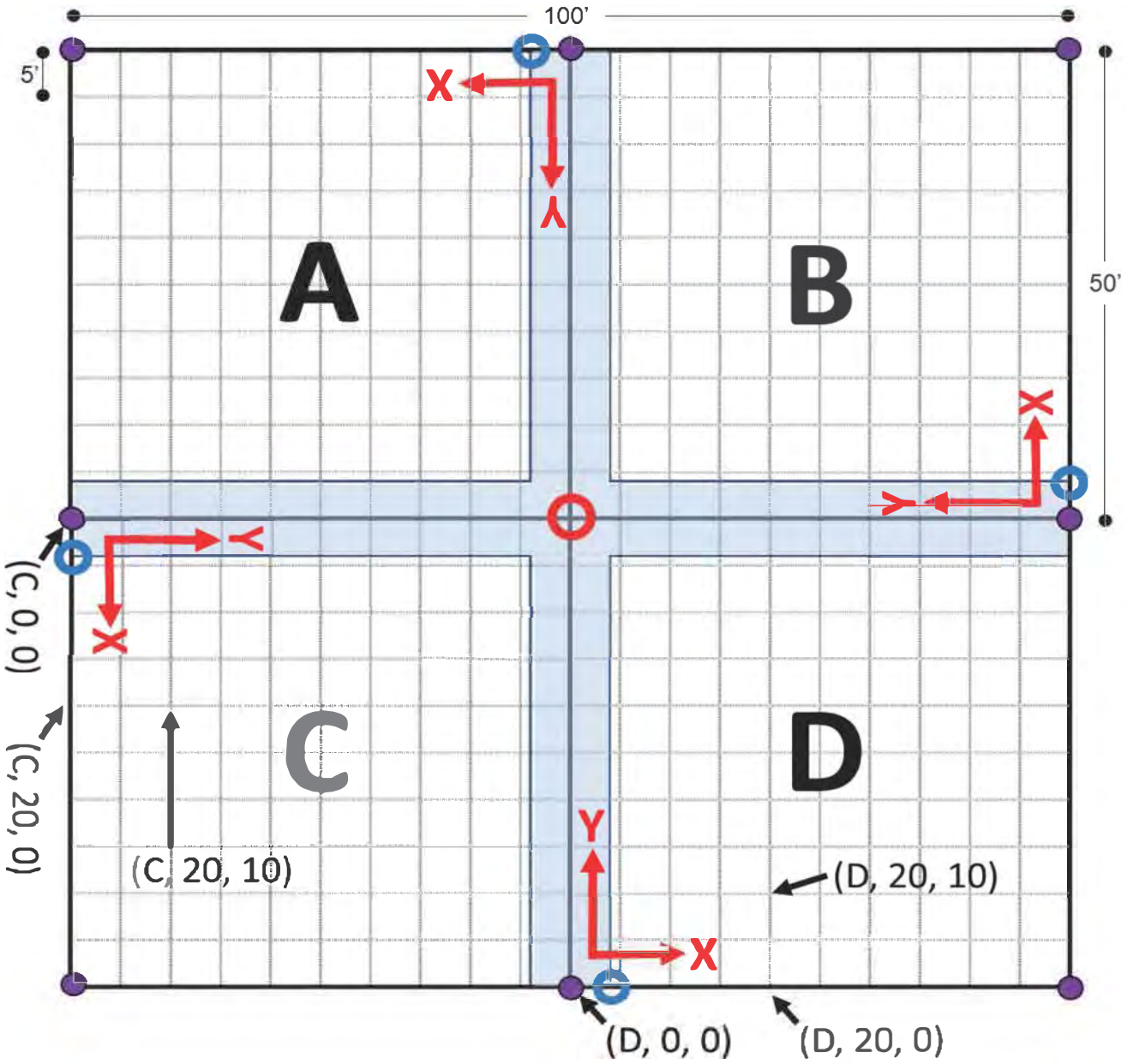
Figure B-4
Test Plot Location - Decision Unit 441
Upper Columbia River SATES Program



Note: The x and y axis orientation for each subplot rotates counterclockwise around the center of the test plot, starting with Subplot D, where the x axis is horizontal and the y axis is vertical. Moving counterclockwise, on he first rotation from Subplot D to Subplot B, the x and y axes rotate 90 degrees and so on for the second and third rotation around the center point.

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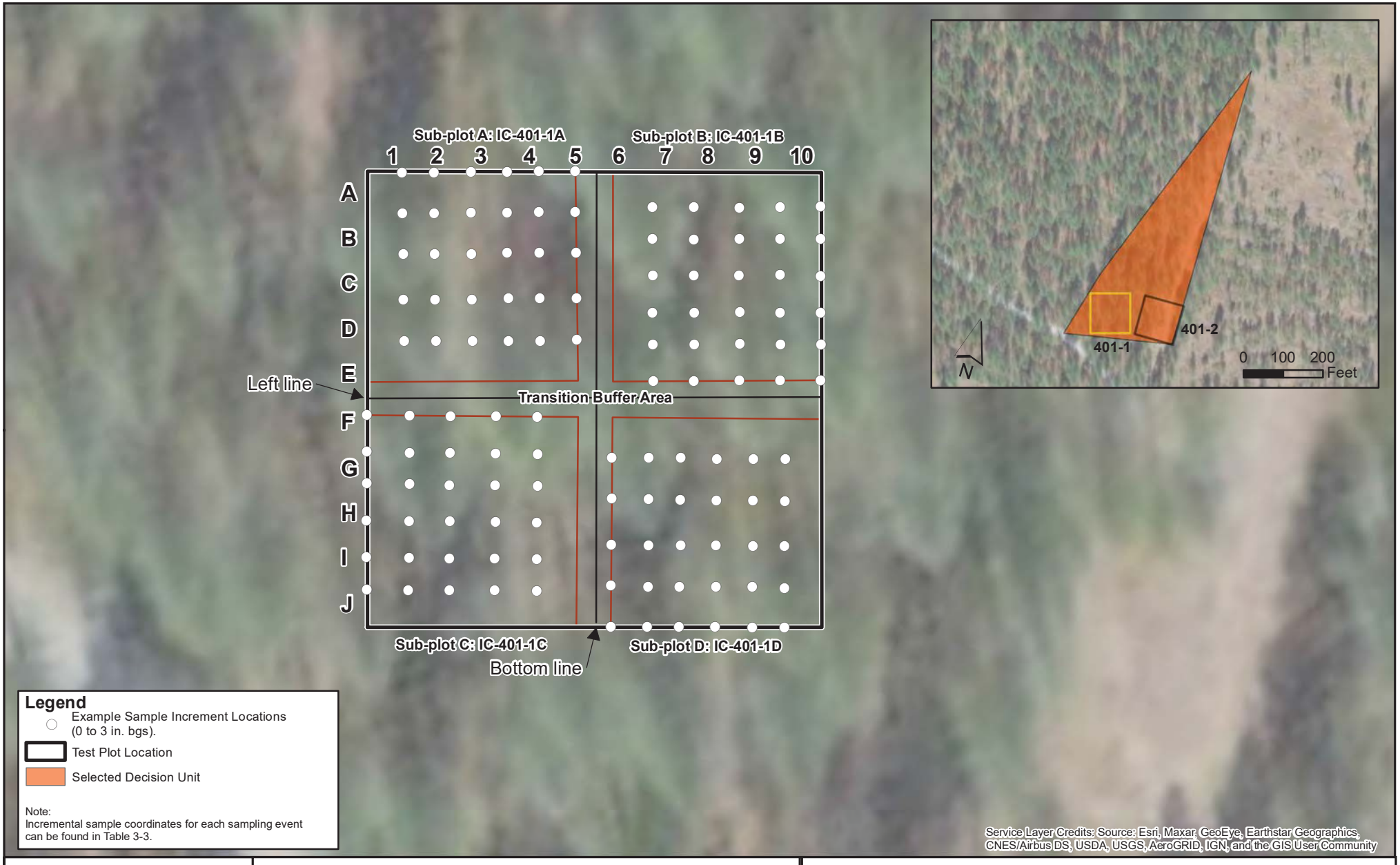
Legend

- Test plot center
- Test plot corner and subplot corner marking stakes
- Soil sampling starting node for each subplot (4,0)

Figure B-5
Test Plot and Subplot Layout for Field-Scale Pilot Testing
Upper Columbia River SATES Program



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DRAFTED BY: JKing | Date: 8/6/2020

0 12.5 25 Meters

0 50 100 Feet

N

Figure B-6
Test Plot 401-1: Example of Soil Increment Sample Location Array
Upper Columbia River SATES Program

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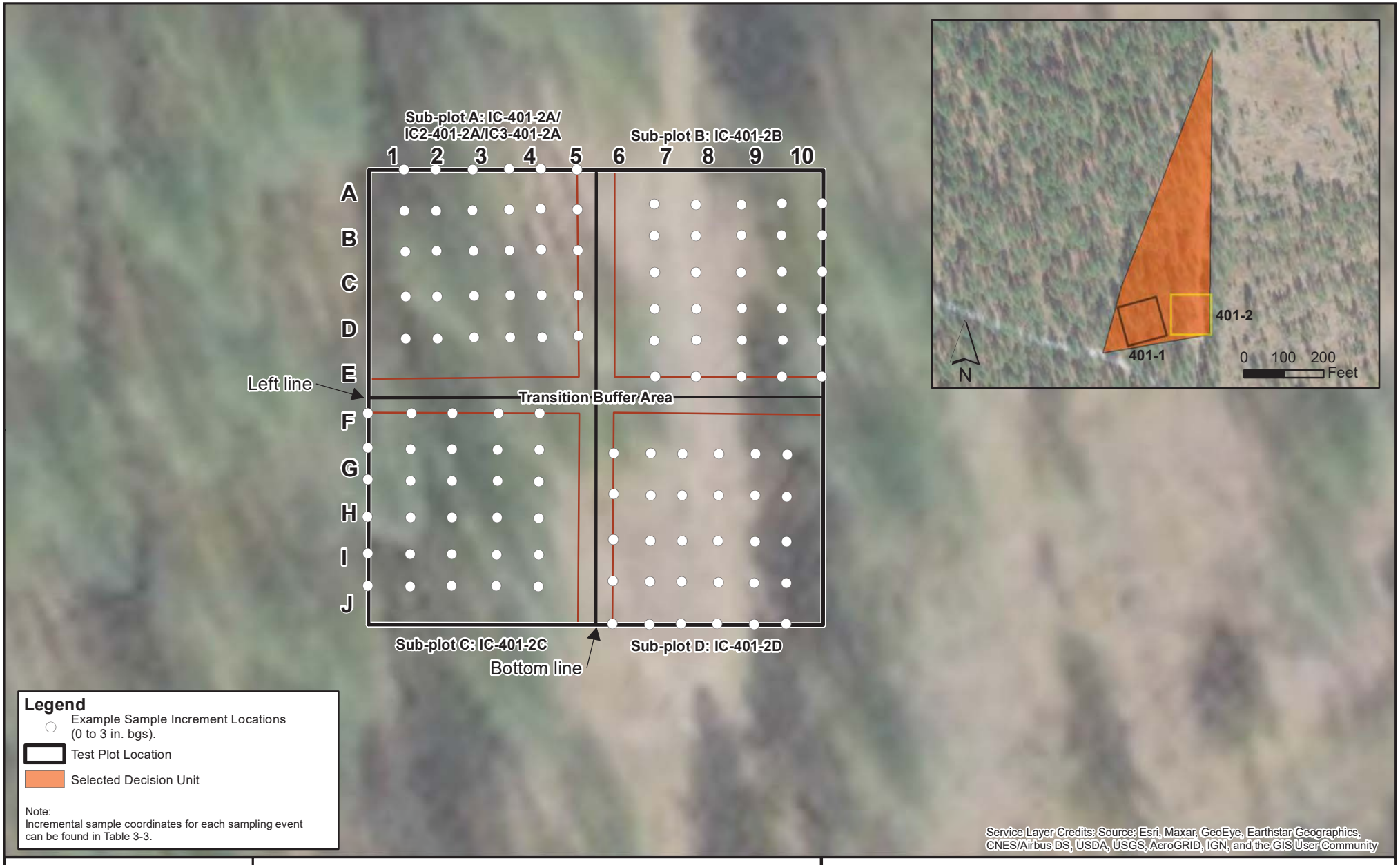
FINAL



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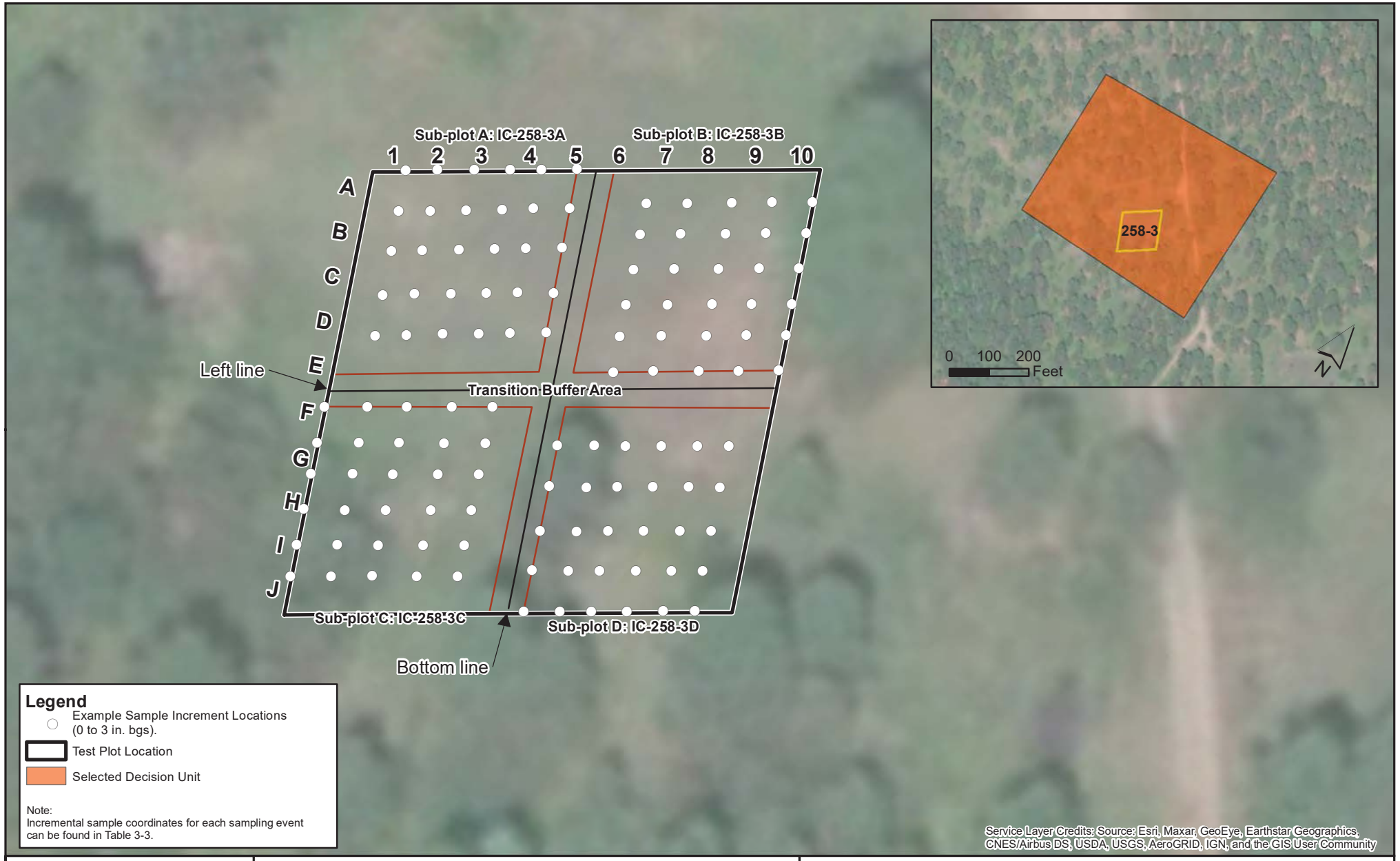
DRAFTED BY: JKing | Date: 8/6/2020

Figure B-7
Test Plot 401-2: Example of
Soil Increment Sample Location Array
Upper Columbia River SATES Program

C:\Projects\C\Projects\1690016456-004\Figure3-4_DU258.3_Adj_TP_Incremental_Characterization.mxd

FINAL



RAMBOLL

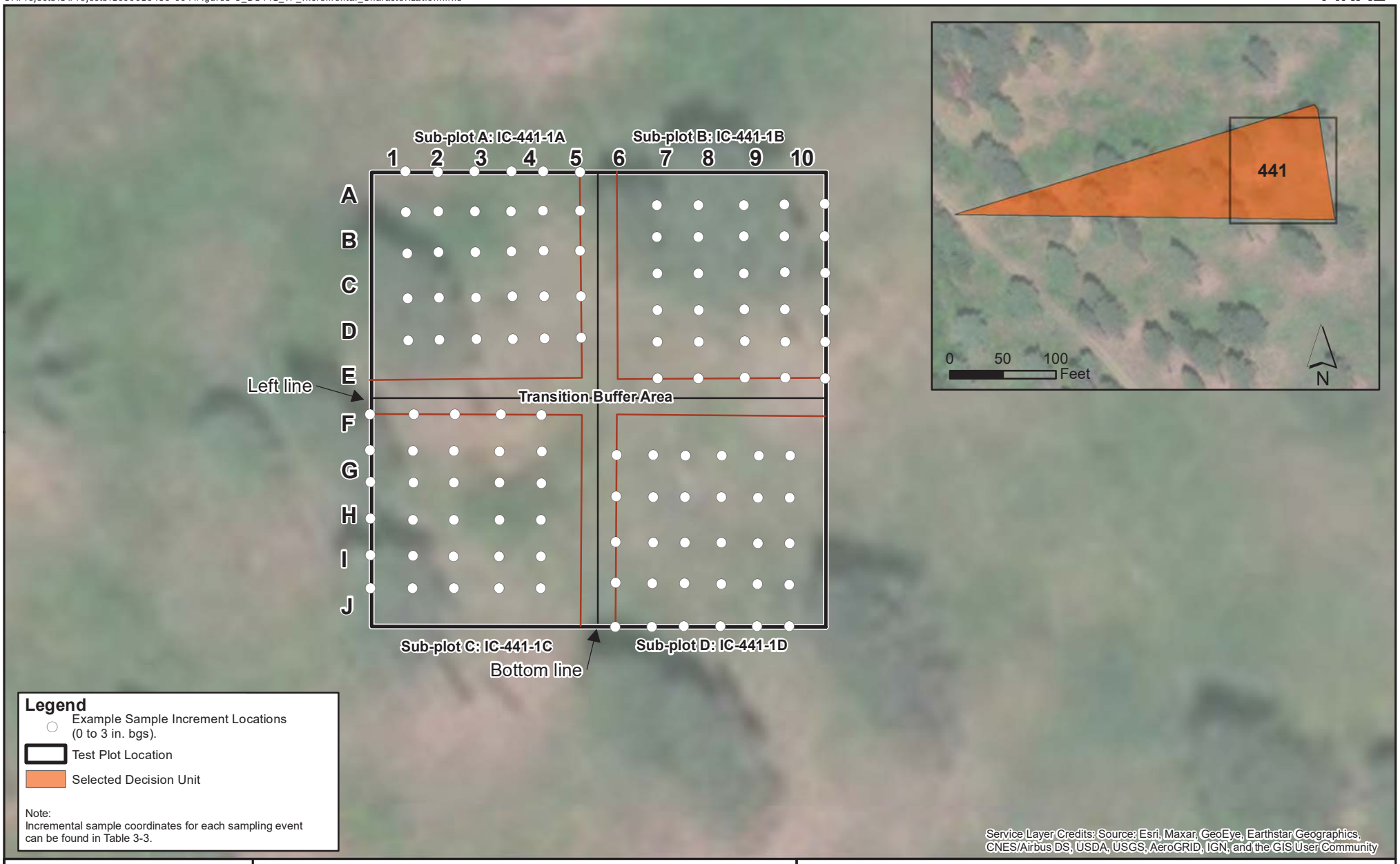
0 12.5 25 Meters

0 50 100 Feet

DRAFTED BY: JKing

Date: 8/6/2020

Figure B-8
Test Plot 258-3: Example of Soil Increment Sample Location Array
Upper Columbia River SATES Program



RAMBOLL

DRAFTED BY: JKing | Date: 8/6/2020

0 12.5 25 Meters

0 50 100 Feet

N

Figure B-9
Test Plot 441-1: Example of Soil Increment Sample Location Array
Upper Columbia River SATES Program

TABLES

Table B-1. Amendment Application Rates by Subplot

Test Plot	Subplot	Treatment	Water (gal)	Amendment (lbs)
401-1	A	Soluble phosphate & biochar	1,800	645 (TSP) 43 (KCl) 574 (biochar)
	B	Soluble phosphate	1,800	643 (TSP) 43 (KCl)
	C	Compost	1,800	2,525
	D	Control	1,800	---
401-2	A	Compost	1,800	2,525
	B	Soluble phosphate & biochar	1,800	645 (TSP) 43 (KCl) 574 (biochar)
	C	Control	1,800	---
	D	Soluble phosphate	1,800	643 (TSP) 43 (KCl)
258-3	A	Compost	1,800	2,525
	B	Control	1,800	---
	C	Soluble phosphate	1,800	643 (TSP) 43 (KCl)
	D	Soluble phosphate & biochar	1,800	645 (TSP) 43 (KCl) 574 (biochar)
441-1	A	Compost	1,800	2,525
	B	Soluble phosphate	1,800	643 (TSP) 43 (KCl)
	C	Control	1,800	---
	D	Soluble phosphate & biochar	1,800	645 (TSP) 43 (KCl) 574 (biochar)

Notes:
KCl = potassium (i.e., potash) fertilizer (0-0-60)
TSP = triple super phosphate (0-45-0)
gal - gallon(s)
lbs - pounds

Table B-2a. Screening Levels for Amendment Materials

Analyte	CAS Number	Units	Maximum Concentration	Source
TAL Metals (6010)				
Aluminum	7429-90-5	mg/kg	80,000	MTCA B NC
Antimony	7440-36-0	mg/kg	32	MTCA B NC
Arsenic	7440-38-2	mg/kg	12	Soil Background
Barium	7440-39-3	mg/kg	16,000	MTCA B NC
Beryllium	7440-41-7	mg/kg	160	MTCA B NC
Cadmium	7440-43-9	mg/kg	2	MTCA A
Calcium	7440-70-2	mg/kg	NS	NS
Chromium	7440-47-3	mg/kg	2,000	MTCA A
Cobalt	7440-48-4	mg/kg	24	MTCA B NC
Copper	7440-50-8	mg/kg	3,200	MTCA B NC
Iron	7439-89-6	mg/kg	56,000	MTCA B NC
Lead	7439-92-1	mg/kg	30	Soil Background
Magnesium	7439-95-4	mg/kg	NS	NS
Manganese	7439-96-5	mg/kg	3,700	MTCA B NC
Mercury	7439-97-6	mg/kg	2	MTCA A
Nickel	7440-02-0	mg/kg	1,600	MTCA B NC
Potassium	7440-09-7	mg/kg	NS	NS
Selenium	7782-49-2	mg/kg	400	MTCA B NC
Silver	7440-22-4	mg/kg	400	MTCA B NC
Sodium	7440-23-5	mg/kg	NS	NS
Thallium	7440-28-0	mg/kg	0.8	MTCA B NC
Vanadium	7440-62-2	mg/kg	400	MTCA B NC
Zinc	7440-66-6	mg/kg	24,000	MTCA B NC
Other Analyses				
Semivolatile Organic Compounds	See Table B-2b			
Electrical Conductivity	NA	dS/m	< 10	Weil, R.R., and N.C. Brady. 2017. The Naturte and Properties of Soils. 15th ed. Pearson Educational Limited, Essex, England.
pH	NA	unitless	5 to 9[1]	EPA Quality Criteria for Water

Notes:

[1]Criteria is pH within this range

CAS = Chemical Abstracts Service

mg/kg = milligrams per kilogram

MTCA A = Washington Model Toxics Control Act Method A Soil for Unrestricted Land Uses

MTCA B NC= Washington Model Toxics Control Act Method B Soil, noncancer

NA = not applicable

NS = No standard available

dS/m = decisiemens per meter

Table B-2b. Screening Levels for Amendment Materials - Semivolatile Organic Compounds

Analyte	Units	CAS Number	Maximum Concentration	Source
SVOCs (8270)				
1,2,4-Trichlorobenzene	mg/kg	120-82-1	34	MTCA B C
1,2-Dichlorobenzene		95-50-1	7,200	MTCA B NC
1,2-Diphenylhydrazine		122-66-7	1.3	MTCA B C
1,3-Dichlorobenzene		541-73-1	NS	NS
1,4-Dichlorobenzene		106-46-7	190	MTCA B C
2,4,5-Trichlorophenol		95-95-4	8,000	MTCA B NC
2,4,6-Trichlorophenol		88-06-2	91	MTCA B C
2,4-Dichlorophenol		120-83-2	240	MTCA B NC
2,4-Dimethylphenol		105-67-9	1,600	MTCA B NC
2,4-Dinitrophenol		51-28-5	160	MTCA B NC
2,4-Dinitrotoluene		121-14-2	3.2	MTCA B C
2,6-Dinitrotoluene		606-20-2	67	MTCA B C
2-Chloronaphthalene		91-58-7	NS	NS
2-Chlorophenol		95-57-8	400	MTCA B NC
2-Methyl-4,6-dinitrophenol		534-52-1	NS	NS
2-Methylnaphthalene		91-57-6	320	MTCA B NC
2-Methylphenol (o-Cresol)		95-48-7	4,000	MTCA B NC
2-Nitroaniline		88-74-4	800	MTCA B NC
2-Nitrophenol		88-75-5	NS	NS
3,3'-Dichlorobenzidine		91-94-1	2.2	MTCA B C
3-Nitroaniline		99-09-2	NS	NS
4-Chloro-3-methylphenol (chlorocresol)		59-50-7	8,000	MTCA B NC
4-Chloroaniline		106-47-8	5	MTCA B C
4-Chlorophenyl Phenyl Ether		7005-72-3	NS	NS
4-Methylphenol (p-Cresol)		106-44-5	8,000	MTCA B NC
4-Nitroaniline		100-01-6	50	MTCA B C
4-Nitrophenol		100-02-7	NS	NS
Acenaphthene		83-32-9	4,800	MTCA B NC
Acenaphthylene		208-96-8	NS	NS
Aniline		62-53-3	180	MTCA B C
Anthracene		120-12-7	24,000	MTCA B NC
Atrazine*		1912-24-9	4.3	MTCA B C
Azobenzene		103-33-3	9.1	MTCA B C
Benz(a)anthracene		56-55-3	0.1	MTCA A
Benzo(a)pyrene		50-32-8	0.1	MTCA A
Benzo(b)fluoranthene		205-99-2	0.1	MTCA A
Benzo(g,h,i)perylene		191-24-2	0.1	MTCA A
Benzo(k)fluoranthene		207-08-9	0.1	MTCA A
Benzoic Acid		65-85-0	320,000	MTCA B NC
Benzyl Alcohol		100-51-6	8,000	MTCA B NC
Biphenyl*		92-52-4	130	MTCA B C
Bis(2-chloroethoxy)methane		111-91-1	NS	NS
Bis(2-chloroethyl) Ether		111-44-4	0.91	MTCA B C
2,2'-Oxybis(1-chloropropane)		108-60-1	NS	NS
Bis(2-ethylhexyl) Phthalate		117-81-7	71	MTCA B C
Butyl Benzyl Phthalate		85-68-7	530	MTCA B C
Caprolactam*		105-60-2	40,000	MTCA B NC
Chrysene		218-01-9	0.1	MTCA A
Dibenz(a,h)anthracene		53-70-3	0.1	MTCA A
Dibenzofuran		132-64-9	80	MTCA B NC
Diethyl Phthalate		84-66-2	64,000	MTCA B NC
Dimethyl Phthalate		131-11-3	NS	NS
Di-n-butyl Phthalate		84-74-2	8,000	MTCA B NC
Di-n-octyl Phthalate		117-84-0	800	MTCA B NC

Table B-2b. Screening Levels for Amendment Materials - Semivolatile Organic Compounds

Analyte	Units	CAS Number	Maximum Concentration	Source
Fluoranthene	mg/kg	206-44-0	3,200	MTCA B NC
Fluorene		86-73-7	3,200	MTCA B NC
Hexachlorobenzene		118-74-1	0.63	MTCA B C
Hexachlorobutadiene		87-68-3	13	MTCA B C
Hexachlorocyclopentadiene		77-47-4	480	MTCA B NC
Hexachloroethane		67-72-1	25	MTCA B C
Indeno(1,2,3-cd)pyrene		193-39-5	0.1	MTCA A
Isophorone		78-59-1	1,100	MTCA B C
Naphthalene		91-20-3	5	MTCA A
Nitrobenzene		98-95-3	160	MTCA B NC
N-Nitrosodimethylamine		62-75-9	0.02	MTCA B C
N-Nitrosodiphenylamine		86-30-6	200	MTCA B C
N-Nitroso-di-n-propylamine		621-64-7	0.14	MTCA B C
Pentachlorophenol		87-86-5	2.5	MTCA B C
Phenanthrene		85-01-8	NS	NS
Phenol		108-95-2	24,000	MTCA B NC
Pyrene		129-00-0	2,400	MTCA B NC
Pyridine*		110-86-1	80	MTCA B NC

Notes:

CAS = Chemical Abstracts Service
mg/kg = milligrams per kilogram
MTCA A = Washington Model Toxics Control Act Method A Soil for Unrestricted Land Uses
MTCA B NC = Washington Model Toxics Control Act Method B Soil, noncancer
MTCA B C = Washington Model Toxics Control Act Method B Soil, cancer
NS = No standard available

Table B-3. Incremental Composite Soil Sampling Location Coordinates for Each Monitoring Event

Location	X	Y
Sub-Plot Datum[a]	0	0
Sample Collection Area Boundary		
Sampling Field Corner 1	4	0
Sampling Field Corner 2	4	50
Sampling Field Corner 3	50	46
Sampling Field Corner 4	46	4

	Baseline Coordinates (ft)		Monitoring 1[b] (ft)		Monitoring 2 (ft)		Monitoring 3 (ft)		Monitoring 4 (ft)		Monitoring 5 (ft)		Monitoring 6 (ft)		Monitoring 7 (ft)		Monitoring 8 (ft)		Monitoring 9 (ft)	
Increment Sampling Points	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
Increment Sampling Point 1	4	0	4	2	4	4	4	6	6	0	6	2	6	4	6	6	8	0	8	2
Increment Sampling Point 2	4	9	4	11	4	13	4	15	6	9	6	11	6	13	6	15	8	9	8	11
Increment Sampling Point 3	4	18	4	20	4	22	4	24	6	18	6	20	6	22	6	24	8	18	8	20
Increment Sampling Point 4	4	28	4	30	4	32	4	34	6	28	6	30	6	32	6	34	8	28	8	30
Increment Sampling Point 5	4	37	4	39	4	41	4	43	6	37	6	39	6	41	6	43	8	37	8	39
Increment Sampling Point 6	12	0	12	2	12	4	12	6	14	0	14	2	14	4	14	6	16	0	16	2
Increment Sampling Point 7	12	9	12	11	12	13	12	15	14	9	14	11	14	13	14	15	16	9	16	11
Increment Sampling Point 8	12	18	12	20	12	22	12	24	14	18	14	20	14	22	14	24	16	18	16	20
Increment Sampling Point 9	12	28	12	30	12	32	12	34	14	28	14	30	14	32	14	34	16	28	16	30
Increment Sampling Point 10	12	37	12	39	12	41	12	43	14	37	14	39	14	41	14	43	16	37	16	39
Increment Sampling Point 11	19	0	19	2	19	4	19	6	21	0	21	2	21	4	21	6	23	0	23	2
Increment Sampling Point 12	19	9	19	11	19	13	19	15	21	9	21	11	21	13	21	15	23	9	23	11
Increment Sampling Point 13	19	18	19	20	19	22	19	24	21	18	21	20	21	22	21	24	23	18	23	20
Increment Sampling Point 14	19	28	19	30	19	32	19	34	21	28	21	30	21	32	21	34	23	28	23	30
Increment Sampling Point 15	19	37	19	39	19	41	19	43	21	37	21	39	21	41	21	43	23	37	23	39
Increment Sampling Point 16	27	0	27	2	27	4	27	6	29	0	29	2	29	4	29	6	31	0	31	2
Increment Sampling Point 17	27	9	27	11	27	13	27	15	29	9	29	11	29	13	29	15	31	9	31	11
Increment Sampling Point 18	27	18	27	20	27	22	27	24	29	18	29	20	29	22	29	24	31	18	31	20
Increment Sampling Point 19	27	28	27	30	27	32	27	34	29	28	29	30	29	32	29	34	31	28	31	30
Increment Sampling Point 20	27	37	27	39	27	41	27	43	29	37	29	39	29	41	29	43	31	37	31	39
Increment Sampling Point 21	35	0	35	2	35	4	35	6	37	0	37	2	37	4	37	6	39	0	39	2
Increment Sampling Point 22	35	9	35	11	35	13	35	15	37	9	37	11	37	13	37	15	39	9	39	11
Increment Sampling Point 23	35	18	35	20	35	22	35	24	37	18	37	20	37	22	37	24	39	18	39	20
Increment Sampling Point 24	35	28	35	30	35	32	35	34	37	28	37	30	37	32	37	34	39	28	39	30
Increment Sampling Point 25	35	37	35	39	35	41	35	43	37	37	37	39	37	41	37	43	39	37	39	39
Increment Sampling Point 26	42	0	42	2	42	4	42	6	44	0	44	2	44	4	44	6	46	0	46	2
Increment Sampling Point 27	42	9	42	11	42	13	42	15	44	9	44	11	44	13	44	15	46	9	46	11
Increment Sampling Point 28	42	18	42	20	42	22	42	24	44	18	44	20	44	22	44	24	46	18	46	20
Increment Sampling Point 29	42	28	42	30	42	32	42	34	44	28	44	30	44	32	44	34	46	28	46	30
Increment Sampling Point 30	42	37	42	39	42	41	42	43	44	37	44	39	44	41	44	43	46	37	46	39

Notes:
[a]See Figure 10 for datum location relative to each sub-plot.
[b]Eaching monitoring heading indicates the monitoring event.

Table B-4. Table descriptions

Table Name	Description	Required[a]	Comment
d_labanal	Analysis dates and aliquot masses/volumes	O	The dates of sample digestion and analysis, and the mass/volume of sample analyzed for each laboratory sample, data package, and method.
d_labcalbatch	Laboratory calibration batch identifiers and descriptions	O	Because instrument calibration data may apply to data in several data packages (SDGs), calibration "batches" can be defined separately from data packages. However, if calibration is performed for each data package, the calibration batch ID and the data package ID may be the same. If the same calibration batch applies to multiple data packages, the calibration batch descriptions need only be provided once, not with every data package.
d_labpkg	Laboratory package (SDG) descriptions	R	Laboratory packages represent distinct sets of samples that are typically analyzed and reported together. Every analytical result for a client sample is linked to a data package description; this table must always be completed.
d_labqcbatch	Laboratory quality control batch identifiers and descriptions	O	Like calibration data, laboratory quality control measurements may apply to data in several data packages (SDGs). Consequently, quality control "batches" can be defined separately from data packages. However, if all quality control measurements are made separately for each data package, the quality control batch ID and the data package ID may be the same. If the same quality control batch applies to multiple data packages, the quality control batch descriptions and data (for LCSs, spikes, blanks, and surrogates) need only be provided once, not with every data package.
d_labqcsamp	Laboratory quality control sample descriptions	O	A list of the identifiers of all quality control samples created by the laboratory (e.g., method blanks and LCSs)
d_labresult	Laboratory analysis results for client samples	R	All of the analytical results for client (database manager) samples.
d_labsample	Laboratory sample identifiers	R	Laboratory sample IDs for each client (database manager) sample number or laboratory quality control sample.
d_lcs	Laboratory control samples	O	Analytical results for LCSs.
d_matrixspike	Laboratory matrix spikes	O	Analytical results for matrix spikes and spike duplicates.
d_methodblank	Laboratory method blanks	O	Analytical results for method blanks.
d_surrogate	Surrogate results	O	Analytical results for surrogates, including both client (database manager) samples and laboratory quality control samples
e_analmethod	Description of laboratory methods (preparation, digestion, analysis)	R	Details of the methods used to prepare, extract, digest, and analyze samples.

Note: LCS - laboratory control sample
SDG - sample delivery group

[a] R = always required; O = optional, depending on work order requirements

Table B-5. Fields per table

Table Name	Column	PK[a]	Data Type	Length Limit	Description	Required	Valid Values[b]	Comments
d_labanal	lab	x	Text	10	Laboratory performing the analysis	x		
	lab_pkg	x	Text	16	Laboratory package (SDG) identifier	x	Per d_labpkg table	
	anal_type	x	Text	10	Type of analysis performed	x	Per d_labpkg table	
	labsample	x	Text	20	Laboratory sample identification	x	Per d_labsample table	
	material_analyzed	x	Text	20	Material analyzed	x	"Soil", "Sediment", "Sediment < 100um", "Porewater", etc.	
	method_code	x	Text	60	Analysis method code	x	Per e_analmethod table	
	date_extracted		Date/Time		Date that the sample was digested or extracted			
	date_analyzed		Date/Time		Date that the sample was analyzed by the specified method			
	mass_gm		Double		Mass of sample (aliquot) analyzed, in grams			
	vol_ml		Double		Volume of sample (aliquot) analyzed in milliliters			
d_labcalbatch	lab	x	Text	50	Name of laboratory performing the analysis	x		
	lab_cal_batch	x	Text	50	Laboratory calibration batch identifier	x		The calibration batch ID may be the same as the data package ID.
	instrument_type		Text	50	Type of laboratory instument used in analysis	x		
	instrument_id		Text	50	Identifier of instument used in analysis	x		The laboratory's identifier for the specific instrument used.
	initial_cal_date		Date/Time		Initial calibration date	x		
d_labpkg	lab	x	Text	10	Laboratory performing the analysis	x		
	lab_pkg	x	Text	16	Laboratory package (SDG) identifier	x		
	anal_type	x	Text	10	Type of analysis performed	x	"Metals", "PestPCBs", "SVOCs", etc.	Should distinguish different types of analyses performed on the same set of samples (typically 20).
	anal_begun		Date/Time		Date the analysis started	x		
	anal_completed		Date/Time		Date the analysis was completed	x		
	analyst		Text	32	Person performing the analysis	x		
	comments		Memo		General notes and information			
d_labqcbatch	lab	x	Text	50	Laboratory performing the analysis	x		
	lab_qc_batch	x	Text	50	Laboratory quality control batch number	x		The laboratory quality control batch ID may be the same as the data package ID.
	prep_date	x	Date/Time		Quality control batch preparation date	x		
	extraction_date	x	Text	50	Date of extraction	x		
d_labqcsamp	lab	x	Text	10	Laboratory performing the analysis	x		
	labqc_samp	x	Text	20	Laboratory quality control sample identifier	x		There should be a matching entry (or entries) in the labqc_samp field of the d_labsample table.
	qc_type		Text	12	Type of quality control sample	x	"MethodBlank", "LCS"	
	comments		Memo		General notes and information			

Table B-5. (cont.)

Table Name	Column	PK[a]	Data Type	Length Limit	Description	Required	Valid Values[b]	Comments
d_labresult	lab	x	Text	10	Laboratory performing the analysis	x		
	lab_pkg	x	Text	16	Laboratory package (SDG) identifier	x	Per d_labpkg table	
	anal_type	x	Text	10	Type of analysis performed	x	Per d_labpkg table	
	labsample	x	Text	20	Laboratory sample identification	x	Per d_labsample table	
	material_analyzed	x	Text	20	Material analyzed	x	"Soil", "Sediment", "Sediment < 100um", "Porewater", etc.	This description should reflect the results of any sample processing in the laboratory that results in a subdivision of the material analyzed, other than just the extraction of an aliquot. Any sample subdivision method should be indicated in the lab_prep_method of the e_analmethod table.
	method_code	x	Text	60	Analysis method code	x	Per e_analmethod table	
	analyte	x	Text	16	Name of analyte measured	x		
	meas_basis	x	Text	10	Measurement basis	x	"Dry", "Total", "Dissolved"	
	lab_rep	x	Text	6	Laboratory replicate identifier	x		
	meas_value		Double		Measured concentration or equivalent value	x		Use the detection limit for undetected measurements.
	units		Text	10	Units associated with the measured value	x		
	std_dev		Double		Standard deviation			Ordinarily carried only for radiological measurements.
	detected		True/False		Was the value detected?			
	detection_limit		Double		Detection limit			
	quantification_limit		Double		Quantification limit			
	maximum_limit		Double		Maximum limit for right-censored data			Applicable only to some types of analyses (e.g., grain size fractions calculated by subtraction) where the "detection limit" is an upper, rather than lower, bound.
	lab_flags		Text	8	Laboratory-assigned process notation flags			Flags should identify undetected values, tentatively identified compounds, and any other result-specific observations that affect data interpretation or usability.
	comments		Memo		General notes and information			
	lab_qc_batch		Text	50	Laboratory quality control batch number		Per d_labqcbatch table	
	lab_cal_batch		Text	50	Laboratory calibration batch number		Per d_labcalbatch table	
d_labsample	lab	x	Text	10	Laboratory performing the analysis	x		
	labsample	x	Text	20	Laboratory sample identifier	x		Analytical sample identifier assigned by the laboratory.
	study_id		Text	25	Client (database manager) study identifier	x[c]		A database manager work order number may be used.
	sample_no		Text	20	Client (database manager) sample number	x[c]		The database manager sample number as on the sample container and COC form.
	labqc_samp		Text	20	Laboratory quality control sample identifier	x[c]		
	receipt_date		Date/Time		Date of written acknowledgment of having received the samples			Relevant only when the sample_no field is used.
	coc_id		Text	12	COC form number			Relevant only when the sample_no field is used.

Table B-5. (cont.)

Table Name	Column	PK[a]	Data Type	Length Limit	Description	Required	Valid Values[b]	Comments
d_lcs	lab	x	Text	10	Laboratory performing the analysis	x		
	lab_qc_batch	x	Text	16	Laboratory quality control batch identifier	x	Per d_labqcbatch table	
	lcs_id	x	Text	25	Laboratory control sample identifier	x		
	analyte	x	Text	10	Name of analyte measured	x		
	meas_basis	x	Text	10	Measurement basis	x		
	lcs_type		Text	1	Laboratory control sample type	x	"S" or "L"	Indicates solid or liquid.
	true_lcs_conc		Double		True laboratory control sample concentration	x		
	meas_lcs_conc		Double		Measured laboratory control sample concentration	x		
	lcs_lowlimit		Double		Laboratory control sample lower limit			
	lcs_highlimit		Double		Laboratory control sample high limit			
	units		Text	10	Units associated with measurement	x	e_unit	
	conc_qual		Text	1	Concentration qualifier		e_concqual	
d_matrixspike	lab	x	Text	10	Laboratory performing the analysis	x		
	lab_qc_batch	x	Text	16	Laboratory quality control batch identifier	x	Per d_labqcbatch table	
	labsample	x	Text	20	Laboratory sample identifier	x	Per d_labsample table	There should be a matching row in the d_labsample table (and rows in the d_labresult table),
	method_code	x	Text	10	Analysis method code	x	Per e_analmethod table	
	analyte	x	Text	16	Name of analyte measured	x		
	meas_basis	x	Text	10	Measurement basis	x		
	spike_no	x	Integer		Spike number (replicate)	x		Ordinarily only one spike (data row) for inorganic analytes, two for organics.
	samp_conc		Double		Sample concentration value	x		Ordinarily this value will also be reported in the d_labresult table.
	initial_qual		Text	1	Initial qualifier			
	spike_added		Double		Amount of spike added	x		
	spiked_conc		Double		Spiked sample concentration value	x		
	final_qual		Text	1	Final qualifier			
	lab_flags		Text	8	Laboratory flags			
	units		Text	10	Units associated with measurement	x		
d_methodblank	lab	x	Text	10	Laboratory performing the analysis	x		
	lab_qc_batch	x	Text	16	Laboratory quality control batch number	x	Per d_labqcbatch table	
	labsample	x	Text	25	Laboratory sample identifier	x	Per d_labsample table	
	method_code	x	Text	15	Analyzation method code	x	Per e_analmethod table	
	analyte	x	Text	16	Name of analyte measured	x		
	lab_rep	x	Text	6	Laboratory replicate identifier	x		
	concentration		Double		Measured concentration or equivalent value			
	retention_time		Double		Column retention time			
	units		Text	10	Units associated with measurement	x		
	lab_flags		Text	8	Laboratory validation flags			

Table B-5. (cont.)

Table Name	Column	PK[a]	Data Type	Length Limit	Description	Required	Valid Values[b]	Comments
d_surrogate	lab	x	Text	10	Laboratory performing the analysis	x		
	lab_qc_batch	x	Text	16	Laboratory quality control batch number	x	Per d_labqcbatch table	
	labsample	x	Text	25	Laboratory sample identifier	x	Per d_labsample table	
	method_code	x	Text	15	Analyzation method code	x	Per e_analmethod table	
	surrogate	x	Text	16	Name of analyte measured	x		
	meas_basis	x	Text	10	Measurement basis	x		
	column_no	x	Text	2	Laboratory column number	x		
	lab_rep	x	Text	4	Laboratory replicate identifier	x		
	recovery		Double		Percent recovery	x		
	out_flag		Text	1	Laboratory validation flag			
e_analmethod	method_code	x	Text	15	Analysis method code	x		
	description	x	Text	255	Narrative description of the analysis method	x		
	lab_prep_method		Text	60	Sample preparation method, if used		"Sieved to 100um", "Filtered", "Centrifuged/supernatant"	Describes any physical subdivision of the sample received that is performed prior to analysis, and that results in analysis of material that is different than material received. Use of a sample preparation method may also affect the values used in the material_analyzed and meas_basis fields of the d_labresult table.
	lab_leach_method		Text	60	Sample leaching method, if used		e_leachmethod	Describes any chemical subdivision of the sample received that is performed prior to analysis. Use of a leaching method may affect the value used in the meas_basis field of the d_labresult table.
	lab_extraction_method		Text	60	Laboratory extraction method		e_labextract	Extraction or digestion method. Required if different from any extraction method implied by the analysis method used.
	lab_anal_method	x	Text	60	Laboratory analysis method		e_labmethod	

Note: LCS - laboratory control sample
SDG - sample delivery group

[a] R = always required; O = optional, depending on work order requirements

[a] Primary key.

[b] Values listed here are only examples; other values may also be used as appropriate.

[c] Either study_id and sample_no or labqc_samp must be included.

APPENDIX C

STANDARD OPERATING PROCEDURES FOR LABORATORY OPERATIONS

STANDARD OPERATING PROCEDURES FOR THE OHIO STATE UNIVERSITY (OSU)

Lead Sorption Test of Potential Remedial Treatments, Johnson 2018
Version 1

1.0 Scope

1.1 This method is for rapid screening of potential remedial treatments ability to sorb and retain Pb from soil solution extracted by SPLP

2.0 Definitions

2.1 Test soil: Contaminated soil used as the source of Pb to test treatments

2.2 Remedial treatments: Treatments added to solution extracted from test soil

2.3 Zero treatment control: Control SPLP extract that has no remedial treatment added

2.4 Control sample: silica sand, which has no capacity for sorbing Pb undergoes the testing procedure

3.0 Equipment and supplies

3.1 SPLP extraction solution – See SPLP SOP but modify extraction fluid to pH 5.00 instead of 4.20

3.2 Soil to generate SPLP extracts

3.3 Remedial treatments

3.4 Reciprocal shaker

3.5 Bottle top dispenser set to 25mL

3.6 0.01M $CaCl_2$

3.7 0.45um vacuum filter

4.0 Method

4.1 Extract test soil in quadruplicate (4x) according to SPLP procedure using pH 5.0 extraction solution at a soil to solution ratio of 6g to 120mL in 250mL centrifuge bottles.

4.1.1 At the conclusion of the extraction, centrifuge samples and vacuum filter solution and combine for next step.

4.1.2 Ensure that at least 475mL of SPLP extract are collected

4.2 Extract test soil in triplicate at the standard 1g to 20mL soil to solution ratio to serve as zero treatment controls

4.2.1 At the conclusion of the extraction, centrifuge samples and syringe filter into separate falcon tubes

4.3 In triplicate, weigh 0.25g of <2mm ground treatment into 50mL centrifuge tubes

4.3.1 Include triplicates of the silica sand test soil

4.4 Add 25mL of filtered SPLP solution extracted from test soil to each tube.

4.5 Shake on reciprocating shaker for 24 hours

4.6 Centrifuge and filter extracts into labeled falcon tubes.

4.7 Rinse the soil remaining in the centrifuge tube three times with 10mL deionized water, centrifuging and disposing of the rinse solution each time

4.8 Dry the sample remaining in the centrifuge tube at 60°C

4.9 Weigh 0.15g of each of the dried treatments into new 50mL centrifuge tubes

4.10 Add 15mL of 0.01M $CaCl_2$ to each of the centrifuge tubes.

4.11 Shake on reciprocating shaker for 24hrs

4.12 Centrifuge and 0.45um syringe filter extracts into labeled falcon tubes.

Soil Carbon and Nitrogen determination by Dry Combustion
Soil Environmental Chemistry Program, The Ohio State University

1.0 SCOPE

1.1 This is an instrumental dry combustion method for determining total Carbon (Nelson and Sommers, 1996) and Nitrogen (Bremner, 1996) in plant and soil like media. The method can also be used to determine organic carbon by employing an acid pretreatment step to remove carbonate minerals.

2.0 DEFINITIONS

2.1 Laboratory Control Sample: The laboratory control sample used for carbon and nitrogen analysis goes through the same preparation procedure as the samples. The composition of carbon and nitrogen in the sample has been determined through repeated intralaboratory measurements.

2.2 Duplicate Samples: A duplicate test involves splitting a sample into sub-samples and processing each through the same sample preparation procedure in order to determine the precision of the method.

2.3 Acid pretreatment: Acid pretreatment involves addition of 10% Hydrochloric acid (HCl) followed by oven drying at 60°C to remove carbonate minerals prior to sample preparation for analysis.

3.0 EQUIPMENT ANND SUPPLIES

3.1 NC2100 soil analyzer CE instruments (Lakewood, NJ).

3.2 Atropina calibration standard (CE instruments, Lakewood, NJ).

3.3 Sulphanilamide calibration check standard (CE instruments, Lakewood, NJ).

3.4 Trace metal grad HCl (Fisher Scientific).

3.5 Tin sample capsules (CE instruments, Lakewood, NJ).

3.6 ≥18 MΩ deionized water.

3.7 Ultra high purity helium.

3.8 Ultra high purity oxygen.

3.9 Compressed air.

4.0 PROCEDURE

4.1 Oven dry samples at 60°C and grind to allow for a homogeneous 50 to 100mg subsample to be taken out for analysis.

4.2 Instrument set up and calibration:

4.3 Perform four point linear calibration curve using an atropine standard (4.84% N, 70.055% C) weighed to the nearest 0.01mg. The instrument linear calibration range is approximately 1mg to approximately 7mg of atropine, corresponding to:

0.0484mg N - 0.339mg N

0.7055mg C - 4.938mg C

4.4 Record Calibration information in Appendix B.

4.5 Weigh samples in duplicate into tin capsules to the nearest 0.01mg and record sample name and mass in Appendix B.

4.6 The mass chosen for the sample should not exceed 100mg and should put the sample C and N within the calibration range.

4.7 Example:

50mg sample weight:

0.0484mg N/50mg sample = 0.0968 %N

0.339mg N/50mg sample = 0.678 %N

0.7055mg C/50mg sample = 1.411 %C

4.938mg C/50mg sample = 9.876 %C

4.8 Input sample masses into Eager 200 software, which allows for results to be given in %C and %N.

4.9 Record Run ID in Carbon Analyzer log.

4.10 Start analysis.

4.11 Maintenance

4.11.1 Soil: Change crucible every 25 samples

4.11.2 Perform routine maintenance in between analytical runs at intervals specified by the manufacturer or when chromatographic quality is suspect.

5.0 QUALITY CONTROL

5.1 Instrument calibration: r^2>0.995 Shall be established for carbon and nitrogen.

5.2 Laboratory Control Sample: The laboratory control sample must fall within ± 20% of the known value. The laboratory control sample must be run with each new calibration of the instrument.

5.3 Sample Duplicates: The relative percent difference (RPD) must be no more than 20%.

$$RPD = 100 \times \frac{/S - D/}{Avg.\ (S,D)}$$

5.4 Initial calibration verification (ICV) is an independent sulphanilimide standard run immediately after calibration Standards must fall within ± 10% of certified value.

5.5 Continuing calibration verification (CCV) is the independent sulphanilimide standard run after every ten samples. Standards must fall within ± 10% of certified value.

5.6 Initial calibration blank (ICB) is a blank tin sample capsule run just prior to the first sample. The blank must not be detectable by the instrument.

5.7 Continuing calibration blank (CCB) is a blank run after every ten samples with the CCV. The blank must not be detectable by the instrument.

6.0 REPORTING

6.1 Fill in Appendix B for sample accounting.

6.2 Complete QC worksheet in appendix A.

6.3 If any of the QC actions fail, the data shall be flagged indicating which QC check failed and determination will be made by the Laboratory Manager if corrective actions should be taken.

7.0 REFERENCES

7.1 Nelson D.W. and Sommers L.E. Total carbon, organic carbon, and organic matter. In Sparks, D. L. Methods of Soil Analysis. Part 3 - Chemical Methods. SSSA Book Series 5. Soil Science Society of America, Madison, WI, 961-1010.

7.2 Bremner J.M. Nitrogen-total. In Sparks, D. L. Methods of Soil Analysis. Part 3 - Chemical Methods. SSSA Book Series 5. Soil Science Society of America, Madison, WI, 1085-1121.

7.3 United States Environmental Protection Agency. Document number ILM04.0b. Contract Laboratory Program Statement of work for inorganic analysis, multi-media, multi-concentration. U.S. EPA: Washington, DC.

Soil Carbon and Nitrogen determination by Dry Combustion Soil
Environmental Chemistry Program, The Ohio State University
Appendix A

Flag	Measurement	QA/QC Check[1]	Frequency	Acceptance Criteria	Corrective Action
a	Calibration	r^2	Calibration	≥0.995	Check calibration stds and recalibrate.
c	Calibration	ICV/LCS	After calibration but before samples.	±10%	Stop analysis, determine and correct problem, and recalibrate.
d	Calibration	CCV/LCS	Every 10 samples	±10%	Stop analysis, determine and correct problem.
f	Instrument Drift/ Sample Carryover	ICB	After calibration but before samples.	Below DL	Stop analysis, determine and correct problem, and recalibrate.
g	Instrument Drift/ Sample Carryover	CCB	Every 10 samples.	Below DL	Stop analysis, determine and correct problem.

Flag	Measurement	QA/QC Check[1]	Frequency	Acceptance Criteria	Corrective Action
i	Method	LCS	1/Run	±20%	Check maintenance and re-analyze.
iii	Reproducibility	Duplicate	Every sample	RPD ±20%	Check sample particle size and homogeneity and re-analyze.

Soil Carbon and Nitrogen determination by Dry Combustion Soil
Environmental Chemistry Program, The Ohio State University
Appendix B

C r^2			N r^2		
Sam	AS		Sam	AS	
1			41		
2			42		
3			43		
4			44		
5			45		
6			46		
7			47		
8			48		
9			49		
10			50		
11			51		
12			52		
13			53		
14			54		
15			55		
16			56		
17			57		
18			58		
19			59		
20			60		
21			61		
22			62		

Soil Carbon and Nitrogen determination by Dry Combustion
Soil Environmental Chemistry Program, The Ohio State University
Appendix B

C r^2			N r^2		
Sam	AS		Sam	AS	
23			63		
24			64		
25			65		
26			66		
27			67		
28			68		
29			69		
30			70		
31			71		
32			72		
33			73		
34			74		
35			75		
36			76		
37			77		
38			78		
39			79		
40			80		

Oxalate Extraction for Reactive Metal Oxides, McKeague and Day, 1966 Soil
Environmental Chemistry Program, The Ohio State University
Version 4

Fill out a New SOP when:

1. The extraction solution is prepared.

Fill out New Appendix when:

2. Previously prepared extraction solution is on a day different than the prepared date.

1.0 SCOPE

1.1 The acid ammonium oxalate extraction (McKeague and Day, 1966) targets poorly crystalline iron and aluminum, while leaving the more crystalline forms of iron and aluminum intact.

2.0 DEFINITIONS

2.1 Laboratory Control Sample: The laboratory control sample is an intralaboratory developed sample whose true value is approximated by the average of repeated measures.

2.2 Duplicate Samples: A duplicate test involves splitting a sample to sub-samples and processing each through the same sample preparation procedure in order to determine the precision of the method.

2.3 Preparation Blank: The Preparation Blank is a sample that contains only the reagents used in the extraction procedure. The preparation blanks is processed through the same preparation procedures as the samples and therefore gives an indication of any contamination picked up during the sample preparation process.

2.4 ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry.

3.0 EQUIPMENT AND SUPPLIES

3.1 Automatic extractant dispenser, 25 mL capability.

3.2 pH Meter accurate to 0.05 units

3.3 Laboratory Balance: Any laboratory balance accurate to within ± 0.0001 grams may be used (all weight measurements are to be within ± 0.001 grams).

3.4 Extraction vessels, 50ml centrifuge tubes

3.5 ≥18 MΩ deionized water (DI)

3.6 Benchtop shaker

3.7 Glass scintillation vials

3.8 15ml Falcon tubes

3.9 High speed centrifuge

3.10 Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$

3.11 Oxalic acid $H_2C_2O_4 \cdot 2H_2O$

3.12 Trace metal grade nitric acid

4.0 PROCEDURE

4.1 Oven dry samples at 60°C.

4.2 Grind samples with either mortar and pestle or puck mill if <250um fraction is being used. No preparation is necessary for >250um size fractions.

4.3 Calibrate pH meter and record result in Appendix.

4.4 0.2M acid ammonium oxalate solution (Ph 3.0).

4.4.1 Solution A: 0.2M Oxalate solution $(NH_4)_2C_2O_4 \cdot H_2O$ (28.3g/L)

4.4.2 Solution B: 0.2M Oxalic acid solution $(H_2C_2O_4 \cdot 2H_2O$ (25.2 g/L)

4.4.3 Mix 700ml of A and 535 ml of B, adjust pH to 3.0 with A or B

4.5 Weigh 0.25 (±0.001g) into 50ml centrifuge tubes and separate into batches of 14 according to analysis sheet labels.

4.6 Check extraction solution pH at time of extraction and record in Appendix.

4.7 Check bottle top dispenser calibration with DI water and record results in Appendix.

4.8 Add 25ml of extraction fluid in batches of 14 samples.

4.8.1 Write start time of extraction on each batch of 14.

4.8.2 Stagger batches by 15 (or more) minutes to allow for centrifugation to stop extraction at exactly four hours.

4.8.3 Cover tubes to allow extraction to take place in darkness and shake for four hours.

4.9 After four hours, remove extractions from shaker and immediately centrifuge for 15 minutes at 9,000 rpm.

4.10 Being careful not to transfer soil, pour off extracts into labeled scintillation vials.

4.11 Dilute extracts x5 with 3% HNO_3 into labeled falcon tubes.

5.0 QUALITY CONTROL

5.1 Laboratory Control Sample (LCS): The laboratory control sample must fall within ± 20% of the known value or within the 95% prediction interval of the certified value. The laboratory control sample must be run with each batch (14) of extractions.

5.2 Sample Duplicates: The relative percent difference (RPD) must be no more than ±20%. At least one sample duplicate must be run with every batch (14) of extractions.

$$RPD = 100 \times \frac{(S - D)}{\text{Avg. } (S,D)}$$

5.3 Preparation Blank: If any analyte concentration is above the method detection limit in the preparation blank, the lowest concentration of the analyte reported in associated samples must be ≥ 10 times the preparation blank concentration. A preparation blank must be run with every batch (14) of extractions.

6.0 REFERENCES

6.1 McKeague, J. and J.H. Day. 1966. Dithionite-and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. of Soil Sci. 46(1): 13-22.

Oxalate Extraction for Reactive Metal Oxides, McKeague and Day, 1966
Soil Environmental Chemistry Program, The Ohio State University
Version 4

Extraction Solution pH at time of extraction

Initials/Date

Pipette Calibration

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

pH Calibration		
pH 2 Buffer	Expiration Date	Start date of use
pH 4 Buffer	Expiration Date	Start date of use
%Slope		

Soil Moisture Holding Capacity, 0 bar
Soil Environmental Chemistry Program, The Ohio State University
Version 5

1.0 SCOPE

1.1 The water holding capacity of soils in pots varies greatly from that of soils in the field. Due to this, a different procedure must be followed to determine the water holding capacity of potted mediums. This procedure outlines a method for determining the water holding capacity of soil and soil like materials in a container.

2.0 DEFINITIONS

2.1 Container capacity, CC: The water holding capacity of a soil medium within a pot or container. It is an equilibrium water content value.

2.2 CC_W: mass water/mass medium

2.3 M_W: mass of water

2.4 M_S: mass of soil

3.0 EQUIPMENT AND SUPPLIES

3.1 Cheesecloth and pots of known base diameter, opening diameter, and side length.

3.2 Balance (capable of measuring >2kg)

3.3 Basins/pools deep enough to all pots to be fully submerged

4.0 PROCEDURE

4.1 Place a piece of cheese cloth in the bottom of each pot to prevent soil loss from the holes in the pot bottom.

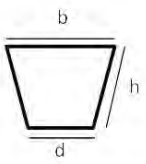
4.2 Weigh the empty pots with cheese cloth and record the mass (determining an average pot/cheesecloth mass may be appropriate when working with a large number of pots).

4.3 Fill the pots with air-dried potting medium and record the mass. All potting material should be thoroughly air dry.

4.4 Saturate pots from below by placing them in a large basins/pools and slowly raising the water level until the pots are submerged. Let the pots sit in the water for 12 hours (overnight).

4.5 Remove pots from the water and situate them, ensuring that they can drain freely. Note: sitting flat on the floor may create water tension around the pot base, preventing free drainage. Allow the pots to drain for 6 hours.

4.6 If a bulk density measurement for the potted material is desired the soil height should be measure at container capacity (after 6 hrs of draining) and the volume of soil calculated using the following equation:



$$V = \frac{\pi h}{12}(d^2 + db + b^2)$$

4.7 Note: in the diagram and equation above, it is difficult to measure b and h directly due to the fact that the pot extends above the soil surface. If Bp and Hp refer to the pot diameter and side length, respectively, then b = d + (h/Hp)(Bp – d). If w refers to the pot side-length that extends from the pot opening to the soil surface, then h = Hp – w.

4.8 Weigh and record the mass of the pots at container capacity. Container capacity determination:

4.8.1 $CC_W = M_W/M_S$

4.9 Bulk density = M_s / volume

5.0 QUALITY CONTROL

6.0 REPORTING

7.0 CORRECTIVE ACTION

8.0 REFERENCES

8.1 Cassel, D.K. and D.R. Nielsen. 1986. Field Capacity and Available Water Capacity. p. 901-926. *In* A. Klute (ed.) Methods of Soil Analysis. Part 1. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

9.0 APPENDIX

10.0 INTERPRETATION

10.1 Container capacity for more than 130 unique soil blends covering a wide range of texture and organic carbon ranged from 14.5 to 49.5%, with a mean of 27.0%. At the time of determining container capacity these soil blends had been allowed several weeks of wetting and drying to form soil structure, and had grass grown on them for 30 days.

Bioaccessible Arsenic and Lead, EPA Method 1340
Soil Environmental Chemistry Program, The Ohio State University
Version 3

1.0 Scope of Method

1.1 This method is typically applicable for the characterization of lead bioaccessibility in soil. The assay may be varied or changed as required and dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. Users are cautioned that deviations in the method from the assay described herein may impact the results (and the validity of the method). The *in vitro* bioaccessibility assay described in this method provides a rapid and relatively inexpensive alternative to *in vivo* assays for predicting relative bioaccessibility of lead in soils and soil-like materials. The method is based on the concept that lead solubilization in gastrointestinal fluid is likely to be an important determinant of lead bioavailability *in vivo*. The method measures the extent of lead solubilization in an extraction solvent that resembles gastric fluid. The fraction of lead which solubilizes in an *in vitro* system is referred to as *in vitro* bioaccessibility (IVBA), which may then be used as an indicator of *in vivo* RBA. Measurements of IVBA using this assay have been shown to be a reliable predictor of *in vivo* RBA of lead in a wide range of soil types and lead phases from a variety of different sites (U.S. EPA, 2007b).

At present, it appears that the relationship between IVBA and RBA is widely applicable, having been found to hold true for a wide range of different soil types and lead phases from a variety of different sites. However, the majority of the samples tested have been collected from mining and milling sites, and it is plausible that some forms of lead that do not occur at this type of site might not follow the observed correlation. Thus, whenever a sample containing an unusual and/or untested lead phase is evaluated by the IVBA protocol, this sample should be identified as a potential source of uncertainty. In the future, as additional samples with a variety of new and different lead forms are tested by both *in vivo* and *in vitro* methods, the applicability of the method will be more clearly defined. In addition, excess phosphate in the sample medium may result in interference (i.e., the assay is not suited to phosphate-amended soils).

2.0 Definitions

2.1 Control Soil (CS): The laboratory control used for the RBALP is a certified reference material (NIST SRM 2711 or 2710) that goes through the same extraction/preparation procedure as the samples. The analyte composition of the laboratory control sample is certified by acid dissolution method 3051a. This SRM should be included in each batch processed.

2.2 Laboratory Control Sample (LCS): A sample which contains only extraction fluid is spiked prior to incubation and run through the complete procedure in order to provide information about the effect of the extraction fluid on bioaccessibility and/or measurement methodology.

2.3 Matrix Spike: A duplicate sample is spiked prior to extraction and run through the complete procedure in order to provide information about the effect of the sample matrix on bioaccessibility and/or measurement methodology.

2.4 Reagent Blank: The Reagent Blank is a sample that contains only the reagents used in the extraction procedure. The preparation blank is processed through the same

preparation procedures as the samples and therefore gives an indication of any contamination picked up during the sample preparation process.

2.5 Duplicate sample: A duplicate of one sample per batch is processed through the same preparation procedures as the samples to determine reproducibility within each batch.

2.6 ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry.

3.0 Equipment and Supplies

3.1 VWR Model 1545 Oven

3.2 Glas-Col Rotator Cat. No. 099A RD50

3.3 Trace metal grade hydrochloric acid.

3.4 Glycine salt

3.5 ≥18 MΩ deionized water (DI).

3.6 175mL high-density polyethylene (HDPE) bottles

3.7 15ml Falcon tubes

3.8 12 ml syringes

3.9 Fisher brand 0.45µm nylon syringe filters

3.10 Spex Certiprep 1000mg/L ICP standard

4.0 Procedure

Review SOP for handling acids prior to beginning the procedure.

4.1 Weigh 1.0 g from each sample to the nearest 0.01 g into a labeled 175 mL acid washed HDPE bottle and record sample mass on analysis sheet.

4.2 Prepare 0.4M glycine extraction solution at 37ºC, adjusting pH to 1.50 +/- 0.5 with trace metal HCl. For a 2L solution, add 60.06g of glycine to a 2L volumetric and fill halfway with lab grade deionized water. To adjust pH to 1.5, start by adding 55 mL of concentrated HCl. Continue to add 1 mL increments of concentrated HCl until the desired pH is met. Before preparing solution, calibrate the pH meter with buffers (2.0, 4.0, and 7.0) that have been heated to 37ºC.

4.2.1 Extraction solution can also be prepared at pH 2.5 for project specific objectives. Note that CS reference values have not been established for pH 2.5.

4.3 Add 100 ± 0.5mL extraction solution with a bottle pipette checked for accuracy (Appendix) to each bottle.

4.4 1mL of 1000 mg/L Pb standard to the blank spike sample and to the matrix spike sample.

4.4.1 Make a Reagent blank spike with 1mL of 1000 mg/L Pb.

4.4.2 Add to the Matrix Spike 1mL of 1000 mg/L Pb.

4.4.3 Check pipette accuracy and record results in appendix prior to spiking the sample.

4.4.4 When using 1000 mg/L standard, pour a small amount into a dixie cup and pipette from the dixie cup. DO NOT return the unused standard to the Certiprep container. Dispose of the unused standard in one of the inorganic waste tubs in the lab.

4.5 Cap the bottle. Properly place the bottles in the rotator and begin rotation. The rotator should be maintained at 30 ± 2 rpm for one hour. If the total time elapsed for the extraction process exceeds 90 minutes (from the time the extraction fluid is added to the final aliquot removal), the test must be repeated

4.6 After the one hour rotation remove a 10mL aliquot of suspension. Syringe filter samples into labeled falcon tubes using dry acid washed syringes and 0.45um nylon syringe filters.

4.7 Measure the pH of the remaining fluid in the extraction bottle and record in analysis sheet. If the fluid pH was not within pH 1.5±0.5, the extraction should be repeated with manual adjustment during the extraction.

4.8 To manually adjust the extraction stop the rotator at 5, 10, 15 and 30 minutes into the extraction and adjust the suspension pH to pH 1.5 ± 0.5 with trace metal grade hydrochloric acid. Discontinue the manual adjustment when the suspension pH remains consistent between adjustment time points.

4.9 Filtered extracts should be stored in the refrigerator at 4°C for preservation until analysis (within one week of extraction). The samples should be analyzed for lead by ICP-AES or ICP-MS (U.S. EPA Method 6010 or 6020, U.S. EPA, 1986).

5.0 Quality Control

5.1 Control Soil (CS): The laboratory control sample must fall within ± 10% of the known value or within the %. The laboratory control sample must be run with each batch of extractions.

NIST SRM 2710a: Analysis of the NIST SRM 2710a standard should yield a mean IVBA result of 67.5% (acceptable IVBA range 60.7-74.2%). For the lead concentration (Pb soil) in the SRM, the median lead concentration presented in the Addendum to the NIST certificate for leachable concentrations determined using Method 3050 (5,100 mg/kg) should be used

NIST SRM 2711a: The NIST SRM 2711a should yield a mean IVBA result of 85.7% (acceptable IVBA range 75.2-96.2%).For the lead concentration (Pb soil) in the SRM, the median lead concentration presented in the Addendum to the NIST certificate for leachable concentrations determined using Method 3050 (1,300 mg/kg) should be used.

5.2 Sample Duplicates: The relative percent difference (RPD) must be no more than ±20%. One sample duplicate must be run with every extraction batch.

$$RPD = 100 \times \frac{(S - D)}{\text{Avg. } (S,D)}$$

5.3 Laboratory Control Sample (LCS): Spike recoveries must fall within the limits of 85-115%. At least one spike analyses (matrix spikes) shall be performed on each batch of extractions. Blank spikes are to be done at the following levels for elements of interest.

Final Spike concentration	mg/L spike solution	mL spike prior to digest
Pb – 10 mg/L	1000	1

5.4 Matrix Spike: Spike recoveries must fall within the limits of 75-125%. At least one spike analyses (matrix spikes) shall be performed on each batch of extractions. Matrix spikes are to be done at the following levels for elements of interest.

Final Spike concentration	mg/L spike solution	mL spike prior to digest
Pb – 10 mg/L	1000	1

5.5 Preparation Blank: If any analyte concentration is above the method detection limit in the preparation blank, the lowest concentration of the analyte reported in associated samples must be ≥ 10 times the preparation blank concentration. A preparation blank must be performed with each for each new preparation of extraction solution.

6.0 Reporting

6.1 If any of the QC actions fail, the data shall be flagged indicating which QC check failed and determination will be made by the Laboratory Manager if corrective actions should be taken.

7.0 References

7.1 United States Environmental Protection Agency. Standard Operating Procedure for an *In Vitro* Bioaccessibility Assay for Lead in Soil. In EPA 9200. 2-86; U.S. EPA: Washington, DC, 2012.

7.2 United States Environmental Protection Agency. Method 6010C. Inductively Coupled Plasma-Atomic Emission Spectrometry. In SW-846; U.S. EPA: Washington, DC, 2007.

7.3 United States Environmental Protection Agency. Method 6020A. Inductively Coupled Plasma-Atomic Mass Spectrometry. In SW-846; U.S. EPA: Washington, DC, 2007.

7.4 Drexler, J.W. and Brattin, W. J. *An In Vitro Procedure for Estimation of Lead Relative Bioavailability: With Validation*. Human and Ecological Risk Assessment (2007, 13, 383-401.

Appendix

Pipette Calibration
Verification

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Mehlich III Extractable Lead and Phosphorus, Mehlich 1984
Soil Environmental Chemistry Program, The Ohio State University
Version 11

1.0 SCOPE

1.1 The Mehlich 3 soil test was developed by Mehlich in 1984 as an improved multi-element extractant for P, K, Ca, Mg, B, Na, Mn, Cu, Fe, and Zn (Mehlich, 1984). It is also applicable to other metals including lead. Today, the Mehlich 3 test is used throughout the United States and Canada because it is well suited to a wide range of soils, both acidic and basic in reaction. The Mehlich 3 is similar in principle to the Bray and Kurtz P-1 test because it is an acidic solution that contains ammonium fluoride. Acetic acid in the extractant also contributes to the release of available P in most soils. A Mehlich 3 value of 45-50 mg P/kg soil is generally considered to be optimum for plant growth and crop yields, higher than the critical values used for other standard soil P tests such as the Bray and Kurtz P-1, Mehlich 1, and Olsen P.

2.0 DEFINITIONS

2.1 Laboratory Control Sample: The laboratory control sample is an intralaboratory developed sample whose true Mehlich 3 value is approximated by the average of repeated measures.

2.2 Duplicate Samples: A duplicate test involves splitting a sample to sub-samples and processing each through the same sample preparation procedure in order to determine the precision of the method.

2.3 Preparation Blank: The Preparation Blank is a sample that contains only the reagents used in the extraction procedure. The preparation blanks is processed through the same preparation procedures as the samples and therefore gives an indication of any contamination picked up during the sample preparation process.

2.4 ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry.

3.0 EQUIPMENT AND SUPPLIES

3.1 Automatic extractant dispenser, 10 mL capability

3.2 pH Meter accurate to 0.05 units

3.3 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.01 grams)

3.4 Extraction vessels, 50ml disposable cups

3.5 ≥18 MΩ deionized water (DI).

3.6 Rotating shaker with a capability of 150 excursions per minute (epm)

3.7 12 ml syringes equipped with 0.45um GMF filters.

3.8 15ml Falcon tubes.

3.9 ACS grade Ammonium fluoride (NH4F)

3.10 EDTA [(HOOCCH2)2NCH2CH2N (CH2COOH)2]

3.11 ACS grade Ammonium nitrate (NH4NO3)

3.12 Glacial acetic acid

3.13 Trace metal grade HNO3

4.0 PROCEDURE

4.1 Mehlich 3 Extracting Solution Preparation: (0.2 M CH3COOH, 0.25 M NH4NO3, 0.015 M NH4F, 0.013 M HNO3, 0.001 M EDTA [(HOOCCH2)2NCH2CH2N (CH2COOH)2].

4.1.1 Add 1000mL of distilled water to a 2 L volumetric flask.

4.1.2 Add 40 g of ammonium nitrate (NH_4NO_3) in the distilled water.

4.1.3 Add 1.11g of ammonium fluoride (NH_4F).

4.1.4 Add 0.585g EDTA.

4.1.5 Add 23 mL glacial acetic acid (99.5%, 17.4 M).

4.1.6 Add 1.6 mL of concentrated nitric acid (HNO3, 68 to 70 %, 15.5 M).

4.1.7 Add distilled water to 2 L final volume and mix well (enough extractant for 200 samples), final pH should be 2.5 ± 0.1.

4.1.8 Check blank and blank filtered solution on ICP prior to analysis. P concentration should be < 0.05 mg/L.

4.2 Weigh 1.00g of soil into extraction cup.

4.3 Calibrate pH meter and record result in Appendix.

4.4 Check extraction solution pH at time of extraction and record in Appendix.

4.5 Check bottle top dispenser calibration with DI water and record results in Appendix.

4.6 Add 10ml of extraction fluid in batches of six samples.

4.7 Shake at 150 or more[a] epm for five minutes at a room temperature at 24 to 27 °C.

4.7.1 The rotation speed should be maintained at an epm that provides vigorous swirling.

4.8 Remove from shaker and immediately 0.45um glass filter (GMF) at least 5ml into falcon tubes.

4.8.1 Rapid filtration is required to limit the extraction time to 5 minutes.

5.0 QUALITY CONTROL

5.1 Laboratory Control Sample (LCS): The laboratory control sample must fall within ± 20% of the known value. The laboratory control sample must be run with each batch of M3 extractions.

5.2 Sample Duplicates: The relative percent difference (RPD) must be no more than ±20%. One sample duplicate must be run with every other batch (1/ 2 batches) of M3 extractions.

$$RPD = 100 \times \frac{(S - D)}{\text{Avg. } (S,D)}$$

5.3 Preparation Blank: If any analyte concentration is above the detection limit in the preparation blank, the lowest concentration of the analyte reported in associated samples must be ≥ 10 times the preparation blank concentration. A preparation blank must be performed with every other batch (1/ 2 batches) of M3 extractions.

6.0 REFERENCES

6.1 Amacher, M.C. 1996. Nickel, Cadmium, and Lead. p. 739-768. *In* J.M. Bartels and J.M. Bigham (ed.) Methods of soil analysis. Part 3. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

6.2 Maynard, D.G., and Y.P. Kalra. 1993. Nitrogen and exchangeable ammonium

6.3 nitrogen. p. 25-26. In M.R. Carter (ed.) Soil Sampling and Methods of Analysis. Lewis Publ., Boca Raton, FL.

6.4 Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15(12): 1409-1416.

6.5 Vitosh, M.L., J.W. Johnson and D.B. Mengel. 1995. Tri-state Fertilizer Recommendations for Corn, Soybeans, Wheat and Alfalfa.

7.0 APPENDIX

Extraction Solution pH day of extraction

Batches completed

Initials/Date

Pipette Calibration

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

pH Calibration		
pH 2 Buffer	Expiration Date	Start date of use
pH 4 Buffer	Expiration Date	Start date of use
%Slope		

8.0 INTERPRETATION

8.1 The Mehlich3 extraction was developed for P, K, Mg, Ca, Mn, Fe, Cu, Zn, B, and Na from acid soils, but is applicable to other metals, including Cd, Cu, Ni, and Pb (Mehlich, 1984, Amacher, 1996, Maynard and Kalra, 1993). The Mehlich3 extraction is commonly used to evaluate plant available nutrients. Table 1 shows critical soil test values for several elements (Vitosh, Johnson, and Mengel, 1995).

Table 1. Mehlich3 critical soil test levels for macronutrients P, K, Ca, and Mg, for corn, soybean, wheat, and alfalfa.

	Corn	Soybean	Wheat	Alfalfa
	——— mg kg^{-1} ———			
P	21-43	21-43	36-57	36-57
K	149-184	149-184	149-184	149
Ca	267	267	267	267
Mg	57	57	57	57

Total TAL Metals (Except Mercury), EPA 3051A
Soil Environmental Chemistry Program, The Ohio State University
Version 12

1.0 SCOPE

1.1 This method is a microwave-assisted extraction using aqua regia and HNO_3. This method is more aggressive in dissolving the sample matrix than methods using conventional heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl), according to EPA Methods 200.2 and 3050. However, because Method 3051a does not accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total content in samples where the analytes are occluded in recalcitrant mineral phases. This method is applicable to the microwave-assisted acid extraction/dissolution‡ of sediments, sludges, and soils, for the following elements: Aluminum (Al)*, Antimony (Sb)*, Arsenic (As), Barium (Ba)*, Beryllium (Be)*, Boron (B), Cadmium (Cd), Calcium (Ca), Chromium (Cr)*, Cobalt (Co), Copper (Cu), Iron (Fe)*, Lead (Pb), Magnesium (Mg)*, Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Potassium (K), Selenium (Se), Silver (Ag)*, Sodium (Na), Strontium (Sr), Thallium (Tl), Vanadium (V)*, Zinc (Zn). *Indicates elements which typically require the addition of HCl to achieve equivalent results with EPA Method 3050, as noted in reference 3. This method is intended to provide a rapid multi-element acid extraction or dissolution prior to analysis. Many types of samples will be dissolved by this method. A few refractory sample matrix compounds, such as quartz, silicates, titanium dioxide, alumina, and other oxides may not be dissolved and in some cases may sequester target analyte elements. These bound elements are considered non-mobile in the environment and are excluded from most aqueous transport mechanisms of pollution.

2.0 DEFINITIONS

2.1 Laboratory Control Sample: The laboratory control used for the microwave digestion is a standard reference material (SRM) or certified reference material (CRM) that goes through the same extraction/preparation procedure as the samples. The analyte composition of the laboratory control sample is certified by acid dissolution method 3051a, 3050, or equivalent.

2.2 Preparation Blank: The Preparation Blank is a sample that contains only the reagents used in the extraction procedure. The preparation blanks is processed through the same preparation procedures as the samples and therefore gives an indication of any contamination picked up during the sample preparation process.

2.3 Interference Check Standards: To verify interelement and background correction factors for the ICP, an Interference Check Samples (ICS) shall be analyzed with each microwave batch. The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP

2.4 Duplicate Samples: A duplicate test involves splitting a sample two sub-samples and processing each through the same sample preparation procedure in order to determine the precision of the method.

2.5 Pre-digestion Spike: A duplicate sample is spiked prior to digestion in order to provide information about the effect of the sample matrix on the digestion and/or measurement methodology.

2.6 ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry.

2.7 ICP-HG-AES: ICP-AES with sample introduction using automated hydride generation

2.8 ICP-MS: Inductively Coupled Plasma-Mass Spectrometry.

3.0 EQUIPMENT AND SUPPLIES

3.1 MARS 1600 watt microwave (CEM corporation, Mathews, NC).

Note: The microwave power output test, power calibration, and temperature probe calibration should be performed according to manufactures specifications every six months.

3.2 Trace metal grade nitric acid.

3.3 Trace metal grade hydrochloric acid.

3.4 ≥18 MΩ deionized water (DI).

3.5 15ml Falcon tubes

3.6 Spex CeriPrep Spike Sample Standard 1 (Cat# SPIKE-1-500)

4.0 PROCEDURE

4.1 Weigh 0.5g of well-mixed samples in duplicate to the nearest 0.01 g into an acid washed Teflon vessel (4.1a) equipped with a controlled pressure relief mechanism.

4.2 Vessels should go through acid bath and DI rinse followed by 3x rinse with 3% acid from squirt bottle, then 3x rinse with reagent DI from squirt bottle.

Note: Store washed vessels inverted in plastic racks.

4.3 Record mass of sample on analysis sheet.

4.4 Add 1.0 mL of spiking solutions to the spike sample. Check pipette accuracy and record results in Appendix prior to spiking the sample.

4.5 Add 3.0 ± 0.1 mL concentrated trace metal grade hydrochloric acid and 9.0 ± 0.1 mL concentrated trace metal grade nitric acid with pipettes checked for accuracy (Section 9.0, Appendix) to each vessel in a fume hood.

4.5.1 Pipette acids from disposable plastic dixie/solo cups.

4.5.2 Any remaining acid should be collected into glass bottle for ICP torch cleaning.

4.5.3 Seal the vessel according to manufacturer's specifications.

4.5.4 Record the mass of each sample+vessel+acids.

4.6 Properly place the vessel in the microwave system according to the manufacturer's recommended specifications.

4.7 Enable appropriate 3051a method in the MARS unit software according to number of samples.

4.8 Once the digests have cooled to less than 75°C, remove from the microwave, remove one vessel at a time and:

4.8.1 Record the mass on sample worksheet.

4.8.2 The mass must be within 1.0 g of the pre-digest mass.

4.9 Remove cap, tare on vessel and add 38 g ≥18 MΩ DI water.

4.10 Return cap and invert several times.

4.11 Allow sediment to settle and pour off approximately 12 ml into labeled falcon tubes.

4.12 Pour off approximately 10ml of ICSA and 10ml of ICSB into labeled falcon tubes.

4.12.1 Make sure ICSA and ICSB are on the analysis sheet (one set/analysis sheet).

5.0 QUALITY CONTROL

5.1 Laboratory Control Sample (LCS): The laboratory control sample must fall within ± 20% of the known value or within the 95% prediction interval of the certified value. The laboratory control sample must be run with each batch of microwave digestions.

5.2 Sample Duplicates: The relative percent difference (RPD) must be no more than ±20%. One sample duplicate must be run with every microwave batch.

$$RPD = 100 \times \frac{(S - D)}{\text{Avg. } (S,D)}$$

5.3 Preparation Blank: If any analyte concentration is above the detection limit in the preparation blank, the lowest concentration of the analyte reported in associated samples must be ≥ 10 times the preparation blank concentration. A preparation blank must be performed with each batch of microwave digests.

5.4 Pre-digestion Spike: Spike recoveries must fall within the limits of 75-125%. At least one spike analyses (matrix spikes) shall be performed on each batch of digests.

5.5 Interference Check Standard: The analytical results for those target analytes with MDLs < 10 ug/L shall fall within + 2x MDL of the analyte's true value (the true value shall be zero unless otherwise stated) in the ICS Solution A (ICSA). For example, if the analysis result(s) for Arsenic (MDL = 10 ug/L, ICSA true value = 0 ug/L) in the ICSA analysis during the run is + 19 ug/L, then the analytical result for Arsenic falls within the + 2x MDL window for Arsenic in the ICSA. Results for the ICP analyses of Solution AB during the analytical runs shall fall within the control limit of +20% of the true value for the analytes included in the Interference Check Samples.

5.6 INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes (mg/L)		Interferents (mg/L)
ICS B		ICS A & ICS B
Se 0.05	Tl 0.1	Al 500
As 0.1	Zn 1.0	Ca 500
Ba 0.5		Fe 200
Be 0.5		Mg 500
Cd 1.0		
Co 0.5		
Cr 0.5		
Cu 0.5		
Mn 0.5		
Ni 1.0		
Pb 0.05		

5.7 REPORTING

5.8 Worksheets: Fill in appendix for pipettes used during the course of this SOP.

6.0 CORRECTIVE ACTION

Pass/ Fail	Flag	Measurement	QA/QC Check[1]	Frequency	Acceptance Criteria	Corrective Action
	i	3051a Method	LCS	1/batch	±20% or w/in 95% PI	Check microwave function and re-digest batch.
	ii	Sample prep	Blank	1/batch	Below MDL or samples >10x	Check ICP for carryover and dish washing procedures re-digest batch.
	iii	Reproducibility	Duplicate	1/batch	RPD ±20%	Check microwave function and re-digest batch.

Pass/ Fail	Flag	Measurement	QA/QC Check[1]	Frequency	Acceptance Criteria	Corrective Action
	lv	3051a Method/ Matrix affects	Pre-Digest Spike	1/batch	±25%	Check microwave function and ICP for signs of matrix affects. Re-digest batch if ICP is acceptable.
	v	Interferences	ICS	1/batch	See 5.5	Determine how to correct the problem with the ICP and re-analyze samples by ICP.

7.0 REFERENCES

7.1 Brobst, R. 1995. Biosolids management handbook. U.S. Environmental Protection Agency, Denver, CO. https://www.epa.gov/sites/production/files/documents/handbook1.pdf.

7.2 USEPA. 2007. Method 3051a. Microwave assisted acid digestion of sediments, sludges, soils, and oils. *In* SW-846. U.S. Environmental Protection Agency, Washington, DC.

7.3 USEPA. 2007. Method 6010C. Inductively coupled plasma-atomic emission spectrometry. *In* SW-846. U.S. Environmental Protection Agency, Washington, DC.

7.4 US Geological Survey. National Geochemical Survey database. US Department of Interior, http://mrdata.usgs.gov/geochemistry/ngs.html.

7.5 APPENDIX

Pipette Calibration Verification

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

Volume	g DI	g DI	g DI	g DI	g DI	date	initials

8.0 INTERPRETATION

8.1 Soil blends and soil blend components should be screened for elemental toxicity according to the USEPA part 503 table 3 limits (Table 1). US Geological Survey background soil data from Ohio (Table 1) should also be used to assess whether soil blend elemental content falls within typical soil ranges.

Table 1. Background soil ranges for the state of Ohio from the US Geological Survey database (USGS), and USEPA Part 503 limits (Brobst, 1995).

Element	Min	Max	Mean	Median	95th	Part 503 Table 3
			mg kg^{-1}			
Ag	<1	<1	.	.	.	
Al	2.87	7.75	5.05	5.00	7.23	
As	4.30	26.6	9.97	9.70	16.9	41
Ba	242	565	438	450	529.5	
Be	0.800	2.80	1.54	1.50	2.45	
Bi	0.110	0.410	0.215	0.210	0.345	
Ca	0.0800	4.29	0.582	0.440	1.625	
Cd	<0.1	0.900	.	0.300	0.8	39
Ce	30.4	101	62.3	60.1	83.85	
Co	3.30	32.4	11.6	10.7	20.55	
Cr	16.0	66.0	38.4	37.0	58	
Cs	<5	10.0	.	5.00	8	
Cu	7.50	55.1	20.4	19.1	37.15	1500
Fe	1.17	4.29	2.48	2.46	3.55	
Ga	5.89	16.8	10.0	9.61	15.15	
Hg	0.0200	0.190	0.0561	0.0500	0.13	17
In	0.0300	0.0800	0.0462	0.0400	0.07	
K	1.03	2.59	1.67	1.68	2.36	
La	14.4	51.4	31.2	30.1	43.4	
Li	14.0	66.0	30.2	28.0	51.5	
Mg	0.160	1.94	0.482	0.420	0.97	
Mn	155	2710	822	684	2200	
Mo	0.690	12.7	2.94	2.25	7.115	
Na	0.210	1.06	0.556	0.530	0.9	
Nb	6.30	14.0	10.7	10.8	13.75	
Ni	7.80	39.3	21.2	20.2	37.1	420
P	310	3840	873	770	1545	
Pb	16.6	148	33.8	29.8	50.75	300
Rb	40.3	126	76.9	76.5	107	
S	0.0200	0.0900	0.0458	0.0500	0.075	
Sb	0.400	1.74	0.781	0.720	1.255	
Sc	3.90	14.0	7.61	7.30	11.9	
Se	0.300	0.900	0.578	0.600	0.85	100
Sn	1.10	11.0	2.27	1.90	5	
Sr	42.0	193	97.3	89.7	167.5	

Table 1. Background soil ranges for the state of Ohio from the US Geological Survey database (USGS), and USEPA Part 503 limits (Brobst, 1995).

Element	Min	Max	Mean	Median	95th	Part 503 Table 3
	mg kg^{-1}					
Te	<0.1	0.300	.	0.100	.	
Th	4.60	16.6	10.6	10.3	14.2	
Ti	0.210	0.420	0.327	0.330	0.41	
Tl	0.300	1.50	0.743	0.700	1.05	
U	1.70	9.00	4.14	3.90	6.2	
V	31.0	120	65.6	66.0	96.5	
W	0.600	2.40	1.24	1.20	1.8	
Y	10.3	30.9	16.9	15.8	26.8	
Zn	33.0	423	91.9	85.0	158	2800

ICP MANUAL

1.0 Scope

1.1 Inductively coupled plasma-atomic emission spectrometry may be used to determine the following trace elements in solution; Aluminum (Al), Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Boron (B), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Potassium (K), Selenium (Se), Silver (Ag), Sodium (Na), Sulfur (S) Strontium (Sr), Thallium (Tl), Vanadium (V), Zinc (Zn).

2.0 Definitions

2.1 Matrix Spike: A duplicate sample is spiked in order to provide information about the effect of the sample matrix on the sample preparation and/or measurement methodology.

2.2 Serial Dilution: A serial dilution consists of a comparison of the results of a sample and another aliquot diluted by a known factor.

2.3 Laboratory Control Sample: The laboratory control samples is a certified QC standard (or dilution) for ICP analysis. The laboratory control sample is SPEX CertiPrep Group LPC standard 1, Fisher Cat. No. LPC-1-100N.

2.4 ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry.

3.0 Instrumentation and Facilities

3.1 ICP-AES and ICP-HG-AES analysis are carried out on a Varian Vista-MPX ICP-OES (Varian Inc., Walnut Creek, CA) at the Soil Environmental Chemistry Lab, The Ohio State University, Dr. Nick Basta, Director.

4.0 Materials and Supplies

4.1 Single element ICP grade standards (SPEX CertiPrep Group, Metuchen, NJ, Assurance ICP Standards).

4.2 Laboratory control sample, SPEX CertiPrep Group LPC standard 1, Fisher Cat. No. LPC-1-100N.

4.3 Periodic table mix 1 for ICP (TraceCert, Sigma-Aldrich 3050 Spruce Street SAINT LOUIS MO 63103 USA)

4.4 Varian/Agilent tuning solution, Varian part no. 190005800.

4.5 Trace metal grade HCl.

4.6 Hamilton Autodiluter.

4.7 15ml Falcon tubes

5.0 Establishing Detection Limits and Linear Range Verification (For SWEL staff only)

5.1 Method detection limits (MDL) are calculated for specific methods and consequent conditions of that method developed for analysis on ICP. The method detection limit is determined as three times the standard deviation of the signal of 10 blanks solutions. MDLs should be established annually.

5.2 Limit of Quantitation (LOQ) is the lowest reportable concentration with a demonstrated accuracy of ± 20%.

5.3 Linear range verification (LRV) is the demonstration of accuracy at concentrations above the highest standard in the calibration curve. LRV is demonstrated accuracy for the maximum concentration test standard. The demonstrated accuracy is ± 15% for Al, Fe, and K and ± 10% for all other elements. LRV should be established annually.

6.0 Maintenance and Optimization (For SWEL staff only) – To be performed after torch, nebulizer, or spray chamber change.

6.1 Detector Calibration: Calibrate while pumping DI water to the spray chamber. Store detector calibration in dark current folder.

6.2 Wavelength Calibration: Calibrate while pumping Varian tuning solution (Varian part no. 190005800) diluted by a factor of 10.

6.3 Nebulizer flow optimization:

6.3.1 Open 01Neboptimize method and open instrument configuration window.

6.3.2 Power = 1.2 KW.

6.3.3 Plasma flow = 15 L/min.

6.3.4 Auxiliary flow = 2.25 L/min.

6.3.5 Adjust nebulizer flow (0.6 to 0.8) by increments of 5 L/min to obtain the maximum net intensity for Mn 257.610. Record results of optimization in the ICP maintenance Log.

6.3.6 Update templates to optimized nebulizer flow.

6.4 Detection Limit Determination:

6.4.1 Detection limits are determined annually for each routinely analyzed sample matrix/nebulizer combination.

6.4.2 If MDL is out of date, open new worksheet from most recent MDL file and save with new date and perform new MDL determination. Note: File saving performed the same way as 7.2.1.

6.4.3 Perform a single point calibration for every element in the method using a 1mg/L standard prepared in the same matrix as the samples.

6.4.4 Analyze a blank.

6.4.5 Determine the method detection limit as 3x standard deviation of the 10 replicate analysis of the blank.

7.0 ICP-OES Procedure

7.1 Creating a Runlist

7.1.1 Create excel run list of ICP samples with similar matrix. Create from analysis sheet or sample list.

7.1.2 Include analysis ID, ICP run name (Year-# run of that year i.e. 18-1), and ICP sample number. Also include operator, nebulizer (seaspray or slurry), ICP tubing configuration (aka pump tubing colors. Usually blk-blk and blu-blu), elements of interest and associated QC checks to be activated in the method.

7.1.3 A template like the one below that contains this information can be found in the "Runlist Template" spreadsheet on the desktop. This will go in the columns to the right of the sample analysis IDs.

Save run list as "ICPyear - #" on the W drive>SECLab>ICP>year>runlist.

ICP #	ICP Run					
18-1	1					
18-1	2					
		Operator:	Alyssa			
		Instrument	Agilent			
		sample	blk blk			
		waste	blu blu			
		nebulizer	Seaspray			
		matrix	3%			
		Run date:				
		QC				
		CRI	0.04	Ba	Ran did not flag	
		ICV	4	Ba		
		CCV	1	Ba		
		Spike				
		0.25 mL LCP/ 5 mL comp				

7.2 Turning on the ICP

7.2.1 Allow 45 minutes for the ICP to warm up before beginning a run

7.2.2 Ensure that the regulator pressure is 115 PSI and the gas tank pressure is >150 PSI. If the tank pressure falls below 150 PSI at any point in the run, turn on the pressure builder. The speed at which this builds pressure varies greatly between tanks (between 3 and 30 minutes). The pressure builder speed can be increased by opening the valve more and vice versa.

7.2.3 Turn on the water cooler and allow 2 minutes before attempting to turn on the ICP. The ICP will give a failure message if the cooler is off or if insufficient cooldown time has passed.

7.2.4 Hook up all tubing: the yellow tube (gray-gray) for the autodilutor rinse, the blk-blk tubing for the sample, and the blu-blu tubing for the waste line. Ensure the tubing is flowing in the proper direction; both pumps rotate clockwise. Check the waste carboy and replace if full. Refill the rinse solution with 3% HCl (square dispenser by the reagent-grade DI. Use another bottle (behind computer) and funnel to transfer 3% into the container, rather than removing the rinse container. This will prevent flow problems.

7.2.5 Ensure that the nebulizer installed on the instrument is appropriate for your run. A seaspray nebulizer is used for most sample types. A slurry nebulizer is needed for high solids samples. A SWEL staff member can change the nebulizer if needed.

7.2.6 Visually inspect the torch for buildup inside of the torch. Buildup at the end of the torch will not impact the run. A flashlight is useful for this. A SWEL staff member can change the torch if needed.  These icons control the pump flow. The leftmost icon turns off the pump, the rightmost pump is high speed, and the middle icon is normal speed. Turn the pump on normal or high speed and that the flow is in the right direction, that there are no blockages in the line, and that there are no leaks at the junctions.

7.2.7  Select this icon to turn on the torch.  Select this icon to turn off the torch.

7.2.8 As you turn on the torch, watch the flame. The flame will initially flicker or may turn orange. This is normal. However, if this continues, or the torch fails to ignite, let a SWEL lab member know.

7.2.9 After the torch ignites, check the lines for good flow. First, ensure that the spray chamber of the nebulizer is filled with mist, rather than clear. This may take several seconds when the ICP is first started if the lines were cleared in the previous run. The mist may be difficult to see, but turning the pump to fast can make it more visible. Ensure that there is no water building up in the spray

chamber- this may be caused by a blocked waste line or backwards tubes. Ensure there is no liquid traveling up into the torch- this may be caused by backwards lines and will cause the torch to flicker or go out. The torch must be replaced if wet.

7.2.10 After the flame and lines have been checked allow the instrument 45 minutes to warm up before beginning a run.

7.3 Making Standards and QC checks

Stock Concentration (ppm)	Dilution Factor	Standard Concentration (ppm)
10	**10**	**1**
10	**20**	**.5**
10	**100**	**.1**
10	**200**	**.05**
10	**1000**	**.01**

7.3.1 Calibration standards are prepared for each method run by serial dilution of "Periodic table mix 1 for ICP". The dilutions should be done into a matrix comparable to the samples. Preparing 10mL of standard allows for 3 calibrations. Label tubes with matrix, concentration, operator initials, and the date. Discard after 1 week.

7.3.2 Table 1 gives a typical standard set that can be used for most runs. This may not be appropriate in some situations, including when elements of interest include species that are difficult to calibrate and give poor results at higher concentrations (including Fe, K, Al, Ca). Elements can be calibrated separately from standards created of single or batched element standards. If needed, consult SWEL staff for advice on crafting a standard set. Standards should have at least 4 in a set.

7.3.3 QC checks are run to ensure the calibration is still valid, that the standard matrix is appropriate for the sample matrix, and that there are no significant matrix effects. Label tubes with matrix, concentration, operator initials, and the date. Discard after 1 week. They are created and run as follows:

7.3.4 Initial calibration verification (ICV) is performed using the LPC diluted by 5x run immediately after instrument calibration. Standards must fall within ± 11% for ICP-OES.

7.3.5 CRI is performed using the LPC diluted by 500x. run immediately after instrument calibration. Standards must fall within ± 22% for ICP-OES

7.3.6 Continuing calibration verification (CCV) is performed by dilution of the calibration standard. One CCV is run after every ten samples. Standards must fall within ± 11% for ICP-AES.

7.3.7 Continuing calibration blank (CCB) is a calibration blank run after every ten samples with the CCV. The calibration blank must fall below the MDL. If a calibration blank is above the detection limit, the instrument must be recalibrated and the previous samples to the last CCB re-run.

7.4 Making Standards and QC checks

7.4.1 A matrix spike and serial dilution is run with a composite sample to ensure the standard matrix is appropriate for the sample matrix and to ensure that there are no matrix effects. These should be analyzed at the very beginning of a run. If the spike or dilution recoveries fall outside acceptable limits, then the samples should be diluted. A comp set should be run for each matrix included in the run.

7.4.2 Make a composite sample (Comp) by pouring into a separate tube 1-2 mL of a number of samples until approximately 14 mL has been obtained. Cap and invert to fully mix. Because the comp may be used to get an estimate of element concentration in relatively homogenous sample sets (and can predict if dilution is needed), it is best to not include blanks or sample spikes when making the comp.

7.4.3 Matrix Spike (Comp Spike): Use 5mL comp to prepare the comp spk. For elements of interest, the spike should be 1ppm if the concentration in the comp is 0-2 ppm. This can be achieved by spiking 5mL comp with 0.250mL LPC.

7.4.3.1 If the element concentration is greater than 2ppm, the sample should be spiked with a concentration 50-100% of the comp concentration. This can be done using the element standards on the autodilutor cart. The “Spike Calculator” spreadsheet (on desktop) can be used to easily calculate spikes.

7.4.3.2 The matrix spike should not consist of more than 10% of the sample volume.

7.4.3.3 Spike recoveries must fall within the limits of 75-125%.

7.4.3.4 Record matrix spike preparations in ICP run list.

$$\%\text{Difference} = 100 * \frac{\text{(comp spike conc. - initial conc.)}}{\text{Spike added}}$$

7.4.4 Serial Dilution (Comp x5): Prepare dilution using an autodiluter.or pipette. A single 5x dilution is typically used.

7.4.4.1 Record dilution preparations in ICP run list. The % difference for the dilution tests must be no more than 15%

7.4.4.2 An error greater than 15% is acceptable when the dilutions are below the reporting limit.

$$\%Difference = 100 * \left(initial - \frac{(diluted * DilutionFactor))}{Initial}\right)$$

7.5 Setting up the method

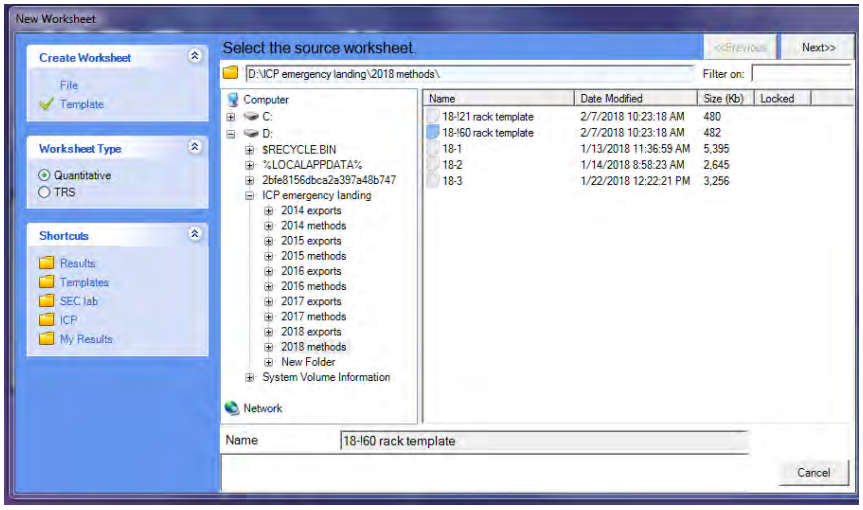
7.5.1 Load method from appropriate template

7.5.2 Agilent: Select File-New…. Under Create Worksheet, select Template.

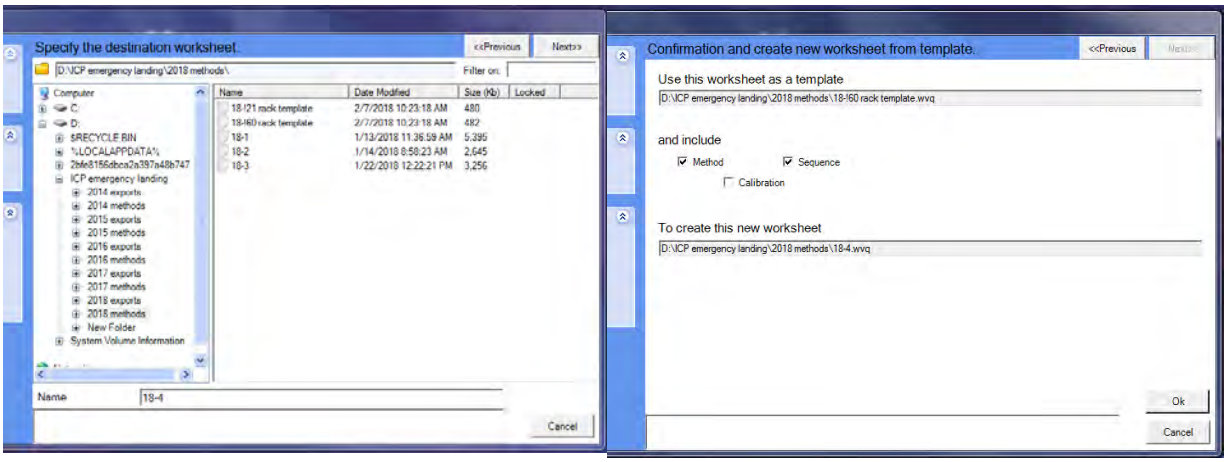
7.5.3 Go to D:\IDP emergency landing\YYYY methods\

7.5.4 A previous run can be used as a template. For a new run, select the 18-21 rack template for 50mL tubes, or the 18-60 rack template for 15mL tubes. Files can be selected in the center pane, not the right pane.

7.5.5 Select next to rename the template to the run name (YYYY-Run#). The run data will be stored in this folder.



7.6 When conduction a new run, select the Method and Sequence options. A new run will be created using the method and sequence of the template run. If the run is to use the same calibration as the template run, select the Calibration option as well.



7.7 Modifying the Method

Select the Method tab>EditMethod…

7.7.1 Adding Elements: The template contains the most commonly run elements. Additional elements can be added in the Element Tab. Select “Add…” to add element. Choose the top two recommended lines. When adding elements, be sure to update the standards and to change the MultiCal parameters to match the other elements (the default values are different than the ones in our template). Update the QC checks and QC blanks (these will automatically be selected for QC actions).

7.7.2 Conditions: For most runs, the template conditions do not need to be changed. For high salt/organic samples, however, increasing the rinse time to 45-60 seconds is recommended.

7.7.3 Standards: The standards in the template correspond to the “Periodic table mix 1 for ICP” standards described above. Standards can be changed or added. Copy and paste are useful functions here. If more than 10 standard solutions are required, then the sequence must be modified (see below). In the template, there are 10 standards but 5 are blanks. While standards can be modified during a run, the number of standards cannot, so blank standards allow additional standards to be added during a run if needed.

7.7.4 QC Test: Checking the boxes turns on QC Actions for an element. Turn on QC Actions for elements on interest for CCV, CRI, and CCB.

7.7.4.1 The QC concentration and % error can be changed here. Changing the QC concentration may be useful for difficult elements if there is high sample concentrations and lower QC conc. are failing.

7.7.5 Most method options cannot be changed once the run is started

7.8 Modifying the Sequence

Select the Sequence tab>Sequence Editor…

7.8.1 If a difference QC set is desired than the one in the template, this can be changed under the Rate generated QC tab of the Sequence Editor.

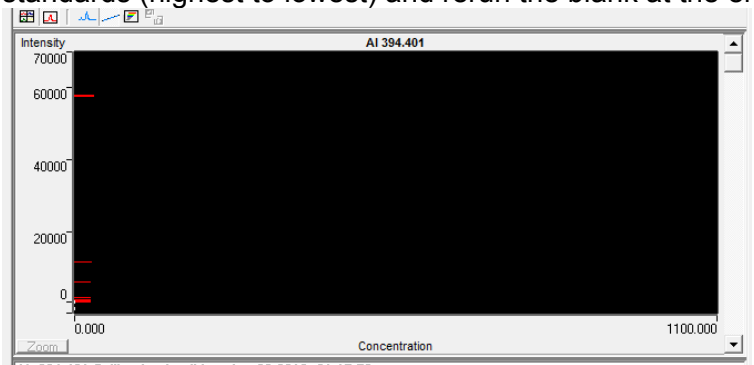
7.8.2 If more than ten standards are required, go to the "Autosampler Setup…" tab to change the standard rack from the 11 rack to the third 60 rack. Under "Rack Properties", change the Type and Use.

7.8.3 Sequence options cannot be changed once the run is started

7.9 Calibration

7.9.1 Go to the Analysis tab. Individual samples cannot be selected until after the run has started. The start arrow will turn green when samples are highlighted. Start and immediately stop the run. Now individual samples can be selected. Selected the blank and run.

7.9.2  Under the Multiple Graphs Spectrum graphs view, inspect the spectrum graphs for each element. While most elements should show no peak, the following elements may have a peak: Ar, B, Be 313, Ca, Cu 324, Fe, K, Mg, Na, S, V, and Zn. If a line is having difficulty calibrating, looking at a previous runlist can help determine whether a blank peak is normal or not. Some elements, notably arsenic, are prone to dirty blanks. If this occurs, rinse on high speed with 24% acid for several minutes. If blank is still dirty, run the standards (highest to lowest) and rerun the blank at the end.



Al 394.401 Calibration (mg/L) on Jan 22 2018, 01:15:58 pm

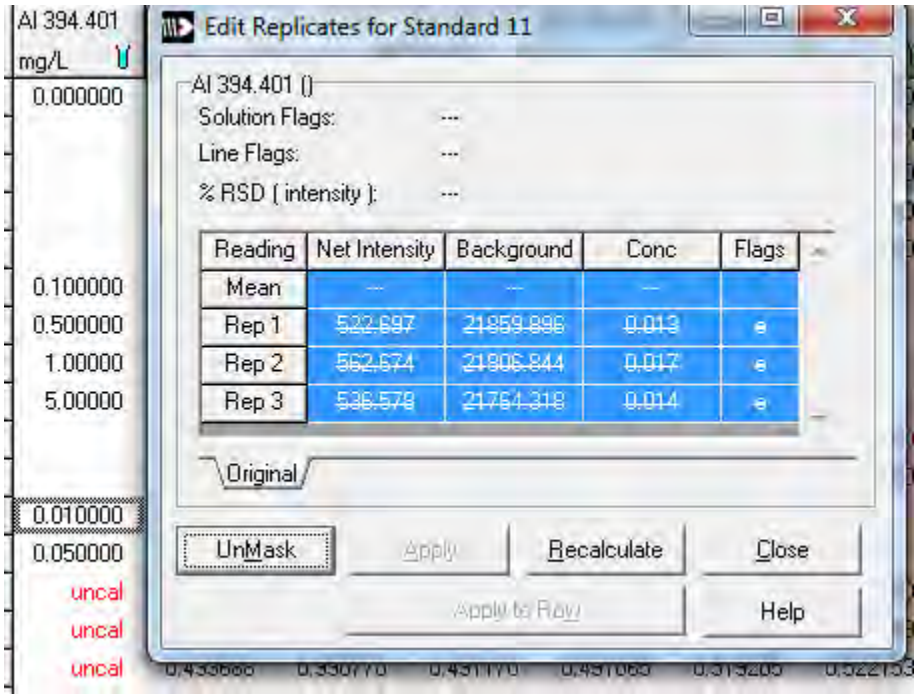
Standard	Flags	Int (c/s)	Std Conc	Calc Conc	Error	%Error
Blank	---	418.2	0.000000	0.003851	0.004	
Standard 5	---	1503.8	0.100000	0.099676	0.000	-0.324
Standard 6	---	5847.6	0.500000	0.483090	-0.017	-3.382
Standard 7	---	11453.1	1.00000	0.977869	-0.022	-2.213
Standard 8	---	57681.6	5.00000	5.05830	0.058	1.166
Standard 11	---	540.6	0.010000	0.014661	0.005	46.613
Standard 12	---	942.1	0.050000	0.050096	0.000	0.191

Correlation Coefficient	0.999967
Status	Maximum error exceeded.
Curve Type	Linear
Curve Coefficient 1:	374.547
Curve Coefficient 2:	11329.312
Blank Offset	374.5

7.9.3 When a clean blank has been obtained, run all standards (including the blank). Once the instrument has run the calibration standards, check to ensure all lines are calibrated. Linear calibration must meet the criteria of: $r^2 = 0.995$, and

calculated concentrations from the regression within 15% for each standard in the calibration. If these conditions are not met, the line will not calibrate. In this case, examine the % error for each element on the "Single Graph Calibration Graph  screen.

7.9.4 Mask values of the calibration with high error. Start with the highest error standard (usually the lowest standard). Right click on that standard and select edit replicates. If the error is low (<20%) and/or there is a clear outlier, mask one replicate and recalculate to try to obtain a curve. Otherwise, mask all replicates and recalculate. This can be repeated with other standards so long as there are at least 3 standards used in the calibration. The reporting limit (RL) for a run is the lowest standard that has at least two replicates.



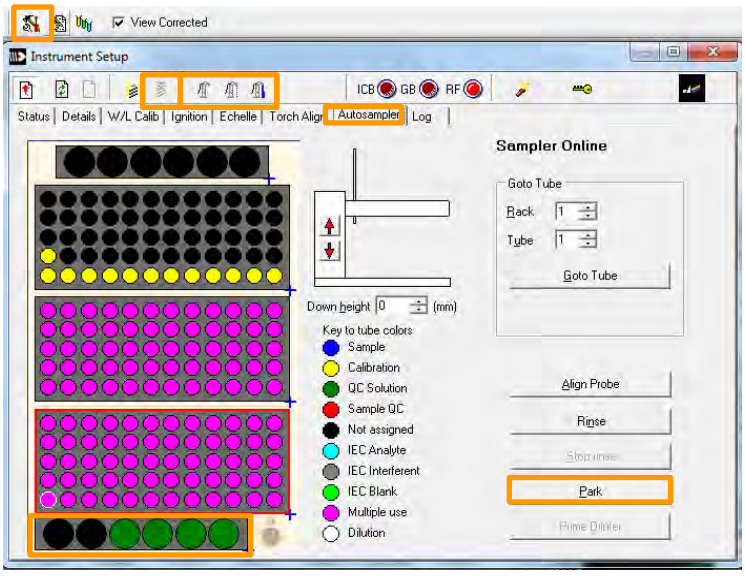
8.0 Running

8.1 After calibration, the run can be started. QC sets are run after the initial calibration and after every 10 samples. QC actions can pause a run if the operator will be nearby (under Sequence Parameters, select "Plasma on & pump slow", or end a run if absent ("Plasma off & pump off").

8.2 In cases where one line is calibrated well but the other line is calibrated poorly or not calibrated, QC actions can be turned off so that the run will not be disrupted by this line. In this case, right click any sample in that line and deselect “QC Actions”.

9.0 Ending a Run

9.1 Operator present: The lines should be rinsed and dried following every run. After all samples have been run, turn the pump speed to fast and rinse with 3% for at least 5 minutes. Subsequently, rinse with DI for at least 10 minutes (fill a 50mL falcon tube with DI and place in an unused space in rack. Open Instrument Setup>Autosampler and double click on the space where the DI tube is located to place the probe there). After rinsing, park the probe and continue pumping until the spray chamber empties. Immediately turn off the ICP (running for prolonged periods without liquid can damage the torch). Pump the lines until dry. Inspect the torch for buildup. Samples high in salts or organic matter can quickly dirty a torch. Inform a SWEL staff member if there is buildup on the torch.



9.2 Operator absent- The rinse procedure after running overnight is the same as described above, but with the ICP off.

10.0 Post-Run and Data Handling

10.1 Methods are stored on D drive during analysis automatically but must be copied to W drive following analysis. (Wdrive>SECLab>ICP>ICP Expert W Drive>year>my results>year.)

10.2 Export data

10.2.1 Highlight samples to be exported (exclude the 10 samples prior to QC failure and failed QC block).

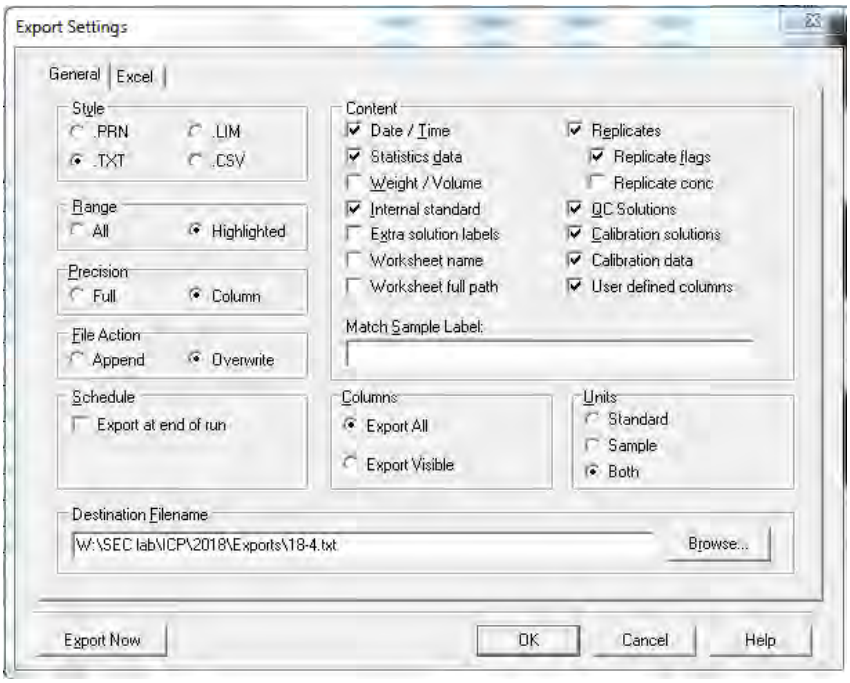
10.2.2 Bring up the Export Settings by pressing ctrl+E or File>Export Settings. The default settings are shown below.

10.2.3 Export selected samples as txt file onto W:\SEC lab\ICP\2018\Exports\YY-#.txt and D:\ICP emergency landing\2018 exports\YY-#.txt

10.2.3.1 YY is the year and # is the ICP number (i.e. 18-5 for the 5th ICP run of 2018)

10.3 Summarize data

10.3.1 See ICP Data Summary and Reporting SOP



11.0 Corrective Action

11.1 Appendix details the quality control checks, frequency, and corrective action procedure for each quality control check.

Flag	Measurement	QA/QC Check[1]	Frequency	Acceptance Criteria	Corrective Action
a	Calibration	r^2	Calibration	≥0.995 ICP-AES	Check calibration stds and recalibrate.
b	Calibration	% Dev	Calibration	±15% ICP-AES	Check calibration stds and recalibrate.
c	Calibration	ICV/LCS	After calibration but before samples.	±10% ICP-AES	Stop analysis, determine and correct problem, and recalibrate.
d	Calibration	CCV/LCS	Every 10 samples	±10% ICP-AES	Stop analysis, determine and correct problem, and recalibrate. Report only values prior to the last good CCV.
e	MDL	LOQ check	After calibration but before samples and after last sample.	±20% ICP-AES	Stop analysis, determine and correct problem, and recalibrate. Report only values prior to the last good LOQ check.
f	Instrument Drift/ Sample Carryover	ICB	After calibration but before samples.	Below MDL	Stop analysis, determine and correct problem, and recalibrate.
g	Instrument Drift/ Sample Carryover	CCB	Every 10 samples.	Below MDL	Stop analysis, determine and correct problem, and recalibrate. Report only values prior to the last good CCB..
h	Linear Range	LRV	Once per analytical run if analyte concentration in the samples is more than 20% greater than highest calibration standard	±10% ICP-AES	If LRV fails, samples with analyte concentrations above the highest calibration standard, must be diluted and re-analyzed.
i	Matrix affects	Matrix spike	One per group of samples with similar matrix type.	±25% ICP-AES	If Matrix spike fails: 1st) Dilute sample, perform matrix spike on diluted sample. If spike still fails or analyte is below MDL then, 2nd) Use internal standard to correct for matrix affect and perform matrix spike using internal correction. If matrix spike still fails then, 3rd) Use standard additions to analyze samples.
j	Matrix affects	Serial Dilution	At least one per group of samples with similar matrix type.	% difference ± 15% if above the RL	If serial dilution fails: 1st) Dilute sample, perform serial dilution on diluted sample. If serial dilution still fails or analyte is below MDL then, 2nd) Use internal standard to correct for matrix affect and perform serial dilution using internal correction. If serial dilution still fails then, 3rd) Use standard additions to analyze samples.

EPA 6010, ICP-AES Data Export and Summary
Soil Environmental Chemistry Program, The Ohio State University
Version 1

1.0 Data export

1.1 Varian Vista MPX

1.1.1 Highlight samples to be exported (exclude the 10 samples prior to QC failure and failed QC block).

1.1.2 Export selected samples as txt onto flash drive.

1.1.3 Transfer txt file onto Wdrive>SEC lab>ICP>year>exports.

1.2 Agilent 720

1.2.1 Highlight samples to be exported (exclude the 10 samples prior to QC failure and failed QC block).

1.2.2 Export selected samples as txt file onto Wdrive>SEC lab>ICP>year>exports.

2.0 Data Summary

2.1 Open txt data file in excel and save as excel file onto Wdrive>SEC lab>ICP>year. This excel file will hereafter be referred to as the "ICP file."

2.2 Copy raw data onto new tab; assign names to new tab (e.g., "rearranged") as well as original tab (e.g., "raw").

2.3 Cut Elements column and insert-paste into column A.

2.4 Select solution label, type, flags, and solution concentration columns (B,C,D,E) and sort by type.

2.5 Delete the "type" column.

2.6 Copy Solution label, flags, and solution concentration columns into ICP no-flag macro (Wdrive>ICP>macro) "r" tab.

2.7 Delete header and run macro according to # of elements and # of replicates (almost always 51, and always 1, respectively).

2.8 The completed macro will appear on the B tab, with column A empty. Copy column A, rows 1-52 of the ICP file into tab B, column A of macro.

2.9 Highlight page (macro, tab B), and copy and paste it onto new tab of ICP file. Label the new tab "post-macro."

2.10 Repeat 2.1-2.9 for all sub-runs (a,b,c, etc.) for the base ICP run (year - #).

2.11 Insert a row at the top of each ICP sub-run and label each column with the sub-run name.

2.12 Make a new tab (e.g., 15-X, a, b,..) on the base ICP file and combine all sub-runs to make an intact sample sequence for the entire run.

2.13 Delete “standards” columns.

2.14 Open ICP run-list file, highlight all cells relating to samples, and copy & transpose-paste them onto a new tab in the ICP run-list file.

2.15 Highlight rows and copy & insert them onto the post-macro tab of the ICP file.

2.16 Shift copied cells over so that “ICP # 1” lines up with sample 1.

2.17 Create min and max columns for CCV, CRI, and ICV. Fill in these columns with the appropriate values.

2.18 Create a max column for ICB and fill it in with the appropriate values.

2.19 Insert MDL (mg/L) and LRV (mg/L) into columns B and C, respectively. MDL and LRV vary according to the sample matrix (e.g., 24% acid), and can be found on the W drive. The matrix identity for the samples in question will be indicated on the ICP run-list file.

2.20 Copy & paste columns relevant to method QC (e.g., duplicates, check soil, blank, ISA, ISB, etc.) onto a new tab in the ICP file. Label this new tab “method QC.” QC measures for all methods are described by the method SOP. Add information necessary to checking QC (e.g., check soil element concentrations) to the “method QC” tab.

2.21 Perform the necessary calculations for checking method QC.

2.22 Create a new tab entitled “summary” that contains starting from column B; MDL (mg/L), LRV (mg/L), ICP QC summary only (min, max), followed by method QC results (% rec, RPD, etc), then samples.

2.23 Create a new tab (“Lines”) and select 1 analytical line for each element based on ICP and method QC results.

EPA LEAD SORPTION TEST METHOD

Outline version of SPLP Biochar Challenge

Extracting Sample Soil with SPLP Extraction Fluid

1. We make up the SPLP extraction solution based upon where the sample soil material is from.
    a. Extraction fluid (#1) pH = 4.20 ± 0.05 for soils from east of the Mississippi River
    b. Extraction fluid (#2) pH = 5.00 ± 0.05 for soils from west of the Mississippi River
2. The extraction fluid is added to the sample soil in a ratio of 20:1, on a weight basis. For every 1 gram of dry soil we add 20 grams of extraction fluid.
3. The extraction fluid and soil are placed in a large plastic bottle with a tight fitting lid. They are placed in an end-over-end rotary mixer.
4. These are mixed at approximately room temperature (23 + 2°C) for 18 ± 2 hours.
5. At the end of the mixing period the supernatant is decanted off into a clean bottle and is then passed through a 0.45 µM membrane filters. The filtered solution is stored in a clean container and kept refrigerated (≈4°) until needed.

Challenging Candidate Biochars with SPLP Solution

1. The next step is to carefully weigh out 0.25 grams of the candidate biochars. [We use 50 ml Falcon or Corning brand centrifuge tubes.] We use a minimum of 3 replicates of each biochar. We also us a minimum of 3 SPLP blanks that are run through the same process with the exception being that they are not exposed to any biochar. We use 3 blanks per 30 samples
2. To each of these we add 25.00 ± 0.05 mls of filtered SPLP solution. For quality control, we weigh the tube, biochar and SPLP solution in the event it's necessary to make any volume addition corrections.
3. We place these on a box shaker in a climate controlled room or space (23 + 2°C) at a vigorous pace of back and forth movement (≈ 100 oscillations per minute). These shake for 24 hours.
4. After 24 hours the samples are again passed through a 0.45 µM membrane filter to separate the SPLP solution from the biochar.
    a. After the filtrate is removed, the biochar on the membrane is washed with copious amounts of MEQ water to remove any remaining un-bound metals.
    b. The membranes containing ≈ 0.25 grams of biochar are placed into clean bottles and placed in a 60°C oven and are dried for at least 24 hours.
5. The filtrates are placed in clean bottles with tight fitting lids and moved to a refrigerator until they can be analyzed via ICP.

Challenging the Sorbed Metals with 0.01M $CaCl_2$ Solution

1. The next step is to carefully weigh out 0.15 grams of the biochars with sorbed metals that were produced earlier and dried at 60°C. Again we weigh the biochar+bottle.
2. To these we add 15 mls of 0.01 M $CaCl_2$. The goal of this extraction is to determine which of the biochars tested give up the least amount of sorbed metals.
3. We place these on a box shaker in a climate controlled room or space (23 + 2°C) at a vigorous pace of back and forth movement (≈ 100 oscillations per minute). These shake for 24 hours.
4. After 24 hours the samples are again passed through a 0.45 µM membrane filter to separate the SPLP solution from the biochar.
    a. After the filtrate is removed, the biochar on the membrane is washed with copious amounts of MEQ water to remove any remaining $CaCl_2$ solution.

   b. The membranes containing ≈ 0.15 grams of biochar are placed into clean bottles and placed in a 60°C oven and are dried for at least 24 hours.
   c. Once dry, these membranes are stored in sealed Falcon or Corning centrifuge
5. The filtrates are placed in clean bottles with tight fitting lids and moved to a refrigerator until they can be analyzed via ICP.

Summarizing the Results

1. This is basically putting together all the gathered information to determine the following:
   a. Which biochar removed which metals?
   b. How does the amount removed compare to the total metal content as determined by running the SPLP solutions that have been through the entire process, but not exposed to biochar?
   c. Once the metals are sorbed onto the biochar, which ones retain the sorbed metals when challenged with the 0.01 M $CaCl_2$ solution?
2. We use stats to help sort all of this out.
3. We also view it graphically.
4. The ultimate goal is to identify those biochars that are effective at removing metals from the SPLP extract and holding onto them when challenged with the 0.01 M $CaCl_2$ solution.

Short Version of EPA Method 1312 – Synthetic Precipitation Leaching Procedure (SPLP)

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

2.0 SUMMARY OF METHOD

2.2 For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3.

Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid. If preferred, a more dilute H_2SO_4/HNO_3 acid mixture may be prepared and used in steps 5.4.1 and 5.4.2 making it easier to adjust the pH of the extraction fluids.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

7.2 Procedure When Volatiles Are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 % solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.9 If the sample contains <0.5% dry solids (see Step 7.1.2), proceed to Step 7.2.13. If the sample contains >0.5 % dry solids (see Step 7.1.1 or 7.1.2), and if particle-size reduction of the solid was needed in Step 7.1.3, proceed to Step 7.2.10. If the sample as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.2.11.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

For dry soils (From 2.2) "The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase." [Since we use a ratio of 100:1, SPLP:Biochar when we use the SPLP solution to challenge the biochars (e.g., 25.0 mls of SPLP:0.25 grams of biochar), we use this information we calculate how much SPLP solution we're going to need and collect what we need plus some to cover the blanks that we'll need.]

Slowly add this amount of appropriate extraction fluid (see Step 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure I rotary (end over end) extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 + 2EC during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 7.2.7.

For final filtration of the 1312 extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

[We use 0.45 µM membrane filters remove any suspended material from the SPLP extract.]

Once we have the filtered SPLP solution we refrigerate it and use it as soon as possible. The hold time for this solution is 180 days (for metals except Hg.). This is the solution that we use to challenge the biochars.

METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

2.0 SUMMARY OF METHOD

2.1 For liquid samples (i.e., those containing less than 0.5 % dry solid material), the sample, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the 1312 extract.

2.2 For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero Headspace Extraction Vessel (ZHE). This device is for use only when the sample is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device and effectively precludes headspace. This type of vessel allows for initial liquid/solid

separation, extraction, and final extract filtration without opening the vessel (see Step 4.3.1). These vessels shall have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psig or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psig, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psig, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.3) refers to pounds-per-square-inch (psig), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the sample is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extraction Vessel (ZHE): When the sample is evaluated for volatiles, the zero-headspace extraction vessel described

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[1]VITON® is a trademark of Du Pont.

in Step 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psig).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the sample is evaluated for other than volatile analytes, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psig or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 %) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are listed in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components of interest. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8-μm . Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with reagent water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to $\pm$ 0.05 units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract when using the ZHE device. These devices listed are recommended for use under the following conditions:

[2]TEDLAR® is a registered trademark of Du Pont.

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1 % of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1 % of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 % solid) or has no significant solid phase (is <0.5% solid) , either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas-tight syringe, pressure filtration unit (see Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid. If preferred, a more dilute H_2SO_4/HNO_3 acid mixture may be prepared and used in steps 5.4.1 and 5.4.2 making it easier to adjust the pH of the extraction fluids.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

5.4.3 Extraction fluid #3: This fluid is reagent water (Step 5.2) and is used to determine cyanide and volatiles leachability.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.5 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 There may be requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of the percent

solids and the particle size. An aliquot may be needed to conduct the nonvolatile analyte extraction procedure. If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the sample is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to extraction).

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Step 8.0 (Quality Control) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary 1312 evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo 1312 extraction. These preliminary evaluations include: (1) determination of the percent solids (Step 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Step 7.1.2); and (3) determination of whether the solid portion of the waste requires particle size reduction (Step 7.1.3).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a representative subsample (100 g minimum) and proceed to Step 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device

discussed in Step 4.3.2, and is outlined in Steps 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: If sample material (>1 % of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.1.5 to determine the weight of the sample that will be filtered.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the sample by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.1.9)}}{\text{Total weight of waste (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Step 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.1.3 to determine whether the solid material requires particle size reduction or to Step 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.1.9 is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 with a fresh portion of the waste if the volatile 1312 analysis is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 $\pm$ 20°C until two successive weighings yield the same value within $\pm$ 1 %. Record the final weight.

Caution: The drying oven should be vented to a hood or other appropriate device to eliminate the possibility of fumes from the sample escaping into the laboratory. Care should be taken to ensure that the sample will not flash or violently react upon heating.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry sample + filter) - tared weight of filter}}{\text{Initial weight of sample (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 if the volatile 1312 analysis is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile 1312 analysis is to be performed, return to the beginning of this Step (7.1) and, with a fresh portion of sample, determine whether particle size reduction is necessary (Step 7.1.3).

7.1.3 Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the sample, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Step 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid:

7.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

7.1.4.2 For wastes and wastewater, extraction fluid #1 should be used.

7.1.4.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.1.5 If the aliquot of the sample used for the preliminary evaluation (Steps 7.1.1 - 7.1.4) was determined to be 100% solid at Step 7.1.1.1, then it can be used for the Step 7.2 extraction (assuming at least 100 grams remain), and the Step 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Step 7.3. The aliquot of the waste subjected to the procedure in Step 7.1.1.7 might be appropriate for use for the Step 7.2 extraction if an adequate amount of solid (as determined by Step 7.1.1.9)

was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 7.2.10 of the nonvolatile 1312 extraction.

7.2 Procedure When Volatiles Are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 % solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the sample (100 gram minimum) and record the weight. If the waste contains <0.5 % dry solids (Step 7.1.2), the liquid portion of the waste, after filtration, is defined as the 1312 extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the 1312 extract. For wastes containing >0.5 % dry solids (Steps 7.1.1 or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the 1312 extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered followed by

filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point if not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

NOTE: If waste material (>1 % of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5, to determine the weight of the waste sample that will be filtered.

NOTE:Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Step 7.2.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the sample contains <0.5% dry solids (see Step 7.1.2), proceed to Step 7.2.13. If the sample contains >0.5 % dry solids (see Step 7.1.1 or 7.1.2), and if particle-size reduction of the solid was needed in Step 7.1.3, proceed to Step 7.2.10. If the sample as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.2.11.

7.2.10 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.1.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 7.2.7. For final filtration of the 1312 extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the 1312 extract as follows:

7.2.13.1 If the sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.2.12 is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 7.2.12 with the initial liquid phase of the sample obtained

in Step 7.2.7. This combined liquid is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Step 7.2.7, is not or may not be compatible with the filtered liquid resulting from Step 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the 1312 extract, and combine the results mathematically, as described in Step 7.2.14.

7.2.14 Following collection of the 1312 extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The 1312 extract shall be prepared and analyzed according to appropriate analytical methods. 1312 extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5 %), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\,(C_1) + (V_2)\,(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles Are Involved

Use the ZHE device to obtain 1312 extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psig), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (see Step 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in Steps 4.6.1-4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Step 7.3, Step 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the sample is 100% solid (see Step 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Step 7.3.5.

7.3.4 If the sample contains <0.5% dry solids (Step 7.1.2), the liquid portion of waste, after filtration, is defined as the 1312 extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing $\geq$0.5% dry solids (Steps 7.1.1 and/or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For samples containing <5% solids (see Step 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Step 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Step 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle-size reduction of the solid portion of the sample was required in Step 7.1.3, proceed to Step 7.3.6. If particle-size reduction was not required in Step 7.1.3, proceed to Step 7.3.7.

7.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Step 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge samples prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate.

Note: If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psig (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the

amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 % solid (see Step 7.1.1), slowly increase the pressure to a maximum of 50 psig to force most of the headspace out of the device and proceed to Step 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psig to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When liquid flow has ceased such that continued pressure filtration at 50 psig does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the 1312 extraction as a solid.

If the original waste contained <0.5 % dry solids (see Step 7.1.2), this filtrate is defined as the 1312 extract and is analyzed directly. Proceed to Step 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (see Steps 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 is used in all cases (see Step 5.4.3).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psig (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psig and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2°C during agitation.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the ZHE is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 7.3.9. All extracts shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured

7.3.14 If the original sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.3.13 is defined as the 1312 extract. If the sample contained an initial liquid phase, the filtered liquid material obtained from Step 7.3.13 and the initial liquid phase (Step 7.3.9) are collectively defined as the 1312 extract.

7.3.15 Following collection of the 1312 extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the 1312 extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume- weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\,(C_1) + (V_2)\,(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Step 8.0 for quality assurance requirements.

8.0 QUALITY CONTROL

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel. Refer to Chapter One for additional quality control protocols.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the 1312 extract and before preservation. Matrix spikes should not be added prior to 1312 extraction of the sample.

8.2.2 In most cases, matrix spike levels should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the

spike concentration may be as low as one half of the analyte concentration, but may not be less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of 1312 extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the 1312 extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%\ \text{Recovery}) = 100\ (X_s - X_u) / K$$

where:

X_s = measured value for the spiked sample
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the 1312 extract is not at least 50% and the concentration does not exceed the appropriate regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standards as the independent variable (x-axis). Solve for the intercept

of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependant variable versus the independent variable. Derive concentrations for the unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo 1312 extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (days)

	From: Field Collection To: 1312 extraction	From: 1312 extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360
NA = Not Applicable				

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Precision results for semi-volatiles and metals: An eastern soil with high organic content and a western soil with low organic content were used for the semi-volatile and metal leaching experiments. Both types of soil were analyzed prior to contaminant spiking. The results are shown in Table 6. The concentration of contaminants leached from the soils were reproducible, as shown

by the moderate relative standard deviations (RSDs) of the recoveries (averaging 29% for the compounds and elements analyzed).

9.2 Precision results for volatiles: Four different soils were spiked and tested for the extraction of volatiles. Soils One and Two were from western and eastern Superfund sites. Soils Three and Four were mixtures of a western soil with low organic content and two different municipal sludges. The results are shown in Table 7. Extract concentrations of volatile organics from the eastern soil were lower than from the western soil. Replicate leachings of Soils Three and Four showed lower precision than the leachates from the Superfund soils.

10.0 REFERENCES

1. Environmental Monitoring Systems Laboratory, "Performance Testing of Method 1312; QA Support for RCRA Testing: Project Report". EPA/600/4-89/022. EPA Contract 68-03-3249 to Lockheed Engineering and Sciences Company, June 1989.

2. Research Triangle Institute, "Interlaboratory Comparison of Methods 1310, 1311, and 1312 for Lead in Soil". U.S. EPA Contract 68-01-7075, November 1988.

Table 1. Volatile Analytes[1]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

Table 2. Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S); 8-vessel extractor (DC20); 12-vessel extractor (DC20B)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2); 4-vessel (3740-4); 6-vessel (3740-6); 8-vessel (3740-8); 12-vessel (3740-12); 24-vessel (3740-24)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 1-liter bottle extractor (YT300RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 $\pm$2 rpm is acceptable.

Table 3. Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C1O2, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT3OO9OHW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device

[1] Any device that meets the specifications listed in Step 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4. Suitable Filter Holders[1]

Company	Location	Model/ Catalogue #	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5. Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7

[1] Any filter that meets the specifications in Step 4.4 of the Method is suitable.

TABLE 6 - METHOD 1312 PRECISION RESULTS FOR SEMI-VOLATILES AND METALS

		Eastern Soil (pH 4.2)		Western Soil (pH 5.0)	
	Amount Spiked (µg)	Amount Recovered* (µg)	% RSD	Amount Recovered* (µg)	% RSD
FORTIFIED ANALYTES					
bis(2-chloroethyl)-ether	1040	834	12.5	616	14.2
2-Chlorophenol	1620	1010	6.8	525	54.9
1,4-Dichlorobenzene	2000	344	12.3	272	34.6
1,2-Dichlorobenzene	8920	1010	8.0	1520	28.4
2-Methylphenol	3940	1860	7.7	1130	32.6
Nitrobenzene	1010	812	10.0	457	21.3
2,4-Dimethylphenol	1460	200	18.4	18	87.6
Hexachlorobutadiene	6300	95	12.9	280	22.8
Acenaphthene	3640	210	8.1	310**	7.7
2,4-Dinitrophenol	1300	896**	6.1	23**	15.7
2,4-Dinitrotoluene	1900	1150	5.4	585	54.4
Hexachlorobenzene	1840	3.7	12.0	10	173.2
gamma BHC (Lindane)	7440	230	16.3	1240	55.2
beta BHC	640	35	13.3	65.3	51.7
METALS					
Lead	5000	70	4.3	10	51.7
Cadmium	1000	387	2.3	91	71.3

* = Triplicate analyses.
** = Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

TABLE 7 - METHOD 1312 PRECISION RESULTS FOR VOLATILES

Compound Name	Soil No. 1 (Western) Avg. %Rec.*	%RSD	Soil No. 2 (Eastern) Avg. %Rec.*	%RSD	Soil No. 3 (Western and Sludge) Avg. %Rec.**	%RSD	Soil No. 4 (Western and Sludge) Avg. %Rec.***	%RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl Alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethane	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl -1-propanol)	0.0	ND	0.0	ND	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloro-ethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloro-ethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloro-ethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloro-ethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichloro-fluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichloro-trifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.2	20.3	7.17	72.8	25.0	61.0	11.8	25.4

* Triplicate analyses
** Six replicate analyses
*** Five replicate analyses

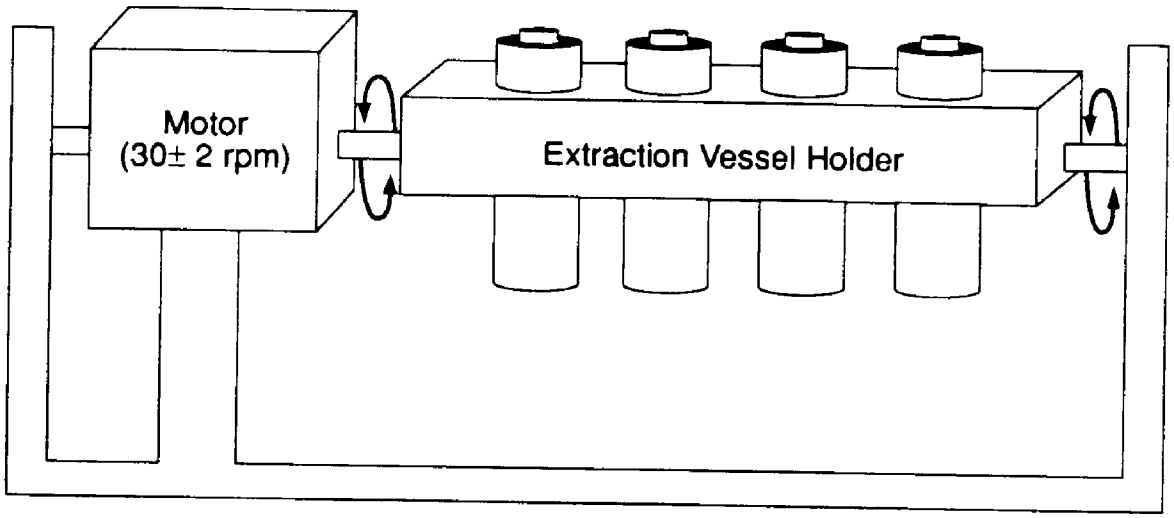


Figure 1. Rotary Agitation Apparatus

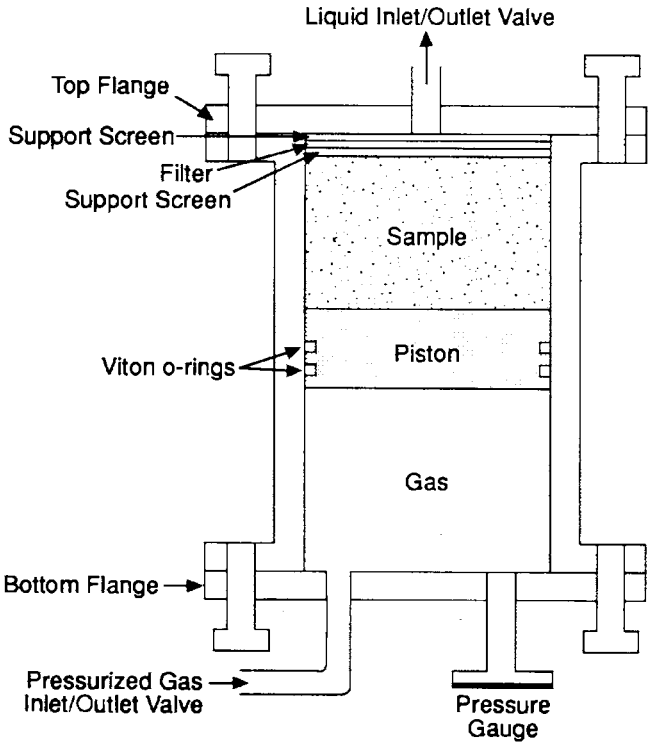
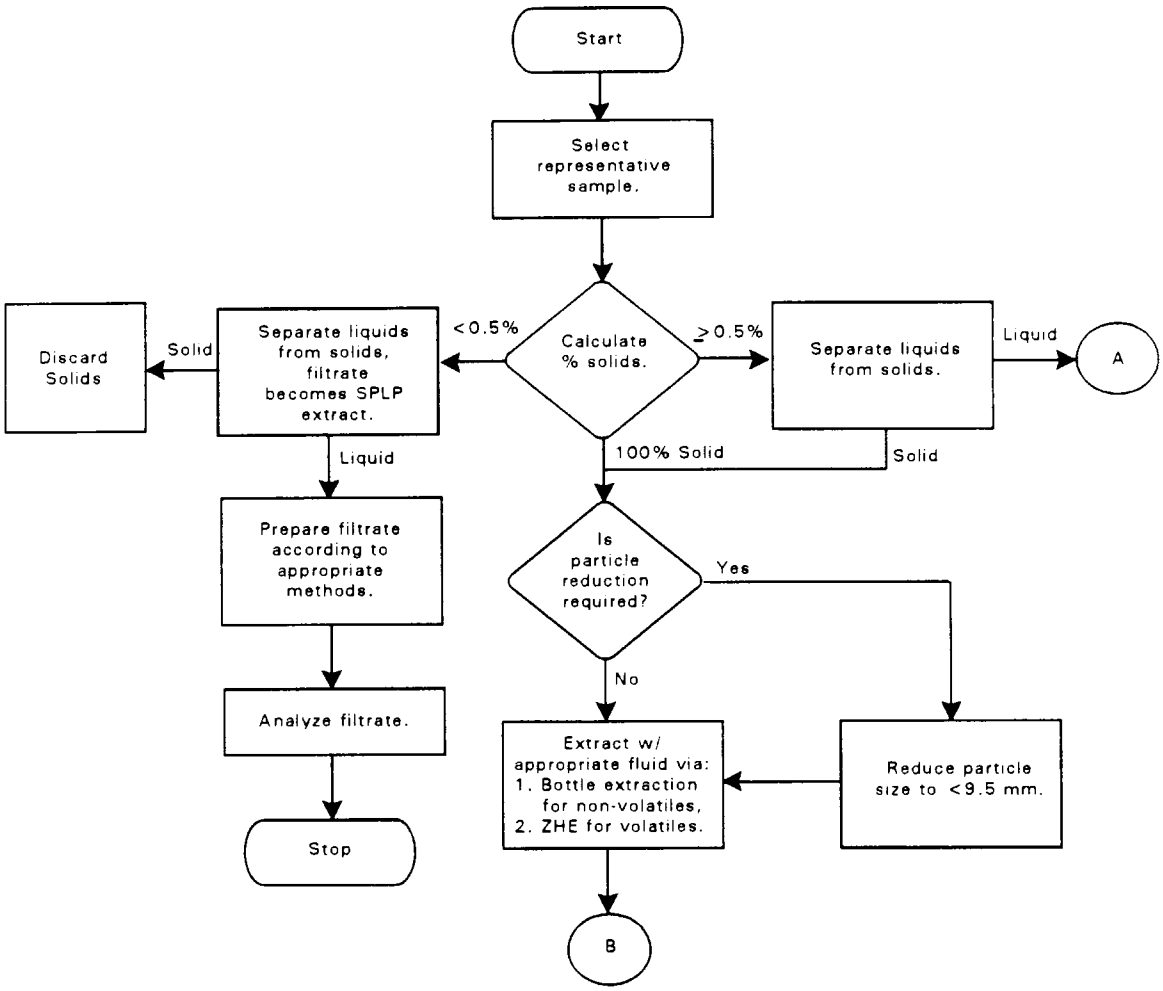
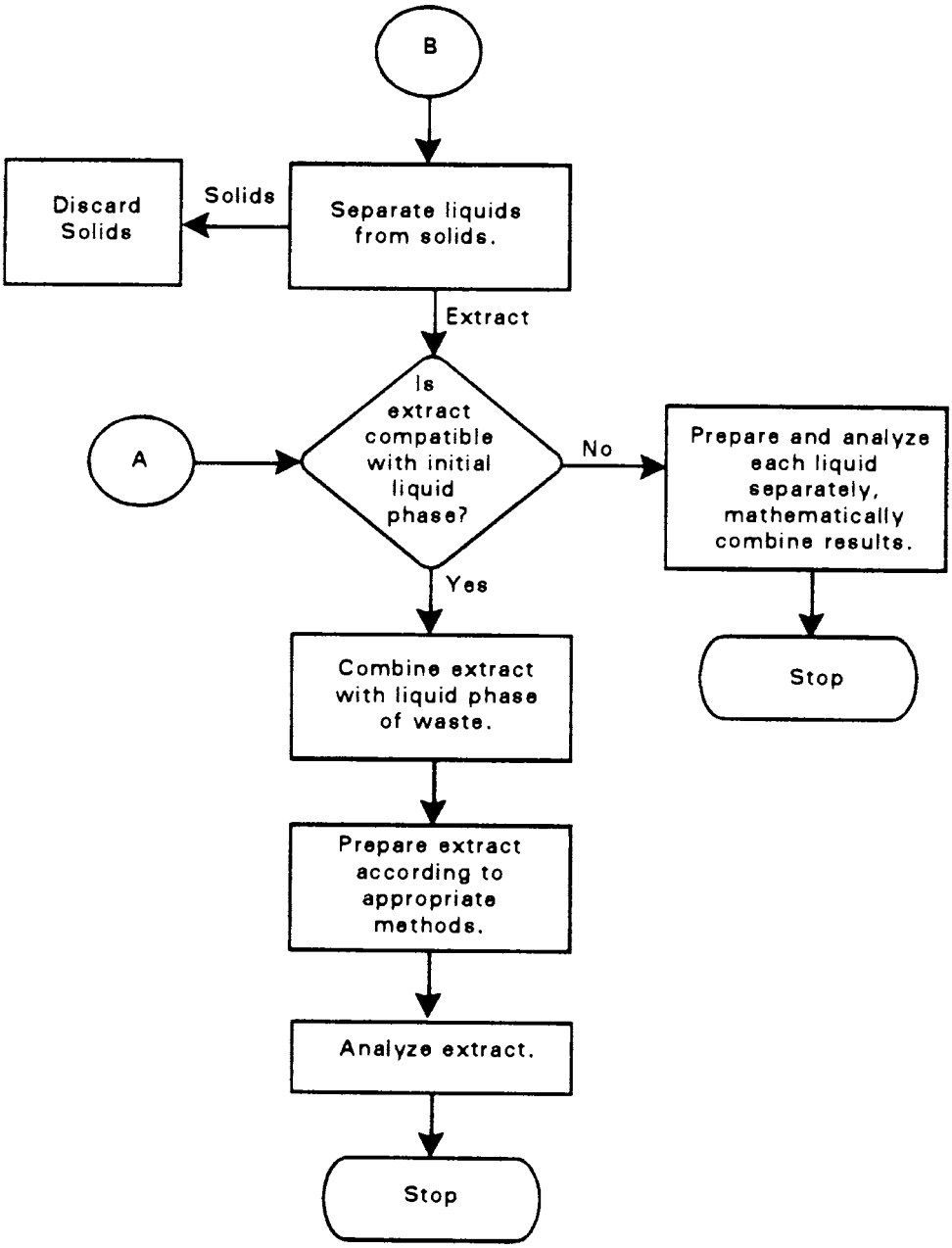


Figure 2. Zero-Headspace Extractor (ZHE)

SYNTHETIC PRECIPITATION LEACHING PROCEDURE



SYNTHETIC PRECIPITATION LEACHING PROCEDURE (continued)



STANDARD OPERATING PROCEDURES FOR ALS

9/18/2020

Subsampling and Compositing of Samples

DOCUMENT ID: SOILPREP-SUBS, REV 2.0

Prepared By: _____ Date: 3/4/2020
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1) Scope & Applicability

1.1 This standard operating procedure describes procedures for obtaining subsamples used for laboratory analysis. The procedure also describes general practices for making composite samples from multiple individual samples. Procedures are given for aqueous, soil, sediment, vegetation and miscellaneous matrices. The SOP does not apply to tissue samples. Procedures for tissue samples are described in the GEN-TISP and MET-TDIG SOPs.

1.2 The SOP describes routine, or default, procedures for samples that do not require VOC analyses. Handling of VOC samples is described in SOP VOC-5035. Program or project-specific requirements may differ from those described in the SOP. Samples analyzed by EPA CLP procedures are specifically excluded from this procedure, and will be handled according to the applicable SOW.

1.3 Multi-increment samples require special handling and subsampling procedures. The procedures for handling multi-increment samples are described in SOP SOILPREP-SUBS.

1.4 This procedure does not apply to situations where the entire sample (container) is used for the analysis.

1.5 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. For example, projects falling under DOD ELAP, QC requirements are defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD%), may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 Obtaining a representative analytical subsample from the field sample submitted is essential to providing meaningful data. The subsample must be taken to most closely reflect the predominant composition of the sample. For aqueous and liquid samples, this is usually accomplished by shaking or inverting the sample. For soil, sediment, powders, and other solids the procedures are more involved. Procedures for subsampling are based on the information given in the references listed.

2.2 Some projects may employ multi-increment (MI) sampling in the field. The primary objective of MI sampling is to control the certain statistical errors associated with discrete sampling. Some studies have shown that MI sampling, using 30+ sample increments within a decision unit (a defined field sampling area) may provide a more representative view of contaminant concentrations than traditional discrete sampling approaches. References listed provide additional background on MI sampling. When this approach is taken it is important that laboratory procedures are consistent with field procedures when taking samples.

2.3 Unique sample matrices such as vegetation, wood and wood chips, mechanical parts and filters, etc. pose additional challenges to obtaining representative samples. For these samples the laboratory staff should consult with the Project Manager to determine the subsampling strategy. These special situations will be handled on a case-by-case basis. Service requests should list any specific sample preparation required.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.2.3 Sample – A portion of material taken from a larger quantity for the purpose of estimating properties or composition of the larger quantity (ASTM).

3.2.4 Subsample – A portion of a sample taken for the purpose of estimating properties or composition of the whole sample (ASTM).

3.2.5 Composite sample – A mixture of multiple samples or subsamples produced to result in one sample representative of multiple field samples.

3.2.6 Representative subsample – A subsample collected in such a manner that it reflects one or more characteristics of interest (a defined by the project objectives) of the laboratory sample from which it was collected (ASTM).

3.2.7 Multilayered sample – A sample consisting of two or more clearly differentiated components (ASTM).

3.2.8 Multi-increment sample (MIS) – A field sample consisting of multiple bulk containers from one decision unit (defined in a MIS sampling plan) submitted to the lab for subsampling into a representative sample for analysis. Also known as Incremental Sampling Methodology (ISM).

3.3 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.4 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts of target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.5 Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

4.2 It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in the *Employee Training and Orientation* (ADM-TRAIN).

5) Interferences

5.1 When obtaining subsamples it is important to minimize any chances for sample contamination or cross-contamination between samples. Work should be performed in an organized and neat manner. Spilling of samples (from overfilled containers, etc.) should be minimized and spills cleaned up. Equipment and laboratory tools used with samples should be cleaned between samples to prevent cross-contamination.

5.2 Analysis-specific interferences are described in the applicable analytical SOP.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

6.3 This method uses Dichloromethane, a known human carcinogen. Refer to the methylene chloride policy document, ENV-HSE-NA-EX-006-EN for proper handling.

6.4 G:\SAFETY\TRAINING\Methylene Chloride\Methylene Chloride - NA 031419.pdf.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Refer to the analytical SOP for sample collection preservation and storage of samples. Subsamples and composite samples held for later analysis should be preserved and stored in the same manner as specified for field samples.

7.2 MIS Projects

7.2.1 Projects for MI samples may include additional instructions not found in the analytical SOP. The analyst should consult with the Project Manager, or refer to the Project Manager's instructions, prior to working with these samples.

7.3 LIMS test codes are used to specify which MIS analytical tests are needed (e.g. ISM-PAH). These test codes will have holding times associated with them that will ensure the completion of the MIS work before the initial analytical holding times (e.g. sample extraction) lapse.

8) Apparatus and Equipment

8.1 Laboratory balance capable of weighing the desired sample mass. There are various makes and models of balances available for use, with each department having balances appropriate for its use. For weighing solids and non-aqueous liquids (wastes), use a top-loader balance. Ensure that the mass (sample + container) to be placed on the pan is within the calibration-verified range of the balance.

8.2 Balance calibration verifications must be performed prior to use on each day of use. The calibration verification weights must bracket the range of use. For additional information, refer to the SOP *Documenting Laboratory Balance and Temperature Checks* (ADM-BAL).

8.3 Wiley laboratory mill, Model 4. Operate the Wiley mill following the manufacturer's recommendations

8.4 Sieve shakers.

8.5 Shatter box.

8.6 Mechanical mixer and/or shaker.

8.7 Stainless steel or Glass mixing bowl

8.8 Metal or disposable spoons and spatulas

8.9 Aluminum foil

8.10 Weighing boats, plastic or aluminum

8.11 Clean sample containers and lids (various sizes) as specified in the applicable test SOP

8.12 Common laboratory glassware/apparatus (beakers, flasks, pipets, syringes, etc.)

8.13 Multi-Increment Samples

8.13.1 Flat spatula, modified to create sides perpendicular to the flat surface used to scoop.

8.13.2 Flat stainless steel masons trowel.

8.13.3 Volatile sample containers.

8.13.3.1 250-500 milliliter (mL) narrow mouth, amber bottles (recommended).

8.13.3.2 4-8 ounce (oz.) amber jars with Teflon lined septum lids.

8.13.4 Large stainless steel spoon or scoop.

8.13.5 Large clean containers (a large stainless steel or glass bowl, Ziploc bags, or 5 gallon bucket).

8.13.6 #10 (2 mm) sieve.

8.13.7 Stainless steel cookie sheet or other tray

9) Standards, Reagents, and Consumable Materials

9.1 All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

9.2 To provide traceability, manufacturer lot numbers of solvents, reagents, standards and supplies used in an analysis shall be recorded on each analytical procedure's batch record, whether it is on the analytical record and/or into a logbook.

9.3 Dichloromethane, acetone, methanol, and acetonitrile may be used during the noted procedures for cleaning and decontamination of equipment Apparatus and Equipment

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described herein. The entry in the log must include: date of event, the initials of who performed the work, and a reference to return to analytical control).

11) Procedure

11.1 Aqueous samples - Subsampling

11.1.1 Examine the sample. Thoroughly mix all samples by vigorous shaking. Immediately open the container and obtain the subsample. Additional filtering of the subsample may be required by the analytical SOP.

11.1.2 If the sample is multi-layered (a water layer with a sand/sediment layer that cannot be mixed or non-aqueous liquid layer) the Project Manager should be consulted on how to proceed with the sample. Additional analyses or sample preparations may be

necessary depending on the client's data needs. Document the condition of the sample and decision made on subsampling.

11.2 General considerations – Non-liquid samples

11.2.1 The analyst must first understand what the sample matrix of interest is. The project information should be consulted. If the sample appears to be homogeneous (other than extraneous materials described below) particle size reduction is not necessary. Particle size reduction should be performed only when required by the project QAPP, project specifications, or client request. If particle size reduction is required, use the appropriate apparatus (Wiley mill, shatter box, etc.) to perform crushing, grinding, milling, or sieving, and document. Refer to ASTM D6323 for guidelines on performing particle size reduction.

11.2.2 Once the matrix of interest is known, examine the sample for presence of extraneous material. The default procedure is to remove these items, or not include in the representative subsample. However, the presence of these materials should be documented in lab records and the Project Manager should be consulted prior to subsampling. Some examples are given below.

- Soil, solid, and sediment samples may include such material as larger, rocks, sticks, leaves, pieces of metal, man-made materials, etc.
- Wood or bark samples may include chunks of soil, mud, rocks, etc.
- Vegetation samples may include chunks of soil, mud, rocks, sticks (not of the sample type, etc.).
- Sediment samples may include rocks, twigs, vegetation, organisms, etc.
- Sediment/marine projects, organisms are typically analyzed under separate sampling and analysis plans.
- Mechanical parts, filters, etc., may include chunks of soil, mud, rocks, sticks, etc.

11.2.3 Examine soil samples to determine if the sample contains significant amounts of water. If the amount of water is greater than approximately 30%, treat the sample as a sediment sample.

11.2.4 Samples which are especially heterogeneous, as well as various special matrices, may require additional preparation. These will be handled on a case-by-case basis after consultation with the appropriate supervisors and Project Manager. Unique matrices for TCLP and other leaching procedures should be handled according to the applicable SOP or reference method.

11.3 Soil/solid Samples

11.3.1 Subsampling samples in jars

11.3.1.1 Using a spatula or other utensil made of an inert material, thoroughly mix and homogenize the sample, making sure to loosen sample from the sides of the container, and continue mixing the entire contents, breaking up soil clumps, etc., until there is no visible segregation of the sample by layer, grain size, color, etc. The sample should appear uniform in color and texture.

11.3.1.2 Once mixed, remove the desired mass of sample for the analysis and document accordingly. Recap the jar and return to storage.

11.3.2 Subsampling samples in sleeves (core samples) and large bulk containers.

11.3.2.1 Empty samples in sleeves into a metal or glass homogenizing container and thoroughly stir using a spatula or other utensil. When homogenized the appropriate sample portions are placed in jars. Perform additional drying and grinding only when specified for the project. Client specifications for drying and grinding will be communicated by the Project Manager.

11.3.2.2 When working with sleeves and resulting homogenized samples or subsamples, always double-check the sample ID on the sleeve against the sample numbers on the samples.

11.3.3 Compositing soil/solid samples

11.3.3.1 Thoroughly mix each individual sample as described above.

11.3.3.2 Combine equal masses from each of the individual samples into a clean stainless steel mixing bowl. The amount used will depend upon the number of analyses to be performed on the composite and/or the amount available. The analyst preparing the composite will document the mass of each individual sample used for the composite, the date and time of compositing, and any other pertinent observations using the Composite Data benchsheet.

11.3.3.3 Thoroughly homogenize the sample using a spatula or other utensil and returned to clean glass jars. The sample container is labeled as a composite and with the sample identification.

11.3.3.4 Return the composite sample and remaining individual samples to storage.

11.4 Sediment Samples - Subsampling

11.4.1 Standard procedure calls for mixing overlying water into the sample. EPA SW-846 methods for organic extractions specify to decant and discard overlying water. However, the Puget Sound Protocols and others have options for decanting and discarding this water, decanting and performing a separate water analysis, or mixing the water into the sample. The analyst should confirm which option is to be used on the sample. For projects not within the scope of the Puget Sound Protocols or similar project plans, the overlying water should be decanted and discarded for organics analysis. For metals and inorganics, mix the overlying water into the sample.

Note: If water is decanted and discarded and percent solids is to be applied or determined, a separate solids determination must be made on the decanted sample.

11.4.2 Thoroughly mix and homogenize the sample, making sure to mix the entire contents of the jar. Additional steps may be needed to homogenize the sample (break up soil clumps, etc.). The sample should be mixed so there is a uniform color and texture.

Note: Sediment samples may contain considerable amounts of organics matter. Ensure that samples are thoroughly mixed. Document the presence of substantial organic matter, shells, etc.

11.4.3 Once mixed, remove the desired mass of sample for the analysis and document accordingly. Recap the jar and return to storage.

11.4.4 The subsample is transferred to an appropriate, labeled container. The sample container is stored in the appropriate refrigerator in sample receiving and any empty sleeve can be stored at room temperature.

11.5 Sediment Samples - Compositing

11.5.1 Thoroughly mix each individual sample as described above.

11.5.2 Combine equal masses from each of the individual samples into a clean stainless steel or glass mixing bowl. The amount used will depend upon the number of analyses to be performed on the composite and/or the amount available. The analyst preparing the composite will document the mass of each individual sample used for the composite, the date and time of compositing, and any other pertinent observations using the Composite Data benchsheet.

Note: Equal masses are used unless otherwise instructed. It may be required to use the entire jar or other measure.

11.5.3 The sample is thoroughly homogenized using a spatula or other utensil and returned to clean glass jars. The sample container is labeled as a composite and with the sample identification, dated, and initialed.

11.5.4 The composite sample and remaining individual samples are returned to storage.

11.5.5 Samples should be received prepared from the field as sample increments. Although unlikely, in cases where proper preparation of increments from large bulk samples does not occur in the field, the following steps will be taken.

11.5.5.1 When obtaining sample increments from a large bulk container (bucket, large jar, large bag, etc.) be sure to sample from the center and remove the soil 1-2 inches deep. Using the large spoon or scoop, collect the sample increment according to the work plan. Scoop approximately 30-60 grams into a large, clean container and move on to the next sample increment location. Be cautious of oversize material, which means more mass may need to be taken from each increment to end with the 30–50 g sub-sample after sieving (a 5 Kg field sample may not be uncommon). Increments can be sieved directly into the bucket, or they can be bagged and sieved later.

11.6 Multi-Incremental Sampling (or Incremental Sampling Methodology (ISM)) – When laboratory subsampling using MIS/ISM is to be used to produce the analytical subsample(s), the following procedures are used. If, after reviewing the project and Service Request information, the analyst has any uncertainty of the MIS approach to take, they must confirm with the Project Manager the protocol to be used. The default procedure is to be used when no other client or project specifications or modifications are given. This section refers to two tables – one specifying default increment amounts for analytical and one listing a "large mass" option that is to be used only when project specified. In addition, the State of Hawaii DOH protocol is to be used when requested.

NOTE: The default procedure is to be used when no other client or project specifications or modifications are given. This section refers to two tables – one specifying default increment amounts for analytical and one listing a "large mass" option that is to be used only when project specified. In addition, the State of Hawaii DOH protocol is to be used when requested. A procedure for the analysis by Method 8330B is also given.

11.6.1 Default procedure

11.6.1.1 After the 30-50 sample increments have been field collected into a container (a 5 Kg field sample may not be uncommon) air dry the entire sample (all received containers) in aluminum pans pre-rinsed three times with DCM (methylene chloride). Note, if Aluminum is a target analyte of interest then substitute the aluminum pans for glass or stainless steel. Air drying may take 2-4 days with occasional stirring.

11.6.1.2 The intent of air drying is to convert the sample to a more manageable form prior to sieving. The sample is considered air-dried when the material appears dry enough to enable disaggregation and sieving. Due to high variability of laboratory samples, sample dryness should be confirmed by a senior analyst or supervisor prior to going further with the procedure. For work performed under DOD QSM, constant weight data will be recorded on the Constant Weight Data Sheet (Hyperlink in Section 20).

11.6.1.3 Rinse all utensils and equipment with DCM three times prior to use (stainless steel tray, mortar & pestle, 2 mm sieve & catch pan, trowel, ISM spatula).

11.6.1.4 Lightly grind the air dried sample with a mortar & pestle in order to break up dirt and clay chunks (do not size reduce rocks or vegetation) and pass sample through a 2 mm sieve.

11.6.1.5 Weigh the remaining +2 mm fraction in an appropriate sized jar and record the weight on the Air Dried Sieve Data benchsheet (Figure 1). Describe the +2mm fraction on the bench sheet (size of rocks, type of any vegetation, etc.).

11.6.1.6 Weigh and record the weight of the -2 mm fraction on the Air Dried Sieve Data benchsheet (Figure 1).

11.6.1.7 Mix the sample, dump on a DCM rinsed stainless steel pan, and spread the sample out with a trowel, forming a rectangle no more than 1cm deep.

11.6.1.8 Divide the sample into a minimum of 30 equal sections (30 to 50 sections is recommended) using the trowel blade. Note that the entire sample should be included in the grid and amount of sample 'outside' the grid outer edges minimized (however, do not overly manipulate the sample in an attempt to create a perfect grid).

11.6.1.8.1 Collect an equal (approximate) amount of sample from each of the sections based on the applicable table (Table 1 or Table 2) and place into a labeled container (see Tables 1 and 2). Scrape the modified flat spatula along the bottom of the tray and pull straight up to make sure all depths and particle sizes are represented in the collection area. Avoid collecting portions from the edge of gridlines (where the slab has been disturbed). Record the exact final weight of sample for each test on the ISM bench sheet and on the jar. All weights shall be measured using an analytical balance.

11.6.1.8.2 Since each laboratory area must analyze the entire contents of the prepared (or submitted) jar, the subsampling process must be repeated for each separate analysis to be performed on the sample. The subsampling process must be performed for each individual QC sample as well. The entire mass in the jar will be analyzed (TOC is the exception). The results may be less defensible if only a subsample or fraction of the jar contents is analyzed.

11.6.1.8.3 If sample amount is sufficient, it is recommended to repeat the process to obtain a backup sample in the event that re-analysis is required. This "As Received" backup is placed back in the original sample jar and returned to sample management/custody.

11.6.1.9 Labeling and storage

11.6.1.9.1 Refer to Table 3 for default storage conditions, which are based on how the MIS sample was prepared and on the stability/volatility of target analytes.

11.6.1.9.2 MIS subsamples do not need to be returned to SMO for barcode labeling. Label the aliquots with labels from "prep App" and deliver them directly to the labs. Document the internal custody transfer directly on the benchsheet that is delivered with the samples.

11.6.1.9.3 Place any remaining -2mm sample into jars labeled as "-2 mm archive." If there are multiple jars, label them as "1 of 3", "2 of 3", etc. All remaining bulk sample jars must be returned to SMO for barcode labeling and storage.

11.6.1.9.4 Usually, the -2 mm archive and test archive (back-up samples) jars are placed in a freezer, while the +2 mm archive and test jars (with QC) are placed on the room temperature shelves.

11.6.2 Procedure for ISM following State of Hawaii DOH Protocol (see references)

11.6.2.1 Samples requesting the Hawaii DOH procedure require wet and/or dry sieving depending on the test/analytes for which subsamples are being prepared. Refer to a copy of the Hawaii DOH procedure and/or the Project Manager for details before beginning.

11.6.2.2 Obtain instructions from the Project Manager or Service Request for increment amounts and test subsample amounts. Also refer to the Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan, November 12, 2008, Section 4.2.2 for guidance on increment/sample amounts.

11.6.2.3 Subsample bulk MI samples to be tested for SVOCs, including TPH-D, some PAHs, Mercury, and unstable pesticides, should be subsampled without drying or sieving in order to minimize chemical loss or alteration and meet holding times for analysis. Refer to Table 2a of Technical Guidance Manual Notes: Decision Unit and Multi-Increment Sample Investigations, March 2011, State of Hawaii, Department of Health, and Reference document number 2011-143-RB.

11.6.2.4 If both SVOC and non-volatile PAHs are targeted contaminants of interest then include testing for both in laboratory subsamples collected from the multi-Increment sample prior to drying and sieving.

11.6.2.5 When creating aliquots for metals, Mercury aliquots should be 5 g and all other materials aliquots should be 10 g.

11.6.2.6 For wet ISM aliquots, organic tests (SVG/SVM) require a larger aliquot size to accommodate for the extra water content. In most cases, low-level organic tests will require a 40 g wet aliquot (max weight capacity for most tests) and normal level tests will require a 20 g wet aliquot (double the target dry weight).

11.6.2.7 Use a separate sample from the wet material and test for soil moisture in order to convert analytical results to dry-weight basis.

11.6.2.8 Not all samples from Hawaii require the State of Hawaii DOH procedure. See service request and/or verify with the Project Manager.

11.7 Analyte-Specific Considerations

11.7.1 Metals

11.7.1.1 It has been proven that grinding can greatly improve the reproducibility for metals analyses. However, erosion of the metals surfaces used in grinding may contribute to a high bias in the samples. It is recommended that the tungsten carbide grinding mill is used when grinding soils in the shatter box thereby limiting the amount of potential bias in the prepared samples.

11.7.1.2 When grinding soil samples that may potentially contain ores of malleable metals (e.g. Lead, Copper, Tin) be aware that the malleable particles may tend to smear during grinding, and may be lost from the samples to equipment surfaces. This anomaly may bias sample results low, decontamination of equipment surfaces may be difficult and could result in high bias in subsequent samples from carry over.

11.7.1.3 Reproducibility for Lead analyses in unground, incrementally sampled (IS) samples from small arms firing ranges may have an unacceptable large variability. The large variability for Lead may be due to single particles of Lead between one and two millimeters in diameter being present in only some of the replicate splits. If the end data is to assess risk of accidental ingestion of Lead, precision for the concentration of lead contained in larger particles may be of less interest then the Lead contained in the finer, less than 0.25 mm, fraction. Using a finer mesh sieve (0.25 mm rather than 2 mm) may improve precision and reproducibility. However, sieving unground samples through sieves finer

than two millimeters is not appropriate if analyzing for high explosives or propellants. Typical mass sizes for energetic analytes are in particles sizes greater than 0.59 millimeters.

11.7.1.4 MI samples collected for Arsenic analyses that contain greater than 20 mg/Kg total Arsenic should be tested for bioaccessible Arsenic. This should be discussed with the project manager. If deemed appropriate, the entire <2 mm fraction of the respective samples should be sieved to a ≤0.25 mm, representatively sub-sampled and analyzed for bioaccessible Arsenic using SBRC methodology, 1-2 grams are required.

11.7.2 Polycyclic Aromatic Hydrocarbons (PAHs)

11.7.2.1 Currently there is little information in published procedures specific to the laboratory processing of ISM samples for PAHs. The default procedure above is used.

11.8 Vegetation samples

11.8.1 Since vegetation samples often are not amenable to standard mixing and homogenization techniques, or because specific sections of the vegetation are targeted, these are handled on a case-by-case basis with instructions from the Project Manager. The PM will obtain sample-specific instructions from the client, and then communicate the specifications to the lab personnel using the ALS Form V or similar project specification document for the project. If the client makes reference to specific procedures, methods, or technical references, the PM will make the document(s) available to the laboratory personnel.

11.9 Paperboard samples

11.9.1 In general, prepare paperboard samples as described below. Project-specific instructions may replace these.

11.9.2 Prepare the FDA Ext first.

- Cut the sheet of paper into one 10" x 10" square.
- Cut the 10" x 10" into strips at the cut lines 7 ½, 5, and 2 ½.
- Cut strips at 7 ½, 5, and 2 ½ inches. This will make a total of 16 2½" squares.
- Place all the squares into a large zip closing bag.

11.9.3 Put one sheet of paper into shredder, run the shredder back and forth to get the entire sample out. Use tongs to remove any remaining sample in bottom of shredder. As a safety precaution, ensure the unit is in the "OFF" position.

11.9.4 Determine the total mass of sample needed to aliquot for all tests. Divide the total mass by the number of samples to be composited. Shred that mass of each sample to be composited together into a single container. Homogenize thoroughly once all the fractions have been shredded. Aliquot each sub sample from this final mass.

11.9.5 Update composites as being done. Open StarLIMS, double click on Ad Hoc by Test (Under Results entry), highlight samples composited and click the Update to Done button at the top of page. Do not add jars when asked. Just click the X on the right hand corner.

12) QA/QC Requirements

12.1 This method shall operate under the formal Quality Assurance Program established at ALS and must maintain records that define the quality of data that is generated. Data shall be compared to established criteria in order to determine if the results meet the performance characteristics of the determinative method(s).

12.2 Ongoing QC Samples required for each sample batch (20 or fewer samples) are described in the SOP *Sample Batches* (ADM-BATCH) and in the determinative SOPs.

13) Data Reduction and Reporting

13.1 All compositing and subsampling data must be recorded into the bench records by the analyst. In addition to sample volumes and masses, sample identifications, etc., this should include descriptions of unique samples or sample components.

13.2 It is the supervisor's responsibility to ensure that analytical data is reviewed and to ensure that all quality control requirements have been met.

14) Method Performance

14.1 Not Applicable.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

15.4 This method uses Dichloromethane and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and recycled off site

16) Contingencies for Handling Our-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Non Conformance and Corrective Action Procedure* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).

- Sample preservation or handling discrepancies due to laboratory or operations error.
- Customer inquiries concerning data quality or services (when applicable). NCAR not required for simple corrections with no impact to the client.
- Data errors reported to clients, non-conforming re-checks.
- Deficiencies found during internal or external audits.
- Login errors or shipping errors.
- IT issues if there is a significant impact to a client.
- Turnaround time complaints

17) Training

17.1 Refer to the SOP *Employee Training and Orientation* (ADM-TRAIN). Training outline

17.1 Training outline

17.1.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to TNI's Initial Demonstration of Capability.

17.2 Training is documented following *Employee Training and Orientation* (ADM-TRAIN).

Note: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 Not Applicable.

19) References

19.1 Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, U.S. Environmental Protection Agency, EPA/600/R-03/027, November 2003.

19.2 Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities, ASTM D 6323, Annual Book of ASTM Standards, 1999.

19.3 Test Methods for Evaluating Solid Waste, EPA SW-846, Final Update III, December 1996.

19.4 Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound, January, 1996.

19.5 Draft Guidance on Multi-Increment Soil Sampling State of Alaska, Department of Environmental Conservation, March 2007.

19.6 Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan, November 12, 2008.

19.7 Technical Guidance Manual Notes: Decision Unit and Multi-Increment Sample Investigations, March 2011, State of Hawaii, Department of Health, 2011-143-RB.

19.8 Standard operating Procedure, In Vitro Method for Determination of Lead and Arsenic Bioavailability; Solubility/Bioavailability Research Consortium, Document 8601-102.011- 0601-1099-RN01.

19.9 TNI Standard, Volume 1- 2009 & 2016.

19.10 DoD Quality Systems Manual for Environmental Laboratories, current version.

20) Changes Since Last Revision

Revision Number	Effective Date	Document Editor	Description of Changes
2.0	9/13/9	T. Caron	Updated to the latest ALS SOP format Typographical, grammatical and formatting revisions. Numerous edits and changes to reflect current practice. Section 6: Added dichloromethane usage into the safety section. Section 11.6 – Expanded description. Section 11.6.3 – 8330B section deleted. Section 11.7.1 – Perchlorate section deleted. Section 111.7.2.1 – Removed part of sentence referencing 8330B.

21) Attachments, Tables, and Appendices

21.1 Analytical Worksheets:

21.1.1 Blank Bench Sheet: R:\Soil Prep\Templates\Blank Bench sheet REV1.xltx.

21.1.2 Constant Weights Data Sheet: R:\Soil Prep\Templates\Constant Weight Data Sheet rev3.xltx

21.1.3 Paperboard Composite Data: R:\Soil Prep\Templates\Paperboard Composite Data REV2.xlsx.

21.1.4 Sieve Data Sheet: R:\Soil Prep\Templates\Sieve Data Sheet REV3.xltx.

21.1.5 Soil Composite Data Sheet: R:\Soil Prep\Templates\Soil Composite Data Sheet REV3.xltx.

21.1.6 Soil Grinding Data Sheet: R:\Soil Prep\Templates\Soil Grinding Data Sheet. REV2.xltx.

21.1.7 Table1- Default Multi-Incremental Sampling Information.

21.1.8 Table 2 - Large Mass Multi-Incremental Sampling Information.

21.1.9 Table 3 - Storage of Multi-Incremental Subsamples.

21.1.10 Figure 1 - Air Drive Sieve Data Sheet:

Table 1
Default Multi-Incremental Sampling Information

Test	Subsample Basis	Aliquot	Approximate Amount per Increment	Container	QC Requirement
Total Solids	Air Dried	15.00 g	0.50 g	2 oz. soil jar	DUP per 10
200.7 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 10
6010 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 20
200.8 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 10
6020 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 20
Mercury	Air Dried	0.5000 g	0.0167 g	Mercury digestion cup	DUP/MS per 20
8081 PEST	As Received	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8081 PEST-LL	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB-LL	Air Dried	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8151	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270 LL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH ULL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
8290/Dioxin	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8330B*	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
Diesel or Residual Range Organics (DRO, RRO)**	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
TOC	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	None
Backup Sample	As Received	30.00 g	1.00 g	Back into original jar	N/A

For DOD projects refer to the DOD 8330B protocols.

** Alaska Methods AK102 and AK103 call for the extraction of from 10-30 g of sample material (soil). For MIS purposes, the minimum required amount of material per analysis is 30 g.

Table 2
"Large Mass" Multi-Incremental Sampling Information

Test	Subsample Basis	Aliquot	Approximate Amount per Increment	Container	QC Requirement
Total Solids	Air Dried	15.00 g	0.50 g	2 oz. soil jar	DUP per 10
200.7 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 10
6010 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 20
200.8 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 10
6020 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 20
Mercury	Air Dried	5.00 g	0.167 g	Mercury digestion cup or 2 oz. soil jar	DUP/MS per 20
8081 PEST	As Received	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8081 PEST-LL	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB-LL	Air Dried	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8151	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270 LL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH ULL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
8290/Dioxin	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8330B*	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
Diesel or Residual Range Organics (DRO, RRO)**	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
TOC	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	None
Backup Sample	As Received	30.00 g	1.00 g	Back into original jar	N/A

For DOD projects refer to the DOD 8330B protocols.

** Alaska Methods AK102 and AK103 call for the extraction of from 10-30 g of sample material (soil). For MIS purposes, the minimum required amount of material per analysis is 30 g.

Table 3
Storage of Multi-Incremental Subsamples

Test	Storage
Total Solids	Room Temperature
200.7 Metals	Room Temperature
6010 Metals	Room Temperature
200.8 Metals	Room Temperature
6020 Metals	Room Temperature
Mercury	Room Temperature
8081 PEST	4 ± 2˚C
8081 PEST-LL	4 ± 2˚C
8082 PCB	Room Temperature
8082 PCB-LL	Room Temperature
8151	4 ± 2˚C
8270	4 ± 2˚C
8270 LL	4 ± 2˚C
PAH	4 ± 2˚C
PAH ULL	4 ± 2˚C
8290/Dioxin	Room Temperature
8330B*	4 ± 2˚C
Diesel or Residual Range Organics (DRO, RRO)*	4 ± 2˚C
TOC	Room Temperature
Backup Sample	4 ± 2˚C

Figure 1 Air Dried Sieve Data

ALS Inc.

Service Request Number(s):

Air Dried Sieve Data

Service Request #	Sample Weight (g)	Weight of Passing Fraction(g)	Weight of Retainied Fraction (g)	Sieve Size
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			
	0.00			

Balance ID:

Analyst:	Date:
Reviewed:	Date:

R:\ICP\misc\digforms\Air Dried Sieve Bench Sheet-Compatible

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

DOCUMENT I.D. MET-ICP

Approved By: _____ Date: 11/19/18
Technical Director, Jeff Coronado

Prepared By: _____ Date: 11/19/18
Quality Assurance Manager, Carl Degner

Prepared By: _____ Date: 11/21/18
General Manager, Ambrose Hughey

Doc Control ID:	_____	Archived Date:	_____

ALS-Kelso SOP Annual Review Statement

SOP Code: MET-ICP
Revision: 27

An annual review of the SOP listed was completed on (date): **2/27/2020**

☒ The SOP reflects current practices and requires no procedural changes.

Supervisor: RRM Date: 2/27/2020

☐ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision

TABLE OF CONTENTS

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

1) Scope & Applicability

1.1 This procedure describes the steps taken for the analysis of soil, sludge surface water and drinking water digestates using EPA methods 6010D and 200.7 for a variety of elements. The digested samples and QC standards are all diluted in a similar acid matrix. A procedure is also given for calculation of hardness by Standard Methods 2340B.

1.2 The Method Reporting Limits (MRLs) for common elements are listed in the lab Data Quality Objective (DQO) tables. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The reported MRL may be adjusted if required for specific project requirements, however, the capability of achieving other reported MRLs must be demonstrated. The Method Detection Limits (MDLs) that have been achieved are listed in the DQO tables. The MDL and MRL may change as annual studies are performed.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP or project which require older versions of EPA methods (i.e. 6010B/6010C). QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD5) may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 A representative aliquot of sample is prepared as described in the applicable digestion SOP. The digestate is analyzed for the elements of interest using ICP spectrometry. The instrument measures characteristic emission spectra by optical spectrometry. The intensity of emission lines are monitored.

2.2 Final results are calculated using the digestion information and the results from the ICP analysis. Data is reported using standard ALS procedures and formats, or following project specific reporting specifications.

2.3 Deviations from the reference method(s): This SOP contains no deviations from the reference methods.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis

sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to

sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8 Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.9 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. The CCV is used to verify that the initial calibration curve is still valid for quantitative purposes.

3.10 Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.11 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4) Interferences

4.1 Interferences from contaminated reagents must be eliminated. The purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the MRL (or above ½ the RL for DoD work).

4.2 Background emission and stray light can be compensated by background correction.

4.3 Spectral overlaps resulting in interelement contributions can be corrected for by using interelement correction factors. Interelement correction factors are established for each instrument and are maintained by the analyst at the workstation.

5) Safety

5.1 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDS prior to beginning this method.

5.2 Hydrochloric, Nitric and Hydrofluoric Acids are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. Safety glasses, lab coat and gloves should be worn while working with the solutions.

5.3 High Voltage - The power unit supplies high voltage to the RF generator which is used to form the plasma. The unit should never be opened. Exposure to high voltage can cause injury or death.

5.4 UV Light -The plasma when lit is a very intense light, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available.

6) Sample Collection, Containers, Preservation, and Storage

6.1 Samples are prepared via procedures in SOPs MET-DIG, MET-3010A, MET-3050, MET-3051M, MET-3052M, or MET-TDIG. Samples are received in the ICP lab as completed digestates. Samples are stored in 16 mL plastic test tubes, 50 mL plastic centrifuge tubes, 100 mL digestion vessels or in 100 mL volumetric flasks.

6.2 Water samples analyzed by EPA method 200.7 are preserved after arrival at the laboratory. These samples are held for a minimum of 24 hours and the pH verified to be <2 prior to digestion.

6.3 Soil samples are diluted prior to instrumental analysis by a factor of 2. This allows the method to meet the required 1 g of sample to 200 mL dilution during digestion.

6.4 Following analysis, digestates are stored until two weeks after all results have been reviewed and then brought to 6< pH <9 and disposed of through the sewer system. The neutralization step is considered hazardous waste treatment and must be documented. See the ALS Lab Waste Management Plan for details.

7) Standards, Reagents, and Consumable Materials

7.1 Standards Preparation

7.1.1 Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. The preparation for all laboratory prepared

reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements. Manufacturer's expiration dates are used to determine the viability of standards.

7.1.2 Calibration standards are prepared from commercially purchased single element 1000 ppm or 10,000 ppm stock standards as well as pre-mixed multi element stock standards. All standards are aliquoted using Class A volumetric pipettes, or calibrated fixed and adjustable volume auto-pipettors. All dilutions are made in Class A volumetric glassware.

The standard mixes for each ICP system vary based on the requirements of each instrument. The composition of the ICAP 6500 standards are outlined in Table 2.

7.1.3 Continuing Calibration Verification (CCV) Standards

CCV standards are analyzed at the midpoint of the calibration. These standards are produced by making a two-fold dilution of each calibration standard. The CCV standards are then run in sequence during the analytical run.

7.1.4 Initial Calibration Verification (ICV) Standards

The ICV working standards are produced by direct dilution of two certified mixed stock solutions (QCP-CICV1 and QCP-CICV3 purchased from Inorganic Ventures or another qualified vendor and various single element stock solutions from sources different than the calibration standards. The composition of these standards is outlined in Table 3.

7.1.5 Interference Check Solutions (ICSA & ICSAB)

The ICSA and ICSAB working standards are produced by direct dilution of certified mixed stock solutions (CLPP-ICS-A and CLPP-ICS-B or equivalent.) Antimony is also added to the ICSAB solution from a 1000 ppm single element stock standard. The composition of these standards is outlined in Table 4.

7.1.6 Low Level Calibration Verification

The CRI, Low Level Continuing Calibration Verification (LLCCV), and Low Level Continuing Calibration Verification (LLCCV) are produced by diluting 1000 or 10000ppm single stock standards into a 100X intermediate standard and then diluted 1/100 to obtain the MRL level. Note: The level used is that of the normal MRL used for both instruments.

7.1.7 The solutions and materials used for the LCS and matrix spikes are described in the applicable digestion SOP.

7.1.8 Standard Log

The analyte, source, initial volume, final volume, final concentration and expiration date are recorded in a standard logbook kept in the ICP lab. The operator who prepares the standard must date and initial the entry in the standards logbook. The operator also places his initials and the date prepared on the standard container. In addition to working standards used in calibration, all other standards used in the analytical run such as ICVs, MRL standards, and other project or client specific standards shall be documented in the standard logbook.

7.2 High Purity Argon.

7.3 Capillary, rinse and peristaltic pump tubing.

7.4 17 x 100 mm polypropylene test tubes.

8) Apparatus and Equipment

8.1 Inductively Coupled Plasma Atomic Emission Spectrometer

8.1.1 Thermo Scientific ICAP 6500 (AES-03).
8.1.2 Thermo Scientific ICAP 6500 (AES-04).

8.2 Concentric nebulizers.

8.3 Microflow nebulizer for ICAP 6500.

8.4 Torches and injector tips for each ICP.

8.5 Cyclonic spray chambers for each instrument.

8.6 Water coolers for each ICP.

8.7 ESI SC4 DX Autosampler with Fast System for ICAP 6500.

8.8 Peristaltic Pumps for each Spectrometer.

8.9 RF Generators for each ICP (internal on the ICAP 6500).

9) Preventative Maintenance

9.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

9.2 Torch, nebulizer, and spray chambers are cleaned as required. All instrument filters are vacuumed monthly. Dirty ICP torches and mixing chambers are soaked in aqua regia overnight, rinsed and placed in a clean dry area. Dirty nebulizers are soaked in dilute HF. If still problematic the unit is returned to the manufacturer for repair.

10) Responsibilities

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the

ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2 It is the responsibility of the department supervisor/manager to document analyst training. Training and proficiency is documented in accordance with the *ALS Kelso – Training Procedure* (ADM-TRAIN).

11) Procedure

11.1 Operating Parameters

11.1.1 For each Thermo Scientific ICAP 6500, the operating parameters are defined in the Method file. Default operating parameters are given in Tools/Options/New Method Parameters. However, each unique set of operating parameters is saved as a new file and the analyst must select and use the correct Method file for the application. Refer to the method files on the workstation for a listing of parameters for each file. The interelement correction factors to be used are established for the ICAP 6500 and are saved on the workstation also. Since these parameters change with method and correction factor updates, and due to the large amount of hardcopy printout for listing these parameters, it is not practical to include the parameters in this SOP.

11.2 Calibration/Standardization

11.2.1 ICAP 6500

11.2.1.1 Plasma is ignited and instrument is allowed to warm up for at least 30 minutes.

11.2.1.2 An internal standard is used for routine analyses on this instrument. Yttrium and Indium are used as internal standards. The internal standard solution is introduced into the analyzed solutions (standards, blanks, QC, samples, etc.) at 4.0 µg/mL for Y, and 8.0 µg/mL for In.

11.2.1.3 Run a peak check standard and adjust peaks as needed.

11.2.1.4 Standardize by running a Blank and a High Standard for each element in the analytical method. Analyst will initial and date the first page of the standardization.

11.3 Analytical Run

11.3.1 Following standardization, the remainder of the run is determined by what analytical method is being performed; 200.7 or 6010D.

11.3.1.1 For 200.7 the sequence is:

- CCVB (aka. IPC): RSD of 4 replicates must be <3% and recovery must be within ± 5%.
- CCVA (aka IPC): RSD of 4 replicates must be <3% and recovery must be within ± 5%.
- ICB: Result should be < ½ MRL.
- ICVB (aka QCS): Recovery must be within ± 5%.
- ICV (aka QCS): Recovery must be within ± 5%.
- CCB: Result should be less than 3 times the standard deviation of the mean background signal.
- LLICV: Spiked at MRL level with the result > MDL and <2x the MRL.
- ICSA: To check validity of Interelement Correction Factors (IECs).
- ICSAB: Recovery must be within ± 20% for the CLPP-ICS-B elements and Sb.
- 10 samples
- CCV: Recovery must be within ± 10%.
- CCB: Result should be less than 3 times the standard deviation of the mean background signal.
- Repeat CCV/CCB standards every 10 samples as needed.

11.3.1.2 For 6010D the sequence is:

- ICVB: Recovery must be within ± 10%.
- ICV: Recovery must be within ± 10%.
- ICB: Result should be < ½ LLOQ.
- CCVB: Recovery must be within ± 10%.
- CCVA: Recovery must be within ± 10%.
- CCB: Result should be < MRL.
- LLICV: Spiked at MRL level with recovery within ± 20%.
- ICSA: To check validity of Interelement Correction Factors (IECs).
- ICSAB: Recovery must be within ± 20% for the CLPP-ICS-B elements and Sb.
- 10 samples
- CCV: Recovery must be within ± 10%.
- CCB: Result should be less than 3 times the standard deviation of the mean background signal.
- Repeat CCV/CCB standards every 10 samples as needed.

11.3.2 Evaluate the initial QC using the following criteria:

11.3.2.1 For methods 200.7 and 6010D, the following criteria apply:

- The ICB and CCB results are evaluated using method specified requirements. The following guidelines should also be used to determine acceptability:

- For 200.7, the result should be less than 3 times the standard deviation of the mean background signal.

- For method 6010D, the result should be less than 1/2 the Lower Limit of Quantitation (LOQ).

- The CCV immediately following standardization must verify within ± 10% of the true values. For 200.7, the first CCV must verify within ± 5% with a RSD of <3% from 4 replicates. Calculate %RSD as follows:

$$\%RSD = \frac{StdDev_{CCV}}{Average_{CCV}} x\,100$$

Where:

StdDevccv = Standard deviation of the replicate integrations
Averageccv = Average of the replicate CCV integrations

- The LLICV or CRI is a low level standard with concentrations at the RL. For DoD projects, the LLICV standard concentrations will be equal to the project RLs. For method 6010D the CRI results should be within 20% of the true value. For 200.7 LLICV/CRI results should be greater than the MDL and less than 2X the MRL.

- The ICSA is run to check the validity of the Interelement Correction Factors (IECs).

Note: DoD QSM requires this to be run at the beginning of each analytical run.

- The ICSAB must be within 20% of the expected value for the CLPP-ICS-B elements and Sb.

11.3.2.2 The ICV, LLICV, ICB, CCV, CCB, CRI, and ICSAB must meet the criteria listed. Reanalyze any elements that fail.

11.3.3 Continuing Calibration Verification

11.3.3.1 CCVs are analyzed after every 10 samples and at the end of the analytical run. They must verify within ±10% of the expected value with a RSD of <10%.

11.3.3.2 CCBs are analyzed after every 10 samples and at the end of the analytical run. CCBs are evaluated as in section 11.3.2.1.

11.3.4 If the CCV or CCB solutions fail, reanalyze any elements to be reported.

12) Quality Assurance/Quality Control Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The accuracy and precision of the procedure must be validated before analysis

of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery for each analyte must meet LCS criteria and the RSD< 30%.

12.2 Method Detection Limits

12.2.1 A Method Detection Limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates at a level near or below the MRL. Follow the procedures in Section 11 to analyze the samples. Refer to the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL).

12.2.2 Calculate the average concentration found (x) and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. MDLs must be performed whenever there is a significant change in the background or instrument response.

12.2.3 A Limit of Detection (LOD) check must be performed after establishing the MDL and at least annually (quarterly if DoD) afterward. A blank is spiked with analytes at 2-4X the MDL and carried through the preparation and analytical procedure. The LOD is verified when the signal/noise ratio is > 3 for all analytes.

12.3 Limit of Quantitation Check (LOQ)/Lower Limit of Quantitation Check (LLQC)

12.3.1 For Method 6010D and drinking waters by method 200.7 a Lower Limit of Quantitation Check (LOQ/LLOQ) sample must be analyzed after establishing the MRL and at least annually (quarterly if DoD) afterward to demonstrate the desired detection capability. The LOQ/LLOQ sample is spiked at 1-2X the MRL and must be carried through the entire preparation and analytical procedure. Limits of quantitation are verified when all analytes are detected within 30% of their true value.

12.4 Linear Dynamic Range

12.4.1 The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing at least three succeeding higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% above or below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and re-analyzed. The LDRs are verified every six months or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in

instrument hardware or operating conditions would dictate they be re-determined.

Method 6010D requires that the linear range for each wavelength be verified on a daily basis. The linear range verification standard must recover within 10% of the true value and can be analyzed anywhere within a particular run. If a linear range verification is not analyzed for a specific element, the highest calibration standard becomes the linear range. All reported sample measurements must fall within the linear range.

12.5 Instrument Detection Limit

12.5.1 The IDLs should be determined annually or after major instrument maintenance. The IDL is determined as the mean of the blank results plus 3 times the standard deviation of 10 replicate analyses of the reagent blank solution.

12.6 Interelement Correction Factors

12.6.1 Spectral Interference Checks (SIC) are performed when an instrument is initially set up, the every six months. During the course of routine work, other interferences may be found. They are verified by the operator during the analytical run and data is manually corrected. Copies of this data are kept on file. Data can be manually corrected or automatically corrected using iTEVA software.

12.7 Internal Standard

12.7.1 Internal standard values are tracked by the instrument software. Values should remain within 60-125% of the value found in the calibration blank. If a sample is found to have and internal standard outside this value, the sample will be diluted to bring the internal standard into range.

12.8 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DoD ELAP must follow requirements defined in the DoD *Quality Systems Manual for Environmental Laboratories.* General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD5). General QC Samples are:

12.8.1 Each sample preparation batch must have a method blank associated with it. The method blank result should be < MRL. If the method blank is found to be contaminated, it may be reported if the concentration in the associated samples is at least 20 times the amount found in the method blank for methods 200.7, otherwise re-digest the batch. For Method 6010D, the method blank may be reported if the concentration in the associated samples is at least 10 times the amount found in the method blank. A contaminated method blank (MB) may also be reported if all of the associated samples are non-detect (ND).

Note: DoD QSM requires contamination in the MB be <1/2 the RL or < 1/10 any sample amount.

12.8.2 A Laboratory Control Sample (LCS) is digested one per batch, or per 20 samples. For soil samples, the recovery must fall within the ranges specified for the reference material. For "blank spike" Laboratory Control Samples recoveries must fall within ± 15% of the true value for 200.7 and ±20% of the true value for 6010D. For specifics on the preparation and composition of LCS samples refer to the appropriate digestion SOP.

12.8.3 A Duplicate sample is digested one per batch, or per 20 samples (i.e. 5%) for 6010D analysis, or per 10 samples (i.e. 10%) for 200.7 analyses. If the RPD is outside acceptance limits, either re-digest the sample batch or flag the data appropriately, depending on the physical nature of the samples (e.g. non-homogenous).

12.8.4 A Laboratory fortified Blank (LFB) at the MRL is digested and analyzed with every batch of drinking water samples (method 200.7). The default acceptance criteria of 50-150% are to be used until sufficient data points are acquired to calculate in-house control limits.

12.8.5 A Matrix Spike sample is digested one per batch, or per 20 samples (i.e. 5%) for 6010D analysis, or per 10 samples (i.e. 10%) for 200.7 analyses. Where specified by project requirements, a matrix spike duplicate may be required. If the recovery is outside acceptance limits, either re-digest the sample batch or flag the data appropriately, depending on the physical nature of the samples (e.g. non-homogenous). If the sample concentration is >4x the spike level, no action is required and data is flagged accordingly. For specifics on the preparation and composition of matrix spike solutions refer to the appropriate digestion SOP.

12.8.6 Acceptance criteria

12.8.6.1 Current ALS control limits and acceptance criteria for ongoing QC analyses are listed in the current ALS-Kelso DQO tables. Criteria are subject to change as statistical data are generated. The default method criteria may be used if statistically generated criteria are broader or insufficient points are available for accurate statistical limits.

12.8.6.2 For all QC analyses, project-specific or program-specific (e.g. DoD) acceptance criteria may supersede ALS criteria.

12.8.7 Matrix Interference

12.8.7.1 When an analyst suspects that there may be any matrix interferences present, a post digestion spike may be performed. The recovery should be ± 20% for method 200.7 and ±25% for 6010D.

12.8.7.2 If the post spike fails, a 1:5 serial dilution test shall be performed. The dilution should be within ± 10% of the original result for 200.7 and ±20% for method 6010D.

12.8.7.3 A 1:5 serial dilution shall be performed for all Tier III or IV deliverables.

12.8.7.4 Post spikes for 6010D shall be performed for Tier III and Tier 1V.

12.9 Additional QC measures include control charting and compiling of QC data for generation of control limits.

12.10 CLP analyses are performed as per the QA/QC guidelines in the most current CLP SOW.

13) Data Reduction and Reporting

13.1 Calculate sample results using the data system printouts and digestion information. The digestion and dilution information is entered into the data system. The data system then uses the calculations below to generate a sample result. The wavelengths used to quantify each metal are summarized in Table 5 for the IRIS and Table 6 for the ICAP6500.

Aqueous samples are reported in µg/L:

$$\mu g/L\,(Sample) = C^{*}\ x\ Digestion\ Dilution\ Factor\ x\ Post\ Digestion\ Dilution\ Factor \times 1000 \mu g/mg$$

Solid samples are reported in mg/Kg:

$$mg/Kg\,(Sample) = C^{*}\ x\ Post\ Digestion\ Dilution\ Factor\ x \frac{Digestion\ Vol.(ml)}{Sample\ wt.(g)}\ x \frac{1mg}{1000ug}\ x \frac{1L}{1000ml}\ x \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in µg/L (in digestate).

13.2 If total hardness is to be reported, use Calcium and Magnesium results to calculate as follows. For reporting calcium hardness, use only the calcium portion of the equation.

$$Hardness, mg\ equivalent CaCO_3/L = 2.497[Ca, mg/L] + 4.118[Mg, mg/L]$$

13.3 A daily run log of all samples analyzed is maintained. All CLP data should be printed and stored after operator has checked for evenness of burns. A copy of this document will go with each package of Tier III or higher data run that day.

13.4 Data Review and Reporting

13.4.1 It is the analyst's responsibility to review analytical data to ensure that all

quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12. The data is then placed in a work order file until complete. When the work order is complete, a report is generated. A final review is performed and the data is delivered to the project management department.

14) Method Performance

14.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional available method performance data.

14.2 The method detection limit (MDL) is established using the procedure described in the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 5-9 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS Lab Waste Management Plan for details.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformance and Corrective Action Procedures* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Refer to the SOP *ALS-Kelso Training Procedure* (ADM-TRAIN) for standard procedures.

17.2 Training outline

17.2.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.2.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.2.3 Perform initial precision and recovery (IPR) study as described above for water or soil samples. Summaries of the IPRs are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.3 Training and proficiency is documented in accordance with the *ALS-Kelso Training Procedure* (ADM-TRAIN).

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 There are no known modifications in this laboratory standard operating procedure from the reference method.

19) Summary of Changes Since Last Revision

19.1 Updated to latest ALS format.
19.2 Separated criteria for 200.7 and 6010D.
19.3 Removed reference to CLP.
19.4 Updated to reference 6010D.
19.5 Updated SOP references as necessary.
19.6 Deleted Section 3.6 (old) surrogate definition.
19.7 Section 6.1 – Updated references for prep methods.
19.8 Section 11.2.1.2 – Updated IS concentrations.
19.9 Deleted sections 11.2.2 and 11.2.3.
19.10 Section 11.3.1.1 and 11.3.2.1 – Updated bullets for ICB.
19.11 Section 12.5 – changed to annually.

20) References and Related Documents

20.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update V, Method 6010D, Revision 4, July 2014.

20.2 USEPA, Methods for Determination of Metals in Environmental Samples, Supplement I, EPA/600/R-94/111, Method 200.7, Revision 4.4, May 1994.

20.3 *Hardness by Calculation, Method 2340B,* Standard Methods for the Examination of Water and Wastewater, 20th ed., 1998.

21) Attachments/Appendices

21.1 Table 1 – Standard A for ICAP 6500 ICP-OES.

21.2 Table 2 – ICP ICV Standards.

21.3 Table 3 – ICP Interference Checks.

21.4 Table 4 – ICAP 6500 Analytical Wavelengths.

TABLE 1
Standard A for ICAP 6500 ICP-OES

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Antimony	(1)	100	5	1000	0.5
Beryllium	(1)	100	5	1000	0.5
Boron	(1)	100	5	1000	0.5
Cadmium	(1)	100	5	1000	0.5
Calcium	Ca stock	1000	0.5	1000	1.0*
Chromium	(1)	100	5	1000	0.5
Cobalt	(1)	100	5	1000	0.5
Copper	(1)	100	5	1000	0.5
Iron	(1)	100	5	1000	0.5
Lead	(1)	100	5	1000	0.5
Magnesium	(1)	100	5	1000	0.5
Manganese	(1)	100	5	1000	0.5
Molybdenum	(1)	100	5	1000	0.5
Nickel	(1)	100	5	1000	0.5
Selenium	(1)	100	5	1000	0.5
Silver	(1)	100	5	1000	0.5
Tin	Elemental Stock	1000	0.5	1000	0.5
Thallium	(1)	100	5	1000	0.5
Titanium	(1)	100	5	1000	0.5
Vanadium	(1)	100	5	1000	0.5
Zinc	(1)	100	5	1000	0.5
Hydrochloric Acid	-	-	50	1000	5%
Nitric Acid	-	-	10	1000	1%

(1) Mixed Standard, QCS-26
* 0.5mL 1000ppm Ca added to 5mL QCS-26(100ppm Ca), 1000mL Final Volume

TABLE 2
ICP ICV Standards

ICV1 Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	QCP-CICV-1	1000	2.5	500	5.0
Antimony	Elemental Stock	1000	1.25	500	2.5
Arsenic	QCP-CICV-3	500	2.5	500	2.5
Barium	QCP-CICV-1	1000	2.5	500	5.0
Beryllium	QCP-CICV-1	25	2.5	500	0.125
Cadmium	QCP-CICV-3	250	2.5	500	1.25
Calcium	QCP-CICV-1	2500	2.5	500	12.5
Chromium	QCP-CICV-1	100	2.5	500	0.5
Cobalt	QCP-CICV-1	250	2.5	500	1.25
Copper	QCP-CICV-1	125	2.5	500	0.625
Iron	QCP-CICV-1	500	2.5	500	2.5
Lead	QCP-CICV-3	500	2.5	500	2.5
Magnesium	QCP-CICV-1	2500	2.5	500	12.5
Manganese	QCP-CICV-1	250	2.5	500	1.25
Molybdenum	Elemental Stock	1000	0.25	500	0.5
Nickel	QCP-CICV-1	250	2.5	500	1.25
Potassium	QCP-CICV-1	2500	2.5	500	12.5
Selenium	QCP-CICV-3	500	2.5	500	2.5
Silver	QCP-CICV-1	125	2.5	500	0.625
Sodium	QCP-CICV-1	2500	2.5	500	12.5
Thallium	QCP-CICV-3	500	2.5	500	2.5
Titanium	Elemental Stock	1000	1.0	500	2.0
Vanadium	QCP-CICV-1	250	2.5	500	1.25
Zinc	QCP-CICV-1	250	2.5	500	1.25
Hydrochloric Acid	-	-	25	500	5%
Nitric Acid	-	-	5	500	1%

TABLE 3
ICP Interference Check Solutions

ICSA Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	CLPP-ICS-A	5000	50	500	500
Calcium	CLPP-ICS-A	5000	50	500	500
Iron	CLPP-ICS-A	2000	50	500	200
Magnesium	CLPP-ICS-A	5000	50	500	500
Hydrochloric Acid	-	-	25	500	5%
Nitric Acid	-	-	5	500	1%

ICSAB Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	CLPP-ICS-A	5000	50	500	500
Antimony	Elemental Stock	1000	0.5	500	1
Barium	CLPP-ICS-B	50	5	500	0.5
Beryllium	CLPP-ICS-B	50	5	500	0.5
Cadmium	CLPP-ICS-B	100	5	500	1
Calcium	CLPP-ICS-A	5000	50	500	500
Chromium	CLPP-ICS-B	50	5	500	0.5
Cobalt	CLPP-ICS-B	50	5	500	0.5
Copper	CLPP-ICS-B	50	5	500	0.5
Iron	CLPP-ICS-A	2000	50	500	200
Lead	CLPP-ICS-B	100	5	500	1
Magnesium	CLPP-ICS-A	5000	50	500	500
Manganese	CLPP-ICS-B	50	5	500	0.5
Nickel	CLPP-ICS-B	100	5	500	1
Silver	CLPP-ICS-B	100	5	500	1
Vanadium	CLPP-ICS-B	50	5	500	0.5
Zinc	CLPP-ICS-B	100	5	500	1
HCl	-	-	25	500	5%
HNO3	-	-	5	500	1%

TABLE 4
ICAP 6500 Analytical Wavelengths

Analyte	Wavelength	
Aluminum	167.0	Low Line
Aluminum	394.4	
Antimony	206.8	
Antimony	217.5	Alternate
Arsenic	189.0	
Barium	455.4	
Beryllium	234.8	
Boron	249.6	
Cadmium	226.5	
Cadmium	214.4	Alternate
Calcium	315.8	
Calcium	393.3	Low Line
Chromium	267.7	
Cobalt	230.7	
Cobalt	228.6	Alternate
Copper	327.3	
Copper	224.7	Alternate
Iron	259.9	
Lead	220.3	
Lithium	670.7	
Magnesium	279.0	High Line
Magnesium	279.5	Low Line
Magnesium	285.2	
Manganese	257.6	
Manganese	260.5	High Line
Molybdenum	202.0	
Nickel	221.6	
Nickel	231.6	Alternate
Phosphorus	214.9	
Phosphorus	178.2	Alternate
Potassium	766.4	
Selenium	196.0	
Silicon	251.6	
Silver	328.0	
Sodium	588.9	Alternate
Sodium	589.5	

TABLE 4 (cont.)
ICAP 6500 Analytical Wavelengths

Analyte	Wavelength	
Strontium	407.7	
Thallium	190.8	
Tin	189.9	
Titanium	336.1	
Vanadium	292.4	
Zinc	206.2	
Zinc	213.8	Alternate

Separatory Funnel Liquid-Liquid Extraction

DOCUMENT ID: EXT-3510 REVISION 13..0

Prepared By: _____ Date: 7/1/2020
Organics Manager, Jonathon Walter

Prepared By: _____ Date: 7/01/2020
Quality Assurance Manager, Bob Di Rienzo

Approved By: _____ Date: 7-1-2020
Laboratory Director, Charles Byrne

1) Scope & Applicability

1.1 This procedure uses techniques described in EPA Method 3510C for extracting nonvolatile and semi-volatile organic compounds from aqueous samples. The procedure also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods.

1.2 This method is applicable to the isolation and concentration of water insoluble and slightly water soluble organics in preparation for a variety of determinative methods which use chromatographic procedures.

2) Summary of Procedure

2.1 A measured volume of sample, usually 100mL-1000mL, is serially extracted at a specified pH with Dichloromethane or Hexane using a separatory funnel.

2.2 The extract is dried, concentrated, and (if necessary) exchanged to an appropriate solvent for the determinative procedure. The extract may undergo additional cleanup steps defined in other procedures.

3) Definitions

3.1 For general definitions applicable to most analyses refer to the SOP for *Sample Batches*, ADM-BATCH.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

5) Interferences

5.1 Phthalate esters can pose difficulties when performing sample extractions for Organochlorine pesticides, PCBs, and other semi-volatile organics. Phthalates are easily extracted or leached from materials containing plastics during laboratory operations. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials.

5.2 Routine cleaning of the extraction glassware is necessary. Refer to the SOP for Organic Extractions Glassware Cleaning.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure as referenced in the ALS Kelso Chemical Hygiene Plan and in the ALS Kelso Lab Waste Management Plan.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Refer to the applicable section in the determinative SOP for sample collection,

preservation, and holding times.

7.2 The extract holding time is 40 days from sample preparation to analysis for most methods; however the determinative SOP must be consulted.

8) Standards, Reagents, and Consumable Materials

8.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP Reagent/Standards Login and Tracking for the complete procedure and documentation requirements.

8.2 All prepared reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

8.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846.

8.4 Sodium hydroxide solution (l0N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 ml.

8.5 Sodium Chloride (granular), NaCl.

8.6 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray.

8.7 Sulfuric acid solution (1:1 v/v), H_2SO_4, purchased. Specific projects may require the use of concentrated HCl.

8.8 Extraction/exchange solvents

8.8.1 Dichloromethane, CH_2Cl_2 - Pesticide quality or equivalent.
8.8.2 Hexane - Pesticide quality or equivalent.
8.8.3 2-Propanol, $CH_3CH(OH)CH_3$ - Pesticide quality or equivalent.
8.8.4 Acetonitrile, CH_3CN - Pesticide quality or equivalent.

8.9 Methyl t-butyl ether (MTBE), Pesticide quality or equivalent.

9) Apparatus and Equipment

9.1 Separatory funnel – Appropriate size, with Teflon stopcock.

9.2 Drying column - modified funnel with ground glass bottom. Glass wool is at bottom covered by sulfate.

9.3 Kuderna-Danish (K-D) apparatus (Kontes K-570025-0500).

9.3.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.
9.3.2 Evaporation flask - 500 ml (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

9.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

9.3.4 Springs - 1/2 inch (Kontes K-662750 or equivalent).

9.4 Boiling chips - Pre-cleaned via DCM rinse, approximately 10/40 mesh (silicon carbide or equivalent).

9.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

9.6 Vials - 2 ml, glass with Teflon lined screw-caps or crimp tops.

9.7 pH indicator paper - pH range including the desired extraction pH.

9.8 Erlenmeyer fleaker - 250 ml.

9.9 Syringe – appropriate size syringe or Eppendorf.

9.10 Graduated cylinder – Appropriate size, Class A or validated general lab grade

9.11 Graduated pipettes, appropriate size.

9.12 Rotary Agitator- 12 and 24 Place Variable Speed Motor.

10) Preventative Maintenance

10.1 Routine cleaning of the extraction glassware is necessary. Refer to the SOP for Organic Extractions Glassware Cleaning.

11) Procedure

11.1 Test-specific benchsheets are attached. These benchsheets list such information as solvents, solvent exchanges, weights, and volumes specified for the determinative method. Use the correct benchsheet and record all extraction and sample information. To assist the analyst, a brief description of the procedure is given on the backside of the benchsheet.

11.2 Procedure for Sample Extraction

11.2.1 Evaluate each sample for settled solid material or sediment.

11.2.1.1 If the sample contains a small amount of material that will not interfere with the separatory funnel extraction, or the material can be suspended in the aqueous layer by shaking, shake the sample to mix the material into the sample and analyze the entire sample. Mark the sample meniscus on each bottle and proceed to the In-Bottle spiking below.

11.2.1.2 If the amount of material is enough to interfere with sample extraction or functioning of the separatory funnel, the Project Manager should be notified to determine the procedure to be used. In this situation the default procedure is to *completely* decant the liquid portion of the sample (without shaking the sample or after re-settling) into a graduated cylinder to measure the volume. It must be documented on the benchsheet when decanting is performed. Proceed to the Graduated Cylinder spiking below.

11.2.2 One set of QC containing matrix spike, duplicate matrix spike, lab control sample and method blank is done for every 20 samples.

Note: It is important that the correct spiking process be used. Addition of surrogate and spike is routinely witnessed by a second analyst to assure completeness. Refer to the SOP for the *Addition of Spikes and Surrogates* (EXT-SAS) for general practices and witnessing procedures. Also:

11.2.2.1 Make sure the tip of the spiking pipette or syringe is just below the surface of the sample. The spiking solution should go into the sample, not disperse on top of it.

11.2.2.2 Make sure the body of a plastic pipette/pipettor does not touch the inside of the bottle or graduated cylinder.

11.2.3 In-Bottle Spiking

11.2.3.1 Add the surrogate spiking solution into the sample in the bottle.

11.2.3.2 For the LCS and sample(s) in each analytical batch selected for matrix spiking, add the prescribed volume matrix spiking standard into the sample bottle.

Note: When spiking into the sample bottle, if the bottle has been filled to the top such that there is no room for the spiking solutions, pipet a small amount of the sample into its separatory funnel prior to spiking.

11.2.3.3 Transfer the sample to the separatory funnel by pouring the entire contents into the funnel (nominally 1L bottle, or smaller). Rinse the sample bottle with a portion of extraction solvent and add the rinsate to the funnel.

NOTE: When measuring out the correct volume to add to the units, be sure to measure the volume of organic free DI water for the LCS and the MB prior to the sample. In this manner less glassware will be generated for the glasswasher.

11.2.3.4 Measure and record the sample volume by filling the bottle to the mark with water and measuring the volume with a Class A TC graduated cylinder. Record the sample volume on the benchsheet.

11.2.4 Graduated Cylinder Spiking – used if a portion of the sample was transferred to a graduated cylinder due to solids content (section 11.2.1.2).

11.2.4.1 Record the sample volume on the benchsheet.

11.2.4.2 Add the surrogate spiking solution into the sample in the graduated cylinder.

11.2.4.3 For the LCS and sample(s) in each analytical batch selected for matrix spiking, add the prescribed volume matrix spiking standard into the designated sample that was transferred to a graduated cylinder. The LCS is a volume of organic free DI water added to a graduated cylinder.

11.2.4.4 Transfer the sample to the separatory funnel by pouring the entire contents into the funnel. Rinse the graduated cylinder with the extraction solvent, but do not rinse the sample bottle containing the remaining solid material. The remaining solid material may be analyzed separately (depending on the Project Manager's instructions) and any remaining target analytes in the solid portion will be accounted for in that analysis.

11.3 Check the pH of the sample by spotting a wide-range pH strip with the sample using a Pasteur pipette. If necessary, adjust the pH for the specific determinative method that will be used to analyze the extract. Adjustments in pH are made by using sodium hydroxide solution and/or sulfuric acid solution. Specific projects may require the use of concentrated HCl.

11.4 Add 15-60 ml of the appropriate solvent to the separatory funnel.

NOTE: Dichloromethane creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted once. Venting of the separatory funnel should be into a hood to avoid needless exposure of the analyst to solvent vapors.

11.5 Seal and shake the separatory funnel venting to release excess pressure. Once vented, the separatory funnels are shaken or tumbled for 1-2 minutes.

11.6 Allow the organic layer to separate from the water phase. If the emulsion is more than one-third the size of the solvent layer, the analyst may employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in a fleaker. If the emulsion cannot be broken, transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid - Liquid Extraction or contact the Project Manager.

11.7 Repeat the extraction two more times using fresh portions of solvent. Combine the three solvent extracts.

11.8 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH. Serially extract three times with 15-60 ml of appropriate solvent, as outlined in Sections 11.4 through 11.6.

11.9 Perform the concentration using the Kuderna-Danish (K-D) Technique.

11.9.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 ml concentrator tube to a 500 ml funnel evaporation flask and rinsing 3 times with DCM. Dry the extract by passing it through a drying column

containing anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer fleaker, which contained the solvent extract and add it to the column to complete the quantitative transfer, ensuring to rinse the funnel.

11.9.2 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 ml of Dichloromethane to the top of the column. Place the K-D apparatus on a hot water bath (15-20-C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 10 ml, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

11.9.3 If a solvent exchange is required, momentarily remove the Snyder column, add 15 ml of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain proper distillation.

11.9.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 ml of Dichloromethane or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in the next section or adjusted to 10.0 ml with the solvent last used. Measure the final extract volume using a 10mL graduated pipette.

11.10 If further concentration is needed, nitrogen blow-down technique is used to adjust the extract to the final volume required.

11.10.1 Place the concentrator tube in a warm water bath (approximately 35ºC) or at room temperature and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Do not let the sample go dry.

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

11.10.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 ml, semivolatile analytes may be lost.

11.11 Take to final volume and transfer the concentrated extract to a labeled autosampler vial (with a Teflon lined screw-cap or crimp top) of storage vial. Measure the final extract volume using a 1mL graduated pipette. The extracts obtained may now be analyzed for the target analytes using the appropriate determinative technique. The extract holding time is 40 days from sample preparation to analysis.

12) QA/QC Requirements

12.1 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). Refer to the SOP for the determinative method for minimum QC requirements.

12.2 Any reagent blanks, laboratory control samples, or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

13) Data Reduction and Reporting

13.1 Preparation of all samples must be documented on a bench sheet. All information regarding the sample(s) extracted, aliquoted, QC spiked, extraction steps, etc. must be documented by the person(s) performing the extraction. Bench sheets are completed and a batch lot number is assigned. The Manufacturer's lot numbers or ID's for the reagents are added to bench sheets.

13.2 The bench sheet must be reviewed by the extraction lead, supervisor, or instrument lab analyst. The instrument lab analyst should sign-off on the bench sheet, thus accepting custody of the extracts.

13.3 Following primary data review, all data is reviewed by a secondary analyst. Refer to the SOP for *Laboratory Data Review Process* (ADM-DREV) for details. The person responsible for final review of the bench sheet should assess the overall validity and quality of the results.

14) Contingencies for Handling Out-of-Control or Unacceptable Data

14.1 Refer to the SOP for Nonconformance and Corrective Action (ADIN-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

15) Method Performance

15.1 Refer to the reference method for additional method performance data available.

16) Pollution Prevention and Waste Management

16.1 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

17) Training

17.1 All analysts performing this analysis are required to read and understand this SOP.

17.2 Training is documented following the *Employee Training and New Employee Orientation* (ADM-TRAIN).

18) Method Modifications

18.1 There are no known modifications in this laboratory standard operating procedure from the reference method.

19) References

19.1 S EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," March 12, 2007.

19.2 EPASW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Method 3510C, Revision 3

19.3 TNI Standard, Volume 1- 2009, TNI Standard, Volume 1 -2016.

20) Changes Since Last Revision

Summary of Revision Changes			
Revision Number	Effective Date	Document Editor	Description of Changes
13.0	7/10/2020	T. Caron	Updated The SOP to the current ALS version/format. Equipment list and Procedural steps were edited in sections 8 and 11 to reflect current practice. Boiler plate sections were reformatted; Definitions, Safety, NCAR and Training.

21) Attachments, Tables, and Appendices

21.1 Active Benchsheets

21.1.1 :R:\Extractions\Active Benchsheets\3510\3510_Fuels-Water.pdf.

21.1.2 R:\Extractions\Active Benchsheets\3510\3510_TCLP_PestPCB.pdf.

21.1.3 R:\Extractions\Active Benchsheets\3510\Add Prep 3510 1,4 dioxane.pdf.

21.1.4 R:\Extractions\Active Benchsheets\3510\Add Prep 3510 DIMP HCL (SVM).pdf.

21.1.5 R:\Extractions\Active Benchsheets\3510\Add Prep 3510 TCLP.pdf.

21.1.6 R:\Extractions\Active Benchsheets\3510\Entrix 3510 prep sheet coextract (alkanes).pdf.

21.1.7 R:\Extractions\Active Benchsheets\3510\Method_ WIDROAlphaPinene_Fuels.pdf.

Metals Digestion - EPA 3010A

DOCUMENT ID: MET-3010, REVISION 16.0

Approved By: _____ Date: 1/13/20
Inorganics Manager, Jeff Coronado

Approved By _____ Date: 1/13/20
Quality Assurance Manager, Carl Degner

Approved By: _____ Date: 1/14/20
General Manager, Ambrose Hughey

1) Scope & Applicability

1.1 This procedure uses techniques described in EPA Method 3010A for acid digestion used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solid. The procedure is applicable to ICP-OES analysis for "Total Metals.

1.2 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DOD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD5)* may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 Nitric acid is added to a representative aliquot of sample and refluxed in a digestion cup. This step is repeated until the digestate is light in color or until the color has stabilized.

2.2 After the digestate has been brought to a low volume, it is refluxed with HCL and brought to volume. Analysis is performed by ICP-OES methods 200.7 and 6010. (see SOP MET-ICP for target elements.

3) .Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5 Laboratory Duplicates (DUP) – Additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6 Method Blank (MB) - An artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7 Laboratory Control Samples (LCS) – An aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8 Critical-volume measurement: Any measurement of volume which has a direct impact on the quantification of target parameters. Examples are: Measurement of standards, sample aliquots, QC standards and spiking solutions, measurement of sample volume, final extract or digestate volume.

3.9 Non-Volumetric Labware: Any container used for measuring initial sample volume or final extract or digestate volume. Examples of this are the centrifuge tubes used to bring metals digestions to final volume and disposable serological pipettes.

3.10 Manufacturer Lot: Labware with unique manufacturer identification referred to as a lot number.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

4.2 It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in the SOP *Employee Training and Orientation* (ADM-TRAIN).

5) Interferences

5.1 Refer to the determinative method for a discussion of interferences.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and gloves appropriate for the solvent being used.

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Kelso Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

6.3 Hydrochloric and/or Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Aqueous samples are preserved with nitric acid (pH<2), then stored at room temperature from receipt until analysis. If properly acid preserved, the sample can be held up to 6 months before analysis.

7.2 Samples acidified at the laboratory must be held for 24 hours, then the pH verified as <2 prior to digestion.

7.3 Metals holding time is six months from sample collection until analysis.

8) Apparatus and Equipment

8.1 Polypropylene digestion tubes, 125mL - Environmental Express.

8.2 Polypropylene ribbed watch glasses.

8.3 Block Digester, calibrated to maintain 95 ± 2°C.

9) Standards, Reagents, and Consumable Materials

9.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Standards, reagents and consumable material documentation shall indicate traceability to purchased neats or compounds. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

9.2 All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

9.3 Reagent water: ASTM Type I water (resistivity $\geq$18 MΩ-cm, conductivity $\leq$0.056 uS/cm).

9.4 Concentrated Nitric Acid: J.T. Baker “Instra-analyzed”, Trace Metals Grade.

9.5 Concentrated Hydrochloric Acid: J.T. Baker “Baker Analyzed” ACS Reagent.

9.6 Metals spiking solutions: Four spiking solutions are needed to prepare the matrix spike sample; SS1, SS3, SS4, and SS5. Follow the formulations laid out on the "Metals Spike Form" (see Attachments for example). These solutions are prepared in acid rinsed Class A volumetric flasks using purchased custom mixed standards or single analyte standards. Aliquots are made using acid rinsed Class A volumetric pipettes of the appropriate size.

9.6.1 SS1 (Al, Ag, Ba, Be, Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Sb, V, and Zn) - Fill a 1000 mL volumetric flask approximately half full with reagent water, add 50 mL of nitric acid and mix. Next add 50 mL 1000 ppm Antimony, then 100 mL of the custom mixed standard (ALS-89) purchased from Inorganic Ventures. Dilute to volume with reagent water, mix thoroughly and transfer to a 1000 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

9.6.2 SS3 (Hg, As, Se, and Tl) - Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 50 mL each of 1000 ppm Arsenic and Selenium. Then add 10 mL 1000 ppm Thallium and 6 mL of 1000 ppm Hg. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

9.6.3 "SS4 (B, Mo, U) - Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 50 mL 1000 ppm Molybdenum, 25 mL 1000 ppm Boron, and 10 mL 1000 ppm Uranium. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution's expiration date is determined by the earliest expiration date of any single component in the solution.

9.6.4 SS5 (K, Na, Mg, Ca) - Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next, add 50 mL of 10,000 ppm Potassium, Sodium, Magnesium, and Calcium. Dilute to volume with reagent water, mix thoroughly and transfer to a Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

10.2 Maintenance for this procedure is generally limited to glassware cleaning, pipette monitoring, and hot plate calibration. Procedures for glassware washing are described in the SOP for *Metals Laboratory Glassware Cleaning* (MET-GC). Procedures for pipette monitoring are given in the SOP *Checking Volumetric Labware* (ADM-VOLWARE).

10.3 Each block digester is uniquely identified and the temperature is verified with each batch of samples. To perform the verification, a certified thermometer is placed in a digestion cup half filled with mineral oil, which is then placed in the block digester. The thermometer does not touch the bottom of the container. The temperature is turned to the 95ºC setting and the mineral oil is allowed to come to temperature. The analyst will verify that the hotplate gives a temperature of 95 ± 2ºC. If not, the

temperature is adjusted until the thermometer reads and maintains 95 ± 2ºC. Each hot block has an assigned calibrated thermometer. The temperature, the correction factor of the assigned thermometer, and the thermometer location is recorded on the digestion bench sheet.

11) Procedure

11.1 Record all digestion and sample information on the applicable bench sheet.

11.2 Shake the sample to mix. Measure a 25 mL aliquot into a 125 mL digestion cup. At this point add the spiking solutions (as described in section 12 of this SOP) to the designated spike sample(s).

11.3 Add 0.750 mL of concentrated HNO3. Place rack of digestion cups in block digester and evaporate to a low volume (5 ml), making certain the sample does not boil and that no portion of the bottom of the digestion cup is allowed to go dry. This should take about 3.5 hours. Cool the digestion cups, add another 0.75 ml portion of HNO3, cover with a watch glass and heat so that a gentle reflux action occurs. (CAUTION: Do not allow sample to go dry. Should this occur, discard sample and re-prepare.) Continue refluxing until digestion is complete. (Additional acid may be required). Digestion is complete when the digestate is light in color or when the color has stabilized.

11.4 Reduce the sample volume to 5 mL, cool the digestion cup and add 1.25 mL of concentrated HCL. Cover the digestion cup and reflux for an additional 15 minutes. If the digest volume reduces to less than 5 mL add approximately 5-10 mL of reagent water and warm for an additional 15 minutes to ensure any precipitates are re-dissolved.

11.5 Remove the digestion cups from the block digester and allow to cool. Rinse down the sides of the digestion cup and the watch glass with reagent water. Dilute to the 25 mL mark on the digestion cup with reagent water. Allow digestates to settle before analysis. If immediate analysis is necessary the digestates may be centrifuged to remove insoluble material.

12) Quality Assurance/Quality Control Requirements

12.1 The 95ºC block digester. temperature must be monitored and documented on a per-batch basis. The actual measured temperature, thermometer correction factor, and corrected temperature must all be recorded.

12.2 Digest one laboratory control sample with each batch. Use the Inorganic Ventures ICV solutions for the liquid laboratory control sample (LCSW) as follows:

12.2.1 0.125 mL of Inorganic Ventures QCP-CICV-1, 0.125 mL of QCP-CICV-3, 0.05 mL of 1000 ppm Sb and 0.25 mL SS4 are added to 25 mL of reagent water in a 150 mL glass beaker and digested as per the procedure.

12.3 Digest one preparation blank (with each samples matrix). Prepare one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use reagent water and follow the digestion procedures.

12.4 Digest one duplicate and one spiked sample with each sample matrix. Prepare one duplicate and spike sample per each digestion batch or per twenty samples whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

12.5 Spike samples are prepared by adding 0.25 mL of SS1, SS3, SS4, and SS5 to the 25 mL aliquot designated for the matrix spike prior to the addition of acids and documented on the digestion bench sheet.

12.6 TCLP/SPLP 3010 Digest

12.6.1 Measure a 25 mL aliquot, using a 125 mL digestion cup. At this point add the spiking solutions to the designated spike sample(s).

12.6.2 The LCS and Matrix Spike are prepared by adding 1.25 mL of SS1, SS3, SS4, and SS5 to the 25 mL aliquot. A matrix spike shall be performed for each waste type (soil, sludge, liquid waste, etc.). The spiked samples must be subjected to the entire sample preparation and analytical process. Matrix spikes are to be added after extraction and filtration and prior to the addition of acids. 0.25 mL TCLP Spike Solution (ALS-57-R1) may be used in place of spiking solutions when appropriate for TCLP 3010 digests.

12.6.3 Following the 3010 digestion procedure, the samples are diluted to a 25 mL final volume.

12.6.4 For additional guidance, refer to the SOPS, MET-TCLP and MET-SPLP.

12.7 CA W.E.T / STLC Procedure, 3010 Digest

12.7.1 Measure a 25 mL aliquot, using a 125 mL digestion cup. At this point add the spiking solutions to the designated spike sample(s).

12.7.2 The LCS and Matrix Spike are prepared by adding 2.50 mL of SS1, SS3, SS4, and SS5 to the 25 mL aliquot. A matrix spike shall be performed for each waste type (soil, sludge, liquid waste, etc.). The spiked samples must be subjected to the entire sample preparation and analytical process. Matrix spikes are to be added after extraction and filtration and prior to the addition of acids.

12.7.3 Following the 3010 digestion procedure, the samples are diluted to a 25 mL final volume.

12.7.3.1 For additional guidance, refer to the SOP MET-STLC.

13) Data Reduction and Reporting

13.1 Digestion data sheets including volumes used are completed and a batch lot number is assigned and attached to the data sheet. The Manufacturer's lot numbers for the reagents used are added to the digestion data sheet.

13.2 Spiking sheets are included with the digestion bench sheet for reference.

13.3 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the *SOP for Laboratory Data Review Process (ADM-DREV)* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Manager to inclusion in the report narrative.

13.4 It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in this SOP. Average, RPD, spike level and spike recovery are entered on the analytical spreadsheet for corresponding samples. All data will be initialed, dated and attached to required data quality worksheet.

14) Method Performance

14.1 Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as in the determinative procedure. The method detection limit(s) and method reporting limit(s) are established for the determinative procedure. See *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* (CE-QA011/ADM-MDL).

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. Refer to the ALS Kelso Chemical Hygiene Plan.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformance and Corrective Action Procedure* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.
- Customer inquiries concerning data quality or services (when applicable). NCAR not required for simple corrections with no impact to the client.
- Data errors reported to clients, non-conforming re-checks.
- Deficiencies found during internal or external audits.

- Login errors or shipping errors.
- IT issues if there is a significant impact to a client.
- Turnaround time complaints.
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Training outline

17.1.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to TNI's Initial Demonstration of Capability.

17.2 Training is documented following *Employee Training and Orientation* (ADM-TRAIN).

17.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 Section 11: The lab uses 25 mL of sample. All acids added to the samples are adjusted accordingly to the 25 mL final volume.

18.2 Digests are not covered with a watch glass during the evaporation process.

19) References

19.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. EPA SW-846, 3rd Edition, Final Update 1, Method 3010A, July 1992.

19.2 SOP: *Metals and Semivolatile Extraction, EPA 1312* (MET-SPLP).

19.3 SOP: *Waste Extraction (WET) Procedure (STLC) for Non-Volatile and Semi-Volatile Parameters, Title 22* (MET-STLC).

19.4 DoD Quality Systems Manual for Environmental Laboratories, current version.

19.5 TNI Standard, Volume 1, 2009 & 2016.

20) Changes Since the Last Revision

Revision Number	Effective Date	Document Editor	Description of Changes
16.0	1/06/20	T. Caron	Reformatted SOP to current ALS SOP format. Minor typographical, grammatical, and formatting changes to improve readability –not affecting content. Removed obsolete references to FLAA analysis. Section 7: Updated this section to be consistent with the MET-DIG SOP. Modified sample preparation to include the use of a hot block digester, as referenced in Summary of Procedures, Apparatus and Equipment, Preventative Maintenance, Procedures and QA requirements. Section 9; and 12: Numerous changes made in this section to reflect current practices. Table A was updated.

21) Attachments, Tables, and Appendices

21.1 Table A: Metals Spiking Solutions Concentrations Form.

Table A

METALS SPIKING SOLUTIONS CONCENTRATIONS FORM

Solution Name	Element	mLs of 1000ppm Solution	Final Volume	Solution Conc. mg/L	Enter mls Added
K-MET SS1 *** Add after HNO3 and before ALS-89 when making the solution	HNO3	50.0	1000ml	-	
	Al	100*	1000ml	200	
	Ag	100*	1000ml	5	
	Ba	100*	1000ml	100	
	Be	100*	1000ml	5	
	Cd	100*	1000ml	5	
	Co	100*	1000ml	50	
	Cr	100*	1000ml	20	
	Cu	100*	1000ml	25	
	Fe	100*	1000ml	100	
	Pb	100*	1000ml	50	
	Mn	100*	1000ml	50	
	Ni	100*	1000ml	50	
	Sb***	50.0	1000ml	50	
	V	100*	1000ml	50	
	Zn	100*	1000ml	50	
K-MET SS2	HNO3	25.0	500ml	-	
	As	2.00	500ml	4	
	Cd	2.00	500ml	4	
	Pb	2.00	500ml	4	
	Se	2.00	500ml	4	
	Tl	2.00	500ml	4	
	Cu	2.00	500ml	4	
K-MET SS3	HNO3	25.0	500ml	-	
	As	50.0	500ml	100	
	Se	50.0	500ml	100	
	Tl	10.0	500ml	20	
	Hg	6.00	500ml	12	
K-MET SS4	HNO3	25.0	500ml	-	
	B	25.0	500ml	50	
	Mo	50.0	500ml	100	
	U	10.0	500ml	20	
K-MET SS5	HNO3	25.0	500ml	-	
	K**	50.0	500ml	1000	
	Na**	50.0	500ml	1000	
	Mg**	50.0	500ml	1000	
	Ca**	50.0	500ml	1000	

K-MET Hydride	HNO3	1.0	100ml	-	
	As, Se	0.25	100ml	.25	
K-MET QCP-CICV-1	Ca, Mg, Na, K	no dilution	-	2500	
	Al, Ba	no dilution	-	1000	
	Fe	no dilution	-	500	
	Co, Mn, Ni, V, Zn	no dilution	-	250	
	Cu, Ag	no dilution	-	125	
	Cr	no dilution	-	100	
	Be	no dilution	-	25	
K-MET QCP-CICV-3	As, Pb, Se, Tl	no dilution	-	500	
	Cd	no dilution	-	250	

* Denotes volume of mixed stock standard.
** Denotes 10,000 ppm individual stock standards.

Standard	mls of standard	ppm	Logbook #	Exp. Date

Mercury in Solid or Semi-Solid Waste

DOCUMENT ID: MET-7471, REV 20.0

Approved By: _____ Date: 12/5/19
Inorganics Manager, Jeff Coronado

Approved By _____ Date: 12/5/19
Quality Assurance Manager, Carl Degner

Approved By: _____ Date: 12/9/19
General Manager, Ambrose Hughey

1) Scope & Applicability

1.1 This Standard Operating Procedure (SOP) describes the procedure used to determine the concentrations of Mercury in soils, sediments, freeze dried tissues, bottom deposits, and sludge-type materials using Method EPA 7471A or 7471B. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix. Method 7471 is a cold-vapor atomic absorption procedure.

1.2 The Method Reporting Limit (MRL) is 0.02 mg/kg. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. A Method Detection Limit (MDL) of 0.002 mg/kg has been achieved using this procedure. Refer to the ALS Kelso DQO Table for current data quality objectives.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DOD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD/ADM-DOD5)* may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 A representative aliquot of sample is prepared as described in this procedure. The mercury is reduced to its elemental state and aerated from solution and measured with an atomic absorption spectrometer. The mercury vapor passes through a cell positioned in the light path of the AA where absorbance is measured as a function of mercury concentration.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not listed. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8 Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.9 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.10 Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.11 Standard Reference Material (SRM) – **A** material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

4.2 It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in the SOP *Employee Training and Orientation* (ADM-TRAIN).

5) Interferences

5.1 Potassium permanganate is added to eliminate possible interference from sulfide. Samples high in chlorides require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which absorbs radiation at 253 nm.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and gloves appropriate for the solvent being used. .

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Kelso Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

6.3 Hydrochloric and/or Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Glass, plastic, and polytetraflouroethylene (PTFE) containers are suitable in most cases.

7.2 Non-aqueous samples are stored at 4 ± 2 ºC from receipt until analysis, unless otherwise dictated by project specifications.

7.3 Samples must be analyzed within 28 days of sampling.

7.4 Non-aqueous samples are stored at 4 ± 2 ºC from receipt until analysis, unless otherwise dictated by project specifications.

8) Apparatus and Equipment

8.1 CETAC M-6100A Mercury Analyzer. See Attachments, Tables and Appendices for instrument parameters.

8.2 Environmental Express Block Digestion Unit.

8.3 Pipettors, Eppendorf and Finn pipette fixed and adjustable volume.

8.4 Polypropylene graduated cylinders, 50 mL.

8.5 125 mL Digestion Vessel tubes.

8.6 Laboratory balance, top-loader capable of readings .001g (3-place). Mettler, Ohaus, or equivalent Standards,

9) Standards, Reagents, and Consumable Materials

9.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Standards, reagents and consumable material documentation shall indicate traceability to purchased neats or compounds. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

9.2 All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

9.3 Mercury stock solution (1,000 mg/L). Commercially prepared certified solution stored at room temperature. The expiration date determined by manufacturer.

9.4 Mercury working standard (100µg/L). Prepared from the intermediate stock solution listed above. Store at room temperature and prepare a new standard daily.

9.5 Laboratory Control Sample – ERA Priority Pollutant/CLP Inorganic Soil reference material. Store at room temperature in the original container and use the vendor expiration date.

9.6 Matrix spike solution (1 mg/L) – Prepare by making a 1:1000 dilution of the mercury stock solution. Store at room temperature and prepare a new standard monthly.

Note: See the Procedure section for details on preparation of calibration and ICV standards. See the Quality Assurance section for QC sample preparation.

9.7 Reagent water - ASTM Type II water (laboratory deionized water).

9.8 Acids - Purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the Method Reporting Limit.

9.8.1 Nitric Acid (HNO_3) 69-70% – JT Baker-Baker Instra-Analyzed® or equivalent.

9.8.2 Sulfuric Acid concentrated (H_2SO_4) – EMD-OmniTrace® or equivalent.

9.8.3 Hydrochloric Acid concentrated (HCL) – VWR – BHD-Aristar® or equivalent.

9.9 Potassium permanganate solution, 5% w/v. To prepare, add 50 g of solid reagent to 1000 mL of DI water and place on magnetic stir plate for approximately 30 minutes until dissolved.

9.10 Sodium chloride/hydroxylamine hydrochloride solution, 12% w/v each. To prepare, add 120 g sodium chloride and 120 g of hydroxylamine hydrochloride to 1000 mL of DI water and place on magnetic stir plate for approximately 15 minutes until dissolved.

9.11 Stannous chloride, 10% w/v in HCl (7% v/v). To prepare, add 100 g stannous chloride crystals and 70 mL of concentrated hydrochloric acid in 1000 mL of D.I. water. Seal lid on mixing bottle and shake until the stannous chloride is dissolved.

9.12 Aqua Regia – Prepare immediately before use by carefully adding 3 parts of concentrated HCL to one part of HNO_3.

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

10.2 ALS staff performs all routine maintenance and troubleshooting. Preventative maintenance activities listed below should be performed when needed as determined by instrument performance (i.e. stability, sensitivity, etc.) or by visual inspection. Repairs of an extraordinary nature may or may not require factory service, depending on the nature of the task.

10.3 Keep the instrument free of dust, deposits, and chemical spills.

10.4 Replace the peristaltic and autosampler rinse tubing.

10.5 Remove and clean the Gas-Liquid separator.

10.6 Remove, dismantle, and clean the optical cells (sample cell and reference cell) including the sapphire windows.

10.7 Replace the Hg lamp bulb when the Lamp Over-Range is triggered. (The new instrument does not display a value).

11) Procedure

11.1 Sample Preparation

11.1.1 Mix the sample thoroughly to achieve homogeneity. For soil, sediment, solids, weigh approximately 0.5 g of well-homogenized sample and place in the bottom of a 125 mL digestion tube and record the weight to the nearest 0.01g. Add 5.0 mL of reagent water and 5.0 mL of aqua regia, then heat in the Block Digestion Unit for 2 minutes at 95ºC.

11.1.2 Cool then add 10 mL of reagent water and 15 mL of potassium permanganate solution. If the purple color does not persist for 15 minutes, add additional potassium permanganate until it does so. Any additional potassium permanganate solution must also be added to the blanks and standards in equal proportion.

Note: Spiking solution is added prior to acidification.

11.1.3 Mix thoroughly and place in the heating block for 30 minutes at 95ºC. The temperature of the block is monitored with a thermometer that is calibrated annually.

11.1.4 Cool and add 6 mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate. Perform this addition under a hood as Cl_2 could be evolved.

11.1.5 Add 27 mL of reagent water and the sample is ready for analysis. (The vapor generator does the step of adding the stannous chloride solution automatically.)

11.2 Calibration

11.2.1 To prepare calibration standards a 10 ppm intermediate stock solution is first prepared by aliquoting 1.0 mL of commercially prepared 1000 ppm stock standard into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This solution must be prepared monthly. Next, a 100 ppb working solution is prepared by aliquoting 1.0 mL of the 10 ppm intermediate stock solution into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This solution must be prepared daily.

Note: All standard aliquots are measured using calibrated fixed or adjustable volume autopipettors or calibrated disposable 5.0 or 10.0 mL pipettes.

11.2.2 Transfer 0, 0.1, 0.25, 0.5, 2.5 and 5.0 mL aliquots of the working solution to a series of labeled 125 mL digestion tubes. Add the appropriate amount of reagent water to bring each bottle to a volume of 5mL. Add 5.0 mL of aqua regia and heat in the heating block for 2 minutes at 95ºC. The final concentrations of the prepared standards are 0, 0.2, 0.5, 1.0, 5.0, 10.0 ppb.

11.2.3 The Initial Calibration Verification (ICV) is prepared by first making a 1000 ppb intermediate solution. 0.10 mL of commercially prepared 1000 ppm stock standard, from a different manufacturer and lot than the calibration standard, is aliquoted into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO_3. This solution must be prepared monthly. Prepare the ICV standard by aliquoting 0.25 mL to a labeled 125 mL digestion tube. Add the 4.75 mL of reagent water and 5.0 mL of Aqua Regia.

11.2.4 Cool and then add 10 mL of reagent water and 15 mL of potassium permanganate solution and return the tubes to the Block Digestion Unit for 30 minutes.

11.2.5 Cool and add 6.0 mL of sodium chloride-hydroxylamine hydrochloride solution. Add 27 mL of reagent water and the standards are ready for analysis.

11.2.6 CETAC Calibration and Sample Analysis

11.2.6.1 Turn on the CETAC instrument, including the Hg lamp, and autosampler. After this is done turn open the operating software (Mercury Analyzer 1.6.5).

11.2.6.2 The rinse station for the autosampler turns on automatically, but the peristaltic pump must be started manually. Make sure all sample uptake and drain tubes are placed correctly on the pump and are secured with the appropriate tension. Place the reagent uptake tube in the stannous chloride and start the pump.

11.2.6.3 From the software's main screen select "File", then: "New From". Under "Template Worksheet", click "Browse" and then select "Kelso Hg Template II". Enter the name of the worksheet and click: OK.

11.2.6.4 Go to the "Sequence Editor" tab to generate a sequence, then enter the QC and field samples to be analyzed in the appropriate order.

11.2.6.5 Transfer the solutions to be analyzed to labeled 12mL polyethylene test tubes and place them in the appropriate spaces on the autosampler trays.

11.2.6.6 Transfer the calibration blank and standards (0.2, 0.5, 1.0, 5.0, and 10 ppb) from their digestion tubes to the standard tubes located behind the autosampler trays. The calibration blank is placed in the left most tube and the other standards are placed in ascending order to the right.

11.2.6.7 Click start and the analysis will begin.

11.2.6.8 After the calibration standards have run the software will use linear regression to create a calibration curve based on the concentration and measured absorbance of each standard. The form of regression line is $y = mx + b$. If the correlation coefficient of the curve is greater than 0.995 the analysis will continue, if not the analysis will be terminated and corrective action will be needed by the analyst.

11.3 As the analysis sequence proceeds, next analyze the following QC standards.

- ICV (5.0 ppb standard prepared from a second source)
- ICB
- CRA (0.2 ppb calibration standard)
- CCV (5.0 ppb calibration standard)
- CCB

11.3.1 If either the ICV or CCV are different from their true values by more than 10% the software will terminate the analysis. If either the ICB or CCB is greater than the MRL the software will terminate the analysis. Method 7471A does not contain criteria for the CRA, however, the result must be a positive measured concentration. For 7471B analyses the criteria are ±30% of the true value. Also, specific project requirements may apply.

Note: For projects falling under DoD QSM requirements, the QSM criteria for CRA standards is ±20% and for ICB and CCB standards no analytes detected > LOD. (The ICV limit is as listed above.)

11.4 Sample Analysis

11.4.1 The samples are analyzed with the CETAC analyzer in the same manner as the calibration standards. The analyzer does the step of adding the stannous

chloride solution automatically. Check the baseline between samples to verify that the spectrometer reading has stabilized at the normal baseline level.

11.4.2 The analytical sequence should be set up to include all samples, QC samples, blanks, and calibration verification standards at necessary intervals. Refer to the SOP for Sample Batches.

11.5 Sample digestion batches are analyzed with a set of CCV and CCB standards which are run at the beginning and end of the analytical run and at a minimum every 10 samples during the run. The same criteria listed above are applied to the CCVs and CCBs and if one is found to be outside these limits the analysis is terminated.

12) QA/QC Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 This method shall operate under the formal Quality Assurance Program established at ALS and must maintain records that define the quality of data that is generated. Data shall be compared to established criteria in order to determine if the results of the analyses meet the performance characteristics of the method. It is required that an initial demonstration of capability and periodic analysis of laboratory reagent blanks, laboratory fortified blanks, and other QC solutions as a continuing check on performance. The accuracy and precision of the procedure must be validated *before* analyses of samples begin, or whenever significant changes to the procedures have been made.

12.1.2 Initial demonstration of capability must be performed by each analyst performing sample analysis and documented in the laboratory records.

12.2 Method Detection Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates with a MDL spiking solution near the MRL and analyze. Refer to *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011/ADM-MDL).

12.2.2 Calculate the average concentration found (x) in µg/L, and the standard deviation of the concentrations (s) in µg/L for each analyte. Calculate the MDL for each analyte. Refer to CE-QA011/ADM-MDL.

Note: Method Detection Limits are subject to change as new MDL studies are completed.

12.3 Limits of Quantification

12.3.1 The laboratory establishes a Limit of Quantitation (LOQ) for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within 70-130% of the true values to verify the data reporting limit. Refer to CE-QA011/ADM-MDL.

12.4 For method 7471B, an LLQC sample (a CRA that is carried through the digestion) must be analyzed to verify accuracy at the MRL. The recovery must be ±30%.

12.5 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual, in *Sample Batches* (ADM-BATCH). For this analysis, these include:

12.5.1 Prepare one method blank (MB) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures. The Method Blank should be < MRL. Re-digest the associated samples if sample levels are <20X MB level.

Note: For projects falling under DoD QSM requirements, the QSM criteria for method blanks is no analytes detected > ½ MRL.

12.5.2 Prepare one Laboratory Control Sample (LCS) per digestion batch, or per 20 samples. Weigh 0.25 g of the current lot of "Environmental Resource Associates Priority Pollutant/CLP Inorganic Soil" prepared reference material in to a 125 mL Digestion vessel tube and prepare as per the procedure.

12.5.3 Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where

X = Concentration of the analyte recovered
TV = True value of amount spiked

Apply LCS recovery criteria from the DQO Table, unless project-specific or in-house limits are established. For method 7471B, the LCS recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range.

Note: For DoD QSM projects, the QSM LCS criterion is 80-120%. If the LCS fails the acceptance criteria, re-digest the batch of samples.

12.5.4 Prepare one sample duplicate and one matrix spike sample per each digestion batch, or per twenty samples, whichever is more frequent. For the matrix spike, add 0.25mL of the matrix spike solution to the designated spike sample, resulting in a spike concentration of 0.5 mg/kg. At times, specific samples will be assigned as duplicates or spikes depending on client requirements.

Note: Duplicate samples are routinely analyzed; however some projects may require a MSD. All DOD projects require a MSD. The MSD sample is prepare as described above.

12.5.5 The RPD criterion for duplicates is 20%. If not, flag the data or re-digest samples. Apply matrix spike recovery criterion listed in the DQO Table, unless project-specific limits are required. For method 7471B, the recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range. For DoD QSM work, MS recoveries are assessed using the QSM LCS control limits. If the MS (and/or MSD where applicable) recovery is outside acceptance limits proceed with the additional interference tests. Based on results of these tests, the physical nature of the sample (e.g. homogeneity), and any specific project requirements, a determination can then be made as to appropriate corrective action (e.g. re-digestion, reporting with a qualifier, alternative methodologies, etc.). If the analyte concentration is >4x the spike level the spike control limit is no longer applicable and no action is required.

Note: For DoD QSM projects, the duplicate RPD limit is 20% and MS recoveries are assessed using the QSM LCS control limits 80-120%.

12.5.5.1 Calculate percent recovery (%R) as:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

12.5.5.2 Calculate Relative Percent Difference (RPD) as:

$$\%\,RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1= Higher Result
R2= Lower Result

12.5.6 Interference Tests: Prepare one post spike for every batch of samples and if samples are sufficiently high (10x the MRL/LOQ) a serial dilution. The serial dilution must agree within 10% of the original sample result. Post spike recovery acceptance limits for method 7471A and 7471B are 80-120% for project falling under SW-846 Update IV. When both the post spike and dilution tests fail all of the samples in the associated preparation batch must be quantified via Method of Standard Additions (MSA).

13) Data Reduction and Reporting

13.1 It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12.

13.2 Record all sample weight, volumes and dilutions on an A.A. benchsheet (see Attachments).

13.3 Solution concentrations are calculated by the Mercury Analyzer software based on the linear regression calibration curve created when the calibration standards are analyzed. The absorbance measured for each sample is applied to the linear regression curve and the final solution concentration is determined and displayed as the instrument result.

13.4 Calculate sample results using the data system printouts and digestion information. The digestion and dilution information is entered into the data system. The data system then uses the calculations below to generate a sample result. Solid samples are reported in mg/Kg:

$$mg/Kg\,(Sample) = C^{*} \times Post\ Digestion\ Dilution\ Factor \times \frac{Digestion\ Vol.(ml)}{Sample\ wt.(g)} \times \frac{1mg}{1000ug} \times \frac{1L}{1000ml} \times \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in ug/L (in digestate).

NOTE: If results are to be reported on a dry weight basis as required by certain projects, the Sample Wt. (g) component of the equation should be the dry-weight derived from a determination of %moisture of a separate aliquot of the sample using the SOP for Total Solids.

13.5 Record all concentrations determined at the instrument and calculate the final results in mg/Kg. Record the final results on the A.A. Benchsheet.

13.6 The data packet for the sequence is submitted for review by supervisor or designee. The results are transferred to the appropriate report form located in the ALS network directory R:\ICP\WIP. Once the results are transferred, the report is reviewed.

13.7 A daily run log of all samples analyzed is maintained. All data should be printed and stored after operator has checked for evenness of burns. A copy of this document will go with each package of Tier III or higher data run that day.

13.8 Refer to the SOP *Laboratory Data Review Process* (ADM-DREV) for general instructions for data review.

14) Method Performance

14.1 Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as in the determinative procedure. The method detection limit(s) and method reporting limit(s) are established for the determinative procedure. See *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* (CE-QA011/ADM-MDL).

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. Refer to the ALS Kelso Chemical Hygiene Plan.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformance and Corrective Action Procedure* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.

- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.
- Customer inquiries concerning data quality or services (when applicable). NCAR not required for simple corrections with no impact to the client.
- Data errors reported to clients, non-conforming re-checks.
- Deficiencies found during internal or external audits.
- Login errors or shipping errors.
- IT issues if there is a significant impact to a client.
- Turnaround time complaints.
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Training outline

17.1.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to TNI's Initial Demonstration of Capability.

17.2 Training is documented following *Employee Training and Orientation* (ADM-TRAIN).

17.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 There are no known modifications in this laboratory standard operating procedure from the reference method.

19) References

19.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update IV, Method 7471B, Revision 2, February 2007.

19.2 DoD Quality Systems Manual for Environmental Laboratories, current version.

19.3 TNI Standard, Volume 1, 2009 & 2016.

20) Changes Since the Last Revision

Summary of Revision Changes			
Revision Number	Effective Date	Document Editor	Description of Changes
20.0	12/10/19	T. Caron	Reformatted SOP to current ALS SOP format. Minor typographical, grammatical, and formatting changes.

21) Attachments, Tables, and Appendices

21.1 Table 1: Analysis Parameters – M 6100 Mercury Analyzer.

21.2 Table 2: Summary of Corrective Actions.

Table 1
Analysis Parameters M-6100 Mercury Analyzer

Analysis Parameters

Instrument M-6100 Mercury Analyzer

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	30.00	60.00	50.00	4	2.00		253.65

Instrumental Zero

Zero before first sample: No

Zero periodically: Yes
Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)
5.00	10.00		

Standby Mode

Enabled: Yes
Standby Options: gas off, lamp off

Autodilution

Enabled: No
Condition:
Tube # range:
If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	Yes	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of
Lower (%)	Upper (%)	Lower (%)	Upper (%)	Determination
75	125	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

Table 2

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 7471A/B	ICAL	Prior to sample analysis	R2 ≥ 0.995	Correct problem then repeat ICAL
EPA 7471A/B	ICV	After ICAL	± 10%	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 7471A/B	CCV	Prior to sample analysis	± 10%	Correct problem then repeat CCV or repeat ICAL
EPA 7471A/B	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 7471A/B	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO	If exceeds limits, re-extract and re-analyze
EPA 7471A/B	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 7471A/B	Sample Duplicates	Include with each analysis batch (up to 20 samples)	≤ 20 % RPD	Re-homogenize and re-analyze if result is > 5 X the MRL

Semivolatile Organic Compounds By GC/MS-Method 8270D

DOCUMENT ID: SVM-8270D, REV 6.0

Prepared By: _____ Date: 11/13/19
Organics Manager, Todd Poyfair

Prepared By: _____ Date: 11/13/19
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Approved By: _____ Date: 11/14/19
General Manager, Ambrose Hughey

1) Scope & Applicability

1.1. This procedure is used to determine the concentrations of Semi-Volatile Organic Compounds in water and soil using EPA Method 8270D. This procedure may also be applicable to various miscellaneous waste samples. Tables 1A and 1B indicate compounds that may be determined by this method and lists their method reporting limits (MRLs) in water and soil. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. The Method Detection Limits (MDLs) will vary depending on the instrument used and preparation method.

1.2. This procedure can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone phase. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. Other compounds than those listed in Tables 1 may be analyzed. Refer to Section 1 of method 8270D.

1.3. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (*ADM-DOD5) may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 This method provides Gas Chromatography/Mass Spectrometry (GC/MS) conditions for the detection of Semi-volatile Organic Compounds. Prior to the use of this method, an appropriate sample preparation method must be used to recover the analytes of interest. An aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a fused silica capillary column. Compounds of interest are detected by a mass selective detector. Identification of the analytes of interest is performed by comparing the retention times of the analytes with the respective retention times of an authentic standard, and by comparing mass spectra of analytes with mass spectra of reference materials. Quantitative analysis is performed by using the authentic standard to produce a response factor and calibration curve, and using the calibration data to determine the concentration of an analyte in the extract. The concentration in the sample is calculated using the sample weight or volume and the extract volume.

2.2 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration and the chromatography for this compound is poor. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, to a chemical reaction in acetone, and can undergo photochemical decomposition. N-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-Dinitrophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Chloroaniline, and Benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the described matrices. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not previously listed. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the

effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6 Surrogate - Surrogates are compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of a surrogate is to evaluate the preparation and analysis of samples. Surrogates are added to blanks, standards, samples and spike samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

3.7 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.8 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.9 Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards.

3.10 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.11 Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.12 Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.13 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or

measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

4.2 It is the responsibility of the department supervisor/manager to document analyst training .and method proficiency, as described in: *Employee Training and Orientation* (ADM-TRAIN).

5) Interferences

5.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation of the samples. Corrective action should be taken to eliminate the interferences.

5.2 Accurate determination of phthalate esters can pose difficulties when using this methodology. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware may occur when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

5.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

6.3 This method uses Dichloromethane, a known human carcinogen. Refer to the methylene chloride policy document, ENV-HSE-NA-EX-006-EN for proper handling.

G:\SAFETY\TRAINING\Methylene Chloride\Methylene Chloride - NA 031419.pdf..

7) Sample Collection, Containers, Preservation, and Storage

7.1 Containers used to collect samples should be purchased pre-cleaned containers. Alternatively, containers used to collect samples for the determination of semivolatile

organic compounds may be soap and water washed followed by methanol (or isopropanol) rinsing. The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may not be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

7.2 Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g., if an automatic sampler is used), run reagent water through the sampler and use the rinsate as a field blank.

7.3 Water and soil samples must be iced or refrigerated at 4 ± 2˚C from time of collection until extraction.

7.4 Water samples must be extracted within 7 days and the extracts analyzed within 40 days following extraction. Soil samples must be extracted within 14 days and the extract analyzed within 40 days following extraction. Extracts are stored at <-10°C

8) Standards, Reagents, and Consumable Materials

8.1 The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

8.2 Solvents: Acetone, methylene chloride, methanol, and other appropriate solvents. Solvents must be of sufficient purity to permit usage without lessening the accuracy of the determination or introducing interferences.

8.3 Stock Standard Solutions (See Table 3)

8.3.1 Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. Commercially prepared stock standards are typically used when available at a concentration of 1000 µg/ml or more. Standard concentrations can be verified by comparison versus an independently prepared standard. Alternatively, prepare stock standard solutions at a concentration of 1000 µg/ml by dissolving 0.0100 g of reference material in methylene chloride or other suitable solvent and diluting to volume in a 10mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Store according to the vendors recommendations.

8.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 ± 2ºC or per manufacturer's recommendation and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

8.3.3 Stock standard solutions must be replaced after one year, or sooner, if comparison with check standards or samples indicates a problem.

8.4 Internal Standard Solutions (See Table 3) - The internal standards are 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12},

and Perylene-d_{12} (See Table 4 for corresponding compounds). The nominal concentration of the standard is 4000 ng/µL. Each 1 ml of sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store at room temperature when not being used. When using premixed certified solutions, store according to the manufacturer's recommendations.

8.5 GC/MS Tuning Standard (See Table 3) - A methylene chloride solution containing 50 ng/µL of Decafluorotriphenylphosphine (DFTPP). The standard should also contain 50 ng/µL each of Benzidine, DDT, and Pentachlorophenol, to verify injection port inertness and GC column performance. Store at 4 ± 2ºC when not being used, or store according to the manufacturer's recommendations.

8.6 Calibration Standards (See Table 3)

8.6.1 A minimum of five initial calibration standards should be prepared from stock solutions. One of the calibration standards should be at a concentration at or below the method reporting limit; the others should correspond to the range of concentrations found in real samples, but should not exceed the working range of the GC/MS system. At least one calibration standard must be at a concentration corresponding to a sample concentration meeting project-specific data quality objectives. Each standard should contain each analyte for detection by this method. Each 1 ml aliquot of calibration standards should be spiked with 10 µL of the internal standard solution prior to analysis. All calibration standards should be stored at <-10ºC or less and should be freshly prepared once a year, or sooner if check standards indicate a problem.

8.6.2 The daily calibration standard (CCV) is prepared at a nominal 80 ng/µL concentration from stock solutions. The CCV is prepared weekly and can be stored at 4 ± 2ºC. The DFTPP standard may be combined with this standard (maintaining 50 ng/µL) providing tuning verification and calibration verification can be done without interferences.

8.7 QC Standards (See Table 4)

8.7.1 Surrogates: Prepare a working solution in methanol containing 2-Fluorophenol, Phenol-d_6, and 2,4,6-Tribromophenol at 150 ng/µL and Nitrobenzene-d_5, 2-Fluorobiphenyl, and Terphenyl-d_{14} at 100 ng/µL. Aliquots of the solution are spiked into all extracted samples, blanks, and QC samples according to the extraction SOP used.

8.7.2 Matrix Spike Standards: Prepare a working solution in methanol containing all analytes of interest ("full list spike") from the standard analyte list (Table1) at 100 ng/µL. Aliquots of the solution are spiked into the selected QC aliquots according to the extraction SOP used.

Note: The spiking level of surrogate and spike may need to be adjusted according to project requirements, if dilutions are expected due to high levels of extracted components, or if a lower calibration range is used.

9) Apparatus and Equipment

9.1 Gas Chromatograph/Mass Spectrometer System

9.1.1 Gas Chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary

column should be directly coupled to the source. Agilent 5890, 6890 or equivalent.

9.1.2 Column: ZB-5MS Guardian- 30 m x 0.25 mm ID x 0.25 µm film thickness silicone-coated fused-silica capillary column. Recommended: Phenomenex with guard.

9.1.3 Mass Spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 2 when 1.0 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

9.1.4 GC/MS Interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

9.1.5 Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number emits. NIST98 Mass Spectral Library is used for spectral comparisons.

9.1.6 Appropriate analytical balance (0.0001 g), volumetric flasks, syringes, vials, and bottles for standards preparation.

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. Maintenance entries should include date, symptom of problem, corrective actions, and description of maintenance, date, and name. The log should contain a reference to return to analytical control.

10.2 Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

10.3 Gas Chromatograph

10.3.1 Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, seal, washer, O-ring, septum, column ferrule, and auto sampler syringe as needed. Liners and seals should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners and seals may be cleaned and re-used.

10.3.2 Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column cutting tool.

10.3.3 Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

10.4 Mass Spectrometer

10.4.1 Tune the MS as needed to result in consistent and acceptable performance while meeting the required ion abundance criteria given in section Table 3.

10.4.2 For units under service contract, certain maintenance is performed by instrument service staff, including pump oil changed, vacuuming boards, etc., as recommended by the manufacturer.

10.4.3 MS source cleaning should be performed as needed, depending on the performance of the unit. This may be done by the analyst or by instrument service staff.

11) Procedure

11.1 Sample Preparation

11.1.1 Water samples

11.1.1.1 Water samples are prepared using continuous liquid-liquid extraction, EPA method 3520C (EXT-3520). In some circumstances, such as rush samples or for TCLP leachates, samples may be prepared using separatory funnel procedures (EXT-3510).

11.1.1.2 Perform the extraction in a 1000 mL aliquot of sample. For TCLP leachates, use 100 mL of sample.

11.1.2 Soil, sediment, and solid samples are prepared using automated soxhlet extraction (SOP EXT-3541). The nominal sample size is 30 g. Sample amounts may be decreased in the case of high-concentration waste samples.

11.1.3 Product samples are prepared using EPA method 3580A.

11.1.4 Cleanup by GPC is performed on solid and waste samples and is optional on water samples.

11.1.5 Following sample preparation, sample extracts are then transferred to the extract storage freezer in the instrument lab. Extracts must be analyzed within 40 days of extraction.

11.2 The recommended GC/MS operating conditions are listed below. The GC conditions may be modified to accommodate specific instrument models and configurations.

Mass range:	35-500 amu
Scan Time:	1 sec/scan
Initial temperature:	40ºC, hold for 3.5 minutes
Temperature program:	40-50ºC at 6ºC/min, 50-270ºC at 15ºC/min, hold for 1.0 min.
Final temperature:	270-320ºC at 6ºC/min, hold for 3 minutes after Benzo[g,h,i]perylene has eluted
Injector temperature:	150ºC ramp to 300ºC
Detector interface temp:	320ºC

Injector:	split, electronic pressure control with pulse
Sample volume:	1.0 µL
Carrier gas:	Helium at 35 cm/secQA/QC Requirements

11.3 Initial Calibration

NOTE: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in the ALS SOP for *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL) are described as follows:

11.3.1 Prior to calibration, analyze the GC/MS tuning standard using instrument conditions used for calibration. Obtain the spectrum for evaluation using one of the following options:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak
- Use one scan at the apex of the peak. Background subtraction is required and must be performed using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be used only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.
- Use one scan either directly preceding or following the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed of instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.
- Use the average across the entire peak up to a total of 5 scans. Peak integration must be consistent with standard operating procedure. If the peak is wider than 5 scans, the tune will consist of the peak apex scan and the two scans immediately preceding and following the apex. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak

11.3.2 Evaluate the spectrum obtained for DFTPP against the tuning criteria in Table 2 (see 8270D, Section 11.3.1 for guidance). The GC/MS must meet the DFTPP ion abundance criteria prior to further analyses.

11.3.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2. See 8270D, Figure 1 for tailing factor calculation. If excessive tailing, poor chromatography, or degradation of >20% is noted, the injection port may require cleaning. It may also be necessary to remove the first 15-30 cm of the GC column. If hardware

tuning criteria cannot be met, the source may need cleaning, filaments replaced or other maintenance.

11.3.4 The internal standards should permit most of the components of interest in the chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Refer to Table 5 for internal standards and corresponding analytes assigned for quantitation (other analytes may be added as needed). Use the base peak ion from the specific internal standard as the primary ion for quantitation (See Table 1 of EPA 8270D). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-Dichlorobenzene-d_4, use 152 m/z for quantitation).

11.3.5 Analyze 1.0 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1 of EPA 8270D). Calculate response factors (RFs) for each compound relative to one of the internal standards as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:
A_x = Area of the characteristic ion for compound being measured.
A_{is} = Area of the characteristic ion for specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

11.3.6 The percent relative standard deviation (%RSD) should be less than or equal to 20% for each compound. It is also recommended that a minimum response factor for the most common target analytes, as noted in Table 6, be demonstrated as a means to ensure that these compounds are performing as expected.

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

where:
RSD = relative standard deviation.
$\overline{RF}$ = mean of initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - RF)^2}{N - 1}}$$

where:
RF_i = RF for each of the calibration levels
N = Number of RF values (e.g., 6)

11.3.7 The relative retention times (RRT) of each compound in each calibration run should agree within 0.06 relative retention time units.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.8 Linearity - If the % RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

11.3.9 If the %RSD for a compound is >20%, then alternative calibration models should be used. Refer to the SOP for *Calibration of Instruments for Organics Chromatographic Analysis* (SOC-CAL) for alternative fit guidance.

11.3.10 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

11.3.11 When calculating the calibration curves using the alternative curve fits, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000C for additional details). It is not necessary to re-analyze a low concentration standard; rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration.

NOTE: Certain project plans (DoD QSM) contain additional initial calibration acceptance criteria (e.g. CCC, SPCC). In these cases, the QAPP-specified criteria are used.

NOTE: Certain state or program protocols have specific procedures for calibration. This may include all or part of Method 8000C. The analyst must ensure that the correct procedures are used. Known uses of 8000C are as follows:

- The use of quadratic regression calibration is not allowed for projects (samples) originating from South Carolina and under the SC DHEC lab certification where historically that analyte responds in a linear manner.

11.3.12 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

11.4 Initial Calibration Verification

11.4.1 Following initial calibration, analyze an ICV standard. The ICV solution must contain all analytes in the calibration standards at a concentration in the middle of the range of the initial calibration. Calculate the concentration using the typical procedure used for quantitation. Calculate the percent difference (%D) from the ICV true value. The maximum allowed % Difference or % Drift is ±30%.

NOTE: DoD ELAP projects may use the acceptance criteria of ±20%.

11.5 Continuing Calibration

11.5.1 Following an acceptable tune, a calibration standard, or standards, at mid-concentration containing all semivolatile analytes, and all required surrogates, must be analyzed every 12 hours during analysis.

Note: When analyzing samples subject to Wisconsin DNR regulations, a second CCV must be analyzed when second order (quadratic) calibrations are used. One will be analyzed at the lower end of the calibration range and one at a point where the curve can no longer be characterized as first order.

11.5.2 If the percent difference or percent drift for each compound is less than or equal to 20%, the initial calibration is assumed to be valid and the analysis of samples may begin.

Calculate the percent drift using:

$$\%\ Drift\ =\ \frac{C_1\ -\ C_c}{C_1}\ x\ 100$$

where:

C_1 = Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

11.5.3 If the percent difference or percent drift for a compound is ≤20%, then the initial calibration for that compound is assumed to be valid. Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the ≤20% criteria. If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.

11.5.4 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit.

11.5.5 Non-detected analytes can be reported from analyses when a CCV exhibit a positive bias (i.e., outside the upper control limit), no further documentation is required.

11.5.6 For situations when the CCV fails to meet the criterion in section 11.5.3, and a confirmed detection exceeds the MRL, the sample must be reanalyzed to ensure accurate quantification. If it is not possible to reanalyze the sample, the result must be reported as an estimated value.

11.5.7 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as required. If the EICP area for any of the internal standards changes by a factor of two (50% to 200%) from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as appropriate. When corrective action is taken, reanalysis of samples analyzed while the system was malfunctioning is required. Update the reference spectra and retention

times in the quantitation database for the instrument method or ID file. The initial calibration average RF or calibration curve is then used in the quantitation of subsequent analyses.

11.5.8 A blank (method blank, GPC blank, or solvent blank) should be analyzed after the CCV, or at any other time during the analytical shift, to prove the system is free of contaminants. If contaminants are found in a method blank or GPC blank, then a solvent blank should be analyzed to help isolate the source of contamination.

11.5.9 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors noted in Table 6.

11.5.10 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination of the front end of the analytical column, and active sites in the column or chromatographic system.

11.6 GC/MS Analysis

11.6.1 Evaluate FID screens if performed and make proper dilution (See FID screening SOP).

11.6.2 Spike the 1 mL extract obtained from sample preparation with 10 µL of the internal standard solution just prior to analysis. Use the same operating conditions as were used for initial calibration.

11.6.3 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

11.6.4 Store the extracts at ≤10ºC or less, protected from light in vials equipped with un-pierced Teflon lined septa. Archive extracts in freezer for 3 months after analysis in the instrument/date specific storage boxes.

NOTE: Client specific QAPPs may require extracts to be kept for a longer period of time.

12) QA/QC Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made. To do this, four clean matrix samples (water or solids) are spiked with the LCS spike solution, then prepared and analyzed.

12.2 Method Detection Limits and Method Reporting Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2 Calculate the average concentration found (x) in µg/L or mg/Kg, and the standard deviation of the concentrations (s) in µg/L or mg/Kg for each analyte. Calculate the MDL for each analyte. Refer to *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011/ADM-MDL). The MDL study must be verified annually (or quarterly, if used for DOD work).

12.3 Limits of Quantification (LOQ)

12.3.1 The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within the LCS acceptance limits to verify the data reporting limit. Refer to *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011/ADM-MDL).

12.3.2 The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit. Current MDLs and LODs can be found in the laboratory Data Quality Objectives.

12.4 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP *Sample Batches* (ADM-BATCH). In general, these include:

12.4.1 Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps minimized. No target analytes should be detected above the MRL in the method blank. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants (phthalate esters, etc.).

Note: DoD requires no analytes detected at >½ the RL or 1/10 the regulatory limit, whichever is greater. For common laboratory contaminates there should be no detection > the RL.

12.4.2 A lab control sample (LCS) must be extracted and analyzed with every batch of 20 or fewer samples. The LCS will routinely contain the entire target analyte list. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

Acceptance criteria for lab control samples are listed in the laboratory Data Quality Objectives (DQO) tables. The accuracy of the analysis is controlled on a subset of target analytes. If the project analyte list is fewer than 20 analytes, all

are considered control analytes. Analytes which are used for control analytes are listed in Table 7. For DoD projects all project target analytes are considered control analytes. If the LCS recovery for any control analyte fails acceptance limits, corrective action is required. If instrument corrective action is not applicable or ineffective, re-extraction of the associated samples is required. If any other analyte fails the advisory acceptance limits, the analyst must evaluate the impact on data quality and take any necessary corrective action, which may include re-extraction of the associated samples. Project-specific requirements may require all compounds to be treated as control analytes, or dictate use of project acceptance criteria.

12.4.3 A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples. The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

WhereR1 = recovered concentration in the higher result
R2 = recovered concentration in the lower result

The acceptance limits for the MS/DMS recovery are listed in the laboratory Data Quality Objectives (DQO) tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken. The RPD acceptance limits are 30% for water and 40% for soils, sediments, and solids. Project-specific requirements may dictate the use of project acceptance criteria.

12.4.4 The acceptance limits for the surrogates are listed in the laboratory Data Quality Objectives (DQO) Tables. If any surrogate recovery is outside acceptance criteria, the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be taken. The sample should be re-analyzed if instrument factors (calibration, injection port) are suspected. If instrument factors are not suspected, re-extraction and re-analysis is required, except in cases of high recovery and no positive hits in the sample for the analyte class represented by the particular surrogate.

12.5 Additional QA/QC measures include control charting of QC sample results.

13) Data Reduction and Reporting

13.1 Qualitative Analysis - The qualitative identification of compounds determined by this procedure is based on retention time, and comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The

reference mass spectrum must be generated by the laboratory using the instrument and conditions used for the sample analysis. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

13.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

13.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

13.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. Use professional judgment in interpretation where interferences are observed.

13.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is <50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks appear to represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification. When analytes co-elute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

13.2 For samples containing components not associated with the calibration standards, a library search may be made of the purpose of tentative identification. Refer to method 8270D for guidance on Tentatively Identified Compound (TIC) identification and quantification.

13.3 Quantitation and Calculations

13.3.1 The GC/MS data stations, in current use, all use the H-P RTE Integrator to generate the raw data used to calculate the standards $\overline{RF}_x$ values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions.

When $\overline{RF}_x$ is used, calculate the extract concentration as follows:

$$C_{ex} = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF}_x)}$$

Where:

C_{ex} = the concentration in the sample extract (ppm);
$Resp_x$ = the peak area of the analytes of interest;
$Resp_{ISTD}$ = the peak area of the associated internal standard;
Amt_{ISTD} = the amount, in ppm, of internal standard added
$\overline{RF}_x$ = the average response from the initial calibration.

13.3.2 The concentration of analytes in the original sample is computed using the following equations:

Aqueous Samples: $Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$

Where Cex = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
Vs = Volume of sample extracted, liters

Non-aqueous Samples: $Concentration\ (mg / Kg) = \frac{(Cex)\ (Vf)\ (D)}{(W)}$

Where Cex = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
W = Weight of sample extracted in grams.

13.4 Tentative identification of compounds (TIC)

13.4.1 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The current library is NIST98.

13.4.2 After a visual comparison of sample spectra with the nearest library searches the analyst assigns a tentative identification. Guidelines for tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 30%.
- (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

13.5 Data Review

13.5.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP for *Laboratory Data Review Process* (ADM-DREV) for details.

13.6 Reporting

13.6.1 Reports are generated in the ALS LIMS by compiling the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file that the Stealth reporting system uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.6.2 Sample concentrations are reported when all QC criteria for the analysis have been met or the results are qualified with an appropriate footnote.

14) Contingencies for Handling Our-of-Control or Unacceptable Data

14.1 Refer to the SOP for *Nonconformance and Corrective Action Procedures* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2 Handling out-of-control or unacceptable data

14.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

14.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.
- Customer inquiries concerning data quality or services (when applicable). NCAR not required for simple corrections with no impact to the client.
- Data errors reported to clients, non-conforming re-checks.
- Deficiencies found during internal or external audits.
- Login errors or shipping errors.
- IT issues if there is a significant impact to a client.
- Turnaround time complaints.

15) Method Performance

15.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2 The method detection limit (MDL) is and related method reporting limit(s) were established using the procedure described in SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL/CE-QA011). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16) Pollution Prevention and Waste Management

16.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

16.2 The laboratory will comply with all Federal, State and local regulations governing waste restrictions as specified in the ALS Lab Waste Management Plan.

16.3 This method uses Methylene Chloride and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and recycled off site.

16.4 This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

17) Training

17.1 Training outline

17.1.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELACs Initial Demonstration of Capability.

17.2 Training is documented following *Employee Training and Orientation* (ADM-TRAIN).

When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 Section 11.5.3, no limit defined in reference method, so lab assigned a limit of 40% based on CLP protocols..

19) References

19.1 *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, Method 8270D, 2007 & 2014.

19.2 *Determinative Chromatographic Separations*, Method 8000C, EPA Test Methods for Evaluating Solid Waste, SW-846, Update III, March 2003.

19.3 *Determinative Chromatographic Separations*, Method 8000D, EPA Test Methods for Evaluating Solid Waste, SW-846, Update IV, February 2007.

19.4 *Determinative Chromatographic Separations*, Method 8000D, EPA Test Methods for Evaluating Solid Waste, SW-846, Update V, July 2014.

19.5 DoD Quality Systems Manual for Environmental Laboratories, current version.

19.6 TNI Standard, Volume 1, 2009 & 2016.

20) Changes Since the Last Revision

Summary of Revision Changes			
Rev. #	Effective Date	Document Editor	Description of Changes
1.0	11/20/19	T.Caron/ C.Degner	Reformatted SOP to current ALS format. Minor typographical, grammatical and format changes to improve readability, not affecting content. Updated Safety (6) and References (19) sections. Section 11.1.4 – Removed reference to screening. Section 11.3.12 is new, regarding identification of structural isomers. Section 13.6 – Removed reference to Excel reporting. Table 1B – Removed Non-Routine Analytes.

21) Attachments, Tables, and Appendices

21.1 Table 1: – Routine Analytes. And MRL/LOQ.

21.2 Table 2 – DFTPP Key IONs and ION Abundance Criteria.

21.3 Table 3; 8270 Standards.

21.4 Table 4: QC Standards.

21.5 Table 5: Internal Standards with Corresponding. Analytes Assigned for Quantitation.

21.6 Table 6: Recommended Minimum Response Factor Criteria.

21.7 Table 7: Control Analytes for Non DoD Projects.

21.8 Table 8: Summary of Corrective Actions.

Table 1
Routine Analytes and MRL/LOQ

ANALYTE	WATER		SOIL/SOLID	
	MRL/LOQ	Units	MRL/LOQ	Units
1,2,4-Trichlorobenzene	10	µg/L	0.33	mg/Kg
1,2-Dichlorobenzene	10	µg/L	0.33	mg/Kg
1,2-Diphenylhydrazine	10	µg/L	0.33	mg/Kg
1,3-Dichlorobenzene	10	µg/L	0.33	mg/Kg
1,4-Dichlorobenzene	10	µg/L	0.33	mg/Kg
2,3,4,6-Tetrachlorophenol	10	µg/L	0.33	mg/Kg
2,4,5-Trichlorophenol	10	µg/L	0.33	mg/Kg
2,4,6-Trichlorophenol	10	µg/L	0.33	mg/Kg
2,4-Dichlorophenol	10	µg/L	0.33	mg/Kg
2,4-Dimethylphenol	10	µg/L	0.33	mg/Kg
2,4-Dinitrophenol	25	µg/L	2	mg/Kg
2,4-Dinitrotoluene	10	µg/L	0.33	mg/Kg
2,6-Dinitrotoluene	10	µg/L	0.33	mg/Kg
2-Chloronaphthalene	10	µg/L	0.33	mg/Kg
2-Chlorophenol	10	µg/L	0.33	mg/Kg
2-Methyl-4,6-dinitrophenol	25	µg/L	2	mg/Kg
2-Methylnaphthalene	10	µg/L	0.33	mg/Kg
2-Methylphenol	10	µg/L	0.33	mg/Kg
2-Nitroaniline	25	µg/L	0.33	mg/Kg
2-Nitrophenol	10	µg/L	0.33	mg/Kg
3,3'-Dichlorobenzidine	25	µg/L	0.33	mg/Kg
3-Nitroaniline	25	µg/L	0.33	mg/Kg
4-Bromophenyl Phenyl Ether	10	µg/L	0.33	mg/Kg
4-Chloro-3-methylphenol	10	µg/L	0.33	mg/Kg
4-Chloroaniline	10	µg/L	0.33	mg/Kg
4-Chlorophenyl Phenyl Ether	10	µg/L	0.33	mg/Kg
4-Methylphenol	10	µg/L	0.33	mg/Kg
4-Nitroaniline	25	µg/L	2	mg/Kg
4-Nitrophenol	25	µg/L	2	mg/Kg
Acenaphthene	10	µg/L	0.33	mg/Kg
Acenaphthylene	10	µg/L	0.33	mg/Kg
Acetophenone	10	µg/L	0.33	mg/Kg
Aniline	25	µg/L	1	mg/Kg
Anthracene	10	µg/L	0.33	mg/Kg
Atrazine	10	µg/L	0.33	mg/Kg
Benz(a)anthracene	10	µg/L	0.33	mg/Kg
Benzo(a)pyrene	10	µg/L	0.33	mg/Kg
Benzo(b)fluoranthene	10	µg/L	0.33	mg/Kg
Benzo(g,h,i)perylene	10	µg/L	0.33	mg/Kg
Benzo(k)fluoranthene	10	µg/L	0.33	mg/Kg
Benzaldehyde	10	µg/L	0.33	mg/Kg
Benzoic Acid	25	µg/L	2	mg/Kg
Benzyl Alcohol	10	µg/L	0.33	mg/Kg
Biphenyl	10	µg/L	0.33	mg/Kg
Bis(2-chloroethoxy)methane	10	µg/L	0.33	mg Kg
Bis(2-chloroethyl) Ether	10	µg/L	0.33	mg/Kg
Bis(2-chloroisopropyl) Ether	10	µg/L	0.33	mg/Kg
Bis(2-ethylhexyl) Phthalate	10	µg/L	0.33	mg/Kg

Butyl Benzyl Phthalate	10	µg/L	0.33	mg/Kg
Caprolactam	10	µg/L	0.33	mg/Kg
Carbazole	10	µg/L	0.33	mg/Kg
Chrysene	10	µg/L	0.33	mg/Kg
Dibenz(a,h)anthracene	10	µg/L	0.33	mg/Kg
Dibenzofuran	10	µg/L	0.33	mg/Kg
Diethyl Phthalate	10	µg/L	0.33	mg/Kg
Dimethyl Phthalate	10	µg/L	0.33	mg/Kg
Di-n-butyl Phthalate	10	µg/L	0.33	mg/Kg
Di-n-octyl Phthalate	10	µg/L	0.33	mg/Kg
Fluoranthene	10	µg/L	0.33	mg/Kg
Fluorene	10	µg/L	0.33	mg/Kg
Hexachlorobenzene	10	µg/L	0.33	mg/Kg
Hexachlorobutadiene	10	µg/L	0.33	mg/Kg
Hexachlorocyclopentadiene	10	µg/L	0.33	mg/Kg
Hexachloroethane	10	µg/L	0.33	mg/Kg
Indeno(1,2,3-cd)pyrene	10	µg/L	0.33	mg/Kg
Isophorone	10	µg/L	0.33	mg/Kg
Naphthalene	10	µg/L	0.33	mg/Kg
Nitrobenzene	10	µg/L	0.33	mg/Kg
N-Nitrosodimethylamine	25	µg/L	2	mg/Kg
N-Nitrosodi-n-propylamine	10	µg/L	0.33	mg/Kg
N-Nitrosodiphenylamine	10	µg/L	0.33	mg/Kg
Pentachlorophenol	25	µg/L	2	mg/Kg
Phenanthrene	10	µg/L	0.33	mg/Kg
Phenol	10	µg/L	0.33	mg/Kg
Pyrene	10	µg/L	0.33	mg/Kg
Pyridine	25	µg/L	0.33	mg/Kg

Table 2
DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-60% of mass 198
365	> 1% of mass 198
441	Present but <24 % of mass 442
442	Base peak, or > 50% of mass 198
443	15-24% of mass 442

Alternate tuning criteria (from Method 625, CLP OLM03.1, or manufacturer's specified criteria) may be used provided that method performance is not adversely affected and that method performance criterion is met. The criteria used must be the same for **all** ion abundance criteria checks associated with a given analysis. For example, initial calibration, continuing calibration(s), QC, and sample analyses for a given sample must all use the same criteria.

Table 3
8270 Standards

CALIBRATION
Recommended: Supelco stock standards (or equivalent from other vendors*):

Supelco EPA CLP Semivolatile Calibration Mix
Supelco EPA 8270 Calibration Mix 4
Supelco EPA 8270 Benzidine Mix
Supelco n-Nitrosodiphenylamine
Absolute 2,3,4,6-Tetrachlorophenol
AccuStandard Method 8270 surrogate standard

Prepare 1 ml of each calibration point from purchased stock standards.
Calibration curve: 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 80 ppm, 100 ppm, 120 ppm, 160 ppm, and 200 ppm.
Add 10 µl internal standard (Z-014J) for each 1 ml calibration standard when curve is prepared. Store all calibration standards in 1 ml amber autosampler vials at -10°C. Expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

ICV
Recommended: AccuStandard catalog # (or equivalent from other vendors*):

CLP-HC-BN-R, 1ml x 2, 2000 ppm BN mix
Z-014E-R3, 1ml x 2, 2000 ppm Composite3 mix
Z-014F, 1ml x 2, 2000ppm Benzidines mix
CLP-HC-AR, 1ml x 2, 2000ppm Acid mix
M-8270-SS-PAK, 1ml x 5, 4000ppm Surrogates mix

Add 10 µl internal standard (Z-014J) for each 1 ml of ICV prepared.
Place in 1 ml amber autosampler vial, recap, and store at -10°C.
Expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

CCV & TUNE
Use the same solutions that were used for the calibration curve

Z-014J, 1ml x 5, 4000ppm Internal Standards mix
M-625C, 1ml x 3, 25000ppm DFTPP (added to CCV)
M-625-TS-20x, 1000ppm (separate tuning standard)

Prepare 1 ml of 80 ppm 8270 CCV standard, place in autosampler vial and cap with a crimp top seal. 80ppm is the nominal concentration. CCV concentrations must be varied periodically.
CCV expiration is set at 1 week from date prepared or expiration date of the parent standard(s), whichever is earliest. Tune standard expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

RECAP AND STORE IMMEDIATELY AFTER INJECTING
Store remaining stock solutions in 1 ml amber vials and store.
Expiration date is one year after ampoule is opened.
Order when down to one unopened ampoule.

* Vendor must be A2LA and/or ISO9000 certified.

Table 4
QC Standards

Supelco Parent	Initial Concentration	Dilution (mixed)*	Final Conc.
8270 Surrogate			
B/N Surrogate Mix (Absolute cat no. 23016)	5000 µg/mL	20mL to 1000mL in MeOH	100 µg/mL
Acid Surrogate Mix (cat no 86-1376)	10000 µg/mL	15mL to 1000mL in MeOH	150 µg/mL
PAH Surrogate Mix (cat no S8522)	5000 µg/ml	20 ml to 1000ml in MeOH	100 µg/ml
8270 Matrix Spike (mixed solution)			
CLP Semivolatile Mix (cat no. 5-06508)	1000 µg/mL	10mL to 100mL in MeOH	100 µg/mL
Benzidines Mix (cat no. 4-8467)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL
N-Nitrosodiphenylamine (cat no. 46702-U)	5000 µg/mL	2mL to 100mL in MeOH	100 µg/mL
8270 Cal Mix 4 (cat no. 86-1148)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL, 200 µg/mL Pyridine
2,3,4,6-Tetrachlorophenol (cat no. 79131)	1000 µg/mL	10mL to 100mL in MeOH	100 µg/mL
1-Methylnaphthalene (cat no. 4-8162)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL
Pyridine (cat. no. App-9-186-20x)	2000 µg/mL	5mL to 100mL in MeOH	200 µg/mL

* For surrogate solution, split the total volume made into 4 bottles for storage and use. To avoid waste, the quantity made can be varied as anticipated for workload.

Standards Expiration: 6 months from preparation date. Purchased standards may be retained past the expiration date for internal R&D, but must be physically separated from standards in active use by placing in a separate, labeled area. Prepared spiking solutions must not be retained past the expiration date. Sequester expired or concentrated spiking solutions in labeled drawers awaiting disposal.

Table 5
Internal Standards with Corresponding analytes Assigned for Quantitation

1,4-Dichlorobenzene-d4 Internal Standard		
N-Nitrosodimethylamine	1,2-Dichlorobenzene	2-Methylphenol
Aniline	1,3-Dichlorobenzene	3- and 4-Methylphenol (co-eluting)
2-Fluorophenol (surrogate)	1,4-Dichlorobenzene	2-Picoline
Bis(2-chloroethyl) Ether	N-Nitrosodi-n-propylamine	Bis(2-chloroisopropyl) Ether
Phenol-d6 (surrogate)	Hexachloroethane	N-Nitrosopyrrolidine
Phenol	Methyl Methanesulfonate	N-Nitrosomorpholine
2-Chlorophenol	N-Nitrosomethylethylamine	*o*-Toluidine
Benzyl Alcohol	Acetophenone	Ethyl Methanesulfonate
Nitrobenzene	N-Nitrosodiethylamine	Pentachloroethane **TABLE**
Pyridine	Nitrobenzene-d5 (surr.)	
Naphthalene-d8 Internal Standard		
	Hexachlorobutadiene	N-Nitrosodi-*n*-butylamine
	2-Methylnaphthalene	N-Nitrosopiperidine
Isophorone	2-Nitrophenol	N,N-Dimethyl-1-phenethylamine
Bis(2-chloroethoxy)methane	2,4-Dimethylphenol	O,O,O-Triethyl Phosphorothioate
1,2,4-Trichlorobenzene	Benzoic Acid	Hexachloropropene
Naphthalene	2,4-Dichlorophenol	*p*-Phenylenediamine
4-Chloroaniline	4-Chloro-3-methylphenol	Safrole
α,α-Dimethylphenethylamine	2,6-Dichlorophenol	1,2,4,5-Tetrachlorobenzene
Acenaphthene-d10 Internal Standard		
2-Fluorobiphenyl (surrogate)	2,4-Dinitrotoluene	1-Naphthylamine
Hexachlorocyclopentadiene	2,6-Dinitrotoluene	2-Naphthylamine
2-Chloronaphthalene	Diethyl Phthalate	2,3,4,6-Tetrachlorophenol
2-Nitroaniline	4-Chlorophenyl Phenyl Ether	Pentachlorobenzene
3-Nitroaniline	Fluorene	1,3-Dinitrobenzene
4-Nitroaniline	4-Nitrophenol	1,4-Naphthoquinone
Dimethyl Phthalate	2,4,6-Trichlorophenol	5-Nitro-*o*-toluidine
Acenaphthylene	2,4,5-Trichlorophenol	Thionazine
Acenaphthene	2,4-Dinitrophenol	Diphenylamine

	Table 5 (Cont.)	
Dibenzofuran	Isosafrole	2-Methyl-4,6-dinitrophenol
1,2-Diphenylhydrazine	N-Nitrosodiphenylamine	
Phenanthrene-d10 Internal Standard		
4-Bromophenyl Phenyl Ether	Pentachlorophenol	Pentachloronitrobenzene
Hexachlorobenzene	1,3,5-Trinitrobenzene	Disulfoton
Phenanthrene	Phorate	2-sec-Butyl-4,6-Dinitrophenol (Dinoseb)
Anthracene	Phenacetin	Methyl Parathion
Di-n-butyl Phthalate	Diallate	4-Nitroquinoline N-Oxide
Fluoranthene	Dimethoate	Parathion
Carbazole	4-Aminobiphenyl	Methapyrilene
Sulfotep	Pronamide	Isodrin
2,4,6-Tribromophenol (surrogate)		
Chrysene-d12 Internal Standard		
Pyrene	Bis(2-ethylhexyl) Phthalate	Chlorobenzilate
Butyl benzyl Phthalate	Chrysene	Kepone
Benzidine	Terphenyl-d14 (surrogate)	3,3'-Dimethylbenzidine
3,3'-Dichlorobenzidine	Total Aramite	Famphur
Benz(a)anthracene	*p*-Dimethylaminoazobenzene	2-Acetylaminofluorene
Perylene-d12 Internal Standard		
Di-n-octyl Phthalate	Indeno(1,2,3-c,d)pyrene	Hexachlorophene
Benzo(b)fluoranthene	Dibenz(a,h)anthracene	3-Methylcholanthrene
Benzo(k)fluoranthene	Benzo(g,h,i)perylene	
Benzo(a)pyrene	7,12-Dimethylbenz(a)anthracene	

Table 6
Recommended Minimum Response Factor Criteria

Compound	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl) Ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitrosodi-n-propylamine	0.500
Hexachloroethane	0.300
Isophorone	0.400
Nitrobenzene	0.200
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2,-Nitroaniline	0.010
Dimethyl Phthalate	0.010
2,6-Dinitrotoluene	0.200

Table 6 (continued)

Compound	Minimum Response Factor (RF)
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

Table 6 (continued)

Compound	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

Table 7
Control Analytes for Non-DoD Projects

1,2,4-Trichlorobenzene
1,4-Dichlorobenzene
2,4-Dinitrotoluene
2-Chloronaphthalene
2-Chlorophenol
4-Bromophenyl Phenyl Ether
4-Chloro-3-methylphenol
4-Nitrophenol
Acenaphthene
Benzo(a)pyrene
Diethyl Phthalate
Hexachloroethane
N-Nitrosodi-n-propylamine
Pentachlorophenol
Phenol
Pyrene

TABLE 8

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C, EPA 8270D	ICAL	Prior to sample analysis	% RSD ≤ 20 COD ≥ 0.990	Correct problem then repeat ICAL
EPA 8000C, EPA 8270D	ICV	After ICAL	± 30% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8000C, EPA 8270D	CCV	Prior to sample analysis	± 20% Diff	Correct problem then repeat CCV or repeat ICAL
EPA 8000C, EPA 8270D	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 8000C, EPA 8270D	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO Table	If exceeds limits, re-extract and re-analyze
EPA 8000C, EPA 8270D	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO Table	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8000C, EPA 8270D	Matrix Spike Duplicates	Include with each analysis batch (up to 20 samples)	W: RPD ≤ 30 S: RPD ≤ 40	Re-homogenize and re-analyze if result is > 5 X the MRL

Total, Fixed, and Volatile Solids in Solid and Semisolid Samples

DOCUMENT ID: SOIL-SOLIDS, REV 2.0

Prepared By: _____ Date: 1/6/2020
Soil Prep Manager, Jonathon Walter

Prepared By: _____ Date: 1/6/2020
Quality Assurance Manager, Carl Degner

Approved By: _____ Date: 1/7/20
General Manager, Ambrose Hughey

1) Scope & Applicability

1.1 This procedure determines percent dry solids in soil, sediment, and solid samples using Standard Methods 2540G, modified EPA Method 160.3 (160.3M) and modified PSEP. These methods are suitable for the determination of solid and semisolid materials produced during water and wastewater treatment.

1.2 This procedure is used to determine volatile solids in soil, sediment and sludge using SM 2540G and modified EPA Method 160.4 (160.4M). This determination is useful because it offers a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge and industrial wastes.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DOD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD5), may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 EPA 160.3M, PSEP, and 2540G - A well-mixed sample is quantitatively transferred to a pre-weighed, metal pan or porcelain crucible and evaporated to dryness at 103–105°C. The pan is weighed and the weight of the residue calculated.

2.2 EPA 160.4M and SM 2540G - The residue from EPA 160.3M, PSEP, or 2540G is ignited to a constant weight at 550°C. The weight loss upon ignition is the volatile solids.

3) Definitions

3.1 Total solids – the residue left in the pan or vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature.

3.2 Total volatile solids, also known as volatile residue, is defined as the total residue obtained from the residue ignited at 550°C in a muffle furnace

3.3 Fixed solids/Volatile Solids – is the term applied to the residue of total, suspended, or dissolved solids after ignition for a specified time at a specified temperature. The weight loss on ignition is called volatile solids.

3.4 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.4.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, all of the same matrix, processed on the same date.

3.5 Sample

3.5.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.5.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.6 Quality System Matrix - The matrix of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.7 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.8 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

4.2 It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in the *ALS-Kelso Training Procedure* (ADM-TRAIN).

5) Interferences

5.1 Sampling and subsampling may introduce serious errors. Homogenize samples thoroughly prior to, and during transfer. Use special handling to insure sample integrity when subsampling.

5.2 The temperature at which the residue is dried has an important bearing on sample results, because weight losses due to the volatilization of organic matter and gases from heat-induced chemical decomposition depend on temperature and time of heating.

5.3 Each sample requires close attention to desiccation after drying. Minimize opening the desiccator to reduce the entry of moist air.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

6.2 Samples must be handled as described in the ALS safety policies and approved methods. Refer to the ALS Chemical Hygiene Plan prior to beginning this method.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Soil samples may be collected in glass jars, sleeves, or other suitable container.

7.2 For soil samples, a minimum of 10 g is required. Collecting 8 oz jars of soil improves subsampling homogeneity.

7.3 Samples should be stored at 4ºC.

7.4 Samples must be analyzed within 7 days of collection.

8) Standards, Reagents, and Consumable Materials

8.1 All equipment cleaning, working solutions and dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

9) Apparatus and Equipment

9.1 Evaporating dishes: dishes of 100 mL capacity made of porcelain.

9.2 Evaporating pans, aluminum

9.3 Desiccators, containing desiccant.

9.4 Drying oven, for operation at 103-105ºC.

9.4.1 Ovens housing an internal temperature recorder/display as part of its operational system are calibrated twice per year by an external, accredited calibration service.

9.4.2 Oven temperature may be monitored by using a thermometer immersed in sand, or other suitable solid material, in a vessel in the oven. The liquid in glass thermometer is verified annually using a reference traceable to NIST.

9.5 Analytical balance capable of weighing to 0.1 mg.

9.6 Balance calibration verification weights, ASTM Class 1.

9.7 Muffle furnace for operation at 550ºC.

9.8 Porcelain Dishes (for 2540G only).

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described herein. The entry in the log must include: date of event, the initials of who performed the work, and a reference to return to analytical control.

10.2 The laboratory utilizes an external calibration service that is accredited to perform calibration or re-certification of ovens housing an internal temperature recorder/display as part of its operational system.

10.3 A bound logbook is used to record all balance measurements. Format the logbook such that the date, initials, balance I.D., weight set ID, measurements, and specifications for the check weights are listed for each balance. Record each calibration verification measurement in the logbook. Entries into logbooks are to be performed in accordance with the SOP for *Making Entries Onto Analytical Records* (CE-QA007). Desiccant should be changed as needed.

11) Procedure

11.1 Total Solids - EPA Method 160.3M and PSEP.

11.1.1 Pre-dry the aluminum pans prior to use by heating at 103-105ºC for one hour. Allow to cool. Label the pans with corresponding sample I.D.s.

11.1.2 Determine and record the tare (dry pan) weight.

11.1.3 Measure 10 g of homogenized sample into the tared weigh pan. Record the pan plus sample weight. If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer (or equivalent); as an alternative, pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves.

11.1.4 Place in a drying oven overnight at 103-105ºC.

11.1.4.1 If solids must be done same day, samples are placed in the oven for four hours. After sample is cooled and weighed, the sample is placed back in oven for an additional 30 minutes, cooled at reweighed for a confirmation weight. Data reported this way must be qualified as estimated.

11.1.5 Remove from the oven and cool to room temperature and weigh.

11.2 Total Solids –SM 2540G.

11.2.1 Pre-dry the porcelain crucible prior to use by heating at 103-105ºC for one hour. Allow to cool. Label the crucibles with corresponding sample I.D.s.

11.2.2 Determine and record the tare (dry crucible) weight.

11.2.3 Measure 25-50 g of homogenized sample into the tared crucible. Record the crucible plus sample weight. If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer (or equivalent); as an alternative, pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves.

11.2.4 Place in a drying oven overnight at 103-105ºC.

11.2.4.1 If solids must be done same day, samples are placed in the oven for four hours. After sample is cooled and weighed, the sample is placed back in oven for an additional 30 minutes, cooled at reweighed for a confirmation weight. Data reported this way must be qualified as estimated.

11.2.5 Remove from the oven and cool to room temperature and weigh.

11.3 Volatile Solids – EPA Method 160.4M and SM 2540G.

11.3.1 Prepare an evaporating dish by igniting a clean evaporating dish at 550ºC for 60 minutes in a muffle furnace.

11.3.2 Cool in a desiccator, weigh and store in desiccator until ready for use.

11.3.3 If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No.7 cork borer (or equivalent); as an alternative, pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves.

11.3.4 Measure 25-50 g of homogenized sample into the pre-weighed, evaporating dish/crucible. Record the weight.

11.3.5 Place in a drying oven overnight at 103-105ºC.

11.3.6 Remove from the oven and cool to balance temperature in a desiccator and weigh. Place samples back in the 105*C oven for 1 hour to repeat drying, cooling, weighing and desiccating steps until weight change is less than 4% or 50 mg, whichever is less.

11.3.7 Weigh samples and record on the bench sheet. Transfer the dried residue to a cool muffle furnace, heat furnace to 550ºC and ignite for one hour.

Note: if the residue contains high amounts or organic matter, refer to SM 2540G for procedure to lessen losses due to reducing conditions.

11.4 Remove from the muffle furnace and cool in a desiccator to balance temperature and weigh. Repeat igniting, cooling, weighing and desiccating steps until weight change is less than 4% or 50 mg, whichever is less.

12) QA/QC Requirements

12.1 This method shall operate under the formal Quality Assurance Program established at ALS and must maintain records that define the quality of data that is generated. Data shall be compared to established criteria in order to determine if the results of the analyses meet the performance characteristics of the method.

12.2 Multi-point balance calibration verifications are required for each day the balance is used and must be performed prior to use. The calibration verification weights must bracket the range of use. For additional information, refer to the SOP *Documenting Laboratory Balance and Temperature Checks* (ADM-BAL).

12.3 For gravimetric determination, prior to, and after each analytical batch, balance calibration verification (CCV) is performed using weights bracketing the sample weights and must be ± 0.5% of the true value.

12.4 A system of documentation (logbook, benchsheet, etc.) must be established for recording the serial number of the Weight Set used for CCV verification.

12.5 Prior to, and after each analytical batch, drying oven temperature check(s) and time(s) shall be recorded.

12.6 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DOD ELAP must follow requirements defined in the DoD Quality Systems Manual for Environmental Laboratories. General QA requirements for DoD QSM are defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD5). General QC requirements are:

$$RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where: R1 = Higher Result

R2 = Lower Result

12.7 Sample Duplicates (DUP) - Run one duplicate per batch of ten samples. Calculate Relative Percent Difference (RPD) for duplicates as:

12.7.1 Duplicate determinations should agree within 5% of their average weight for SM 2540G and 10% for 160.3M, 160.4M, and PSEP..

NOTE: For samples analyzed under PSEP protocol, samples must be analyzed in triplicate.

12.7.2 Duplicate are required for 10% of all samples (one for every ten samples).

12.8 One method blank (MB) per batch of 20 samples for TVS is required.

13) Data Reduction and Reporting

13.1 For soils, sediments, and solids, calculate % solids as follows:

(tare + dry weight) - tare = dry weight

dry weight ÷ wet weight x 100 = % solids

13.2 For Volatile Solids:

$$\% \text{ Total Solids} = \frac{(A - B) \times 100}{C - B}$$

$$\% \text{ Volatile Solids} = \frac{(A - D) \times 100}{A - B}$$

$$\% \text{ Fixed Solids} = \frac{(D - B) \times 100}{A - B}$$

A = weight of dry residue + dish (mg)
B = weight of dish (mg).
C = weight of wet sample + dish (mg)
D = weight of residue = dish after ignition (mg).

13.3 Reporting

13.3.1 Refer to *Data Reporting and Report Generation* (ADM-RG) for reporting guidelines.

13.3.2 Reports are generated in the ALS LIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.4 Data review and Assessment

13.4.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP for *Laboratory Data Review Process* (ADM-DREV) for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Manager to inclusion in the report narrative).

14) Method Performance

14.1 Refer to the reference method for additional method performance data available.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

16) Contingencies for Handling Our-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Non Conformance and Corrective Action Procedure* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc).
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Refer to the SOP *Employee Training and Orientation* (ADM-TRAIN). Training outline

17.1.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDS for all reagents and standards used. Following these reviews, observe the procedure performed by an experienced analyst at least three times.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.2 Training is documented following the *Employee Training and Orientation* (ADM-TRAIN).

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 The EPA 160.3 procedure is modified to determine percent dry solids in soil, sediment, and solids (160.3M). 10 g of samples used instead of 25-50 g for total solids only analysis.

18.2 The EPA 160.4 procedure is modified to determine percent dry solids in soil, sediment, and solids (160.4M). 25-50 g of samples is used for Total Volatile Solids.

18.3 PSEP procedure is modified to determine percent dry solids in soil, sediment, and solids using 10 g of samples used instead of 25 g for total solids only analysis. Pre-dry the aluminum pans are used in place of porcelain crucible.

19) References

19.1 *Total solids dried at 103-105ºC*, SM 2540B-2011.

19.2 *Residue, Total*, Method 160.3 EPA 600/4-79-020.

19.3 *Total, Fixed and Volatile Solids in Solids and Semisolid Samples*, SM 2540G-2011.

19.4 *Residue, Volatile*, Method 160.4 EPA 600/4-79-020, Revised March, 1983.

19.5 TNI Standard, Volume 1, 2009 and 2016.

19.6 DoD Quality Systems Manual for Environmental Laboratories. Current version.

19.7 Conventional Sediment Variables – Particle Size, March 1986, Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound, January, 1996.

20) Changes Since Last Revision

Revision Number	Effective Date	Document Editor	Description of Changes
2.0	01/24/2020	C. Degner	Minor typographical, grammatical, and formatting revisions. Revised ID to from SOILPREP to SOIL. Section 1.1 – Revised. Section 2 – Revised SM 2540B to PSEP. Section 11.1 – Added PSEP. Section 12.7.1 – Added criteria. Section 18.3 – Added modification to PSEP procedure. Section 19.7 – Added reference for PSEP.

21) Attachments, Tables, and Appendices

21.1 TS Bench sheet: R:\Soil Prep\Templates\TS Fixed SOIL Rev4.xltx.

21.2 TVS Bench Sheet: R:\Soil Prep\Templates\TVS SOIL Rev3.xltx.

Closed Vessel Digestion - EPA 3051A

DOCUMENT ID: MET-3051M, REV 6.0

Approved By: _____ Date: 12/5/19
Inorganics Manager, Jeff Coronado

Approved By _____ Date: 12/5/19
Quality Assurance Manager, Carl Degner

Approved By: _____ Date: 12/9/19
General Manager, Ambrose Hughey

1) Scope & Applicability

1.1 This method is utilized to perform total metals analysis on waste oil and other organic based samples. This procedure is based upon EPA method 3051A and is applicable to sediments, sludges, soils, oils and various miscellaneous matrices.

1.2 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DOD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD/ADM-DOD5)* may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 A representative aliquot of sample is added to a Teflon digestion vessel along with 15% concentrated nitric acid. If sample is being analyzed by ICP 15% concentrated nitric and 5% concentrated hydrochloric acid is used. The digestion vessel is then sealed and placed in a 105ºC oven for a minimum of 12 hours. (Note: ALS - Kelso has substituted the use of a microwave oven with a conventional oven.) After cooling the sample is transferred to centrifuge tube and diluted to 20 mL final volume with de ionized water.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.3 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.4 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not previously described. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.5 Miscellaneous matrices - These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix

3.4 Method Blank (MB) - An artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.5 Laboratory Control Samples (LCS) – An aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.6 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.7 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.8 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance program.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

4.2 It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in the SOP *Employee Training and Orientation,* (ADM-TRAIN).

5) Interferences

5.1 Solvents, reagents, and other sample processing hardware may yield artifacts and or interferences to sample analysis. All of these must be demonstrated to be free from interferences under the conditions of analysis by analyzing method blanks.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and gloves appropriate for the solvent being used. .

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Kelso Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

6.3 In addition great care must be taken with the use of Teflon digestion vessels as high pressures and toxic vapors are generated. Only open the digestion vessel after cooling to room temperature in a fume hood.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Soil and sludge samples are stored at 4ºC ± 2°C from sample receipt until analysis. Oil and miscellaneous matrix samples are stored at room temperature from sample receipt until analysis.

7.2 The recommended holding time is 6 months from collection.

8) Apparatus and Equipment

8.1 Teflon digestion vessels.

8.2 3-place balance.

8.3 Conventional oven capable of maintaining 105ºC. (Oven must be vented).

8.4 Pipettes.

9) Standards, Reagents, and Consumable Materials

9.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Standards, reagents and consumable material documentation shall indicate traceability to purchased neats or compounds. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

9.2 All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

9.3 All acids are pre-tested prior to use to ensure no impurities are present

9.3.1 Concentrated nitric acid

9.3.2 Concentrated hydrochloric acid

9.4 Standards

9.4.1 Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. The vendor-assigned expiration date is used.

9.4.2 Metals spiking solutions - Five solutions are needed to prepare the matrix spiking standards: SS1, SS2, SS3, SS4, and SS5.

9.4.3 Follow the formulations laid out in Table 2. These solutions are prepared in acid rinsed Class A volumetric flasks using purchased custom mixed standards or 1000 ppm single analyte standards. Aliquots are made using acid rinsed Class A volumetric pipettes of the appropriate size.

9.4.4 SS1 (Al, Ag, Ba, Be, Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Sb, V, and Zn) - Fill a 1000 mL volumetric flask approximately half full with reagent water, add 50 mL of nitric acid and mix. Next add 50 mL 1000 ppm Antimony, then 100 mL of the custom mixed standard (ALS-89) purchased from Inorganic Ventures. Dilute to volume with reagent water, mix thoroughly and transfer to a 1000 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

9.4.5 SS2 (As, Cd, Pb, Se, Tl and Cu) - Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 2.0 mL each of 1000 ppm Arsenic, Cadmium, Lead, Selenium, Thallium and Copper. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

9.4.6 SS3 (Hg, As, Se, and Tl) - Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 50 mL each of 1000 ppm Arsenic and Selenium. Then add 10 mL 1000 ppm Thallium and 6 mL of 1000 ppm Hg. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

9.4.7 SS4 (B, Mo, U) - Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 50 mL 1000 ppm Molybdenum, 25 mL 1000 ppm Boron, and 10 mL 1000 ppm Uranium. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution's expiration date is determined by the earliest expiration date of any single component in the solution.

9.4.8 SS5 (K, Na, Mg, Ca) - Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next, add 50 mL of 10,000 ppm Potassium, Sodium, Magnesium, and Calcium. Dilute to volume with reagent water, mix thoroughly and transfer to a Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook. Pertinent information must be in the logbook. Maintenance entries should include date, symptom of problem, corrective actions, and description of maintenance, date, and name. The log should contain a reference to return to analytical control.

10.2 Maintenance for this procedure is generally limited to glassware cleaning, pipette monitoring, and hot plate calibration. Procedures for glassware washing are described in the SOP *Metals Laboratory Glassware Cleaning* (MET-GC). Procedures for pipette monitoring are given in the SOP *Checking Volumetric Labware* (ADM-VOLWARE).

11) Procedure

11.1 Weigh 0.200 g of well mixed sample to the nearest 0.001 g into an acid rinsed Teflon digestion vessel. Add the appropriate spiking solutions directly into the designated MS and LCS samples prior to addition of reagents. The amount and mix of spiking solutions is typically 0.4 mL SS1, SS3, SS4, and SS5. Fill out a spiking data sheet and keep it with the digestion data sheets. If the sample(s) are being analyzed for Si, add 3.0 mL of DI water before the addition of HNO3. Add 3.0 mL of concentrated nitric acid (Add the acid in a fume hood and check for a rigorous reaction. If the sample reacts upon addition of acid allow the reaction to subside before sealing the vessel). Seal the vessels with the wrenches provided for this purpose. Place the sealed digestion vessels in an oven at 105ºC for minimum of 12 hours.

11.2 After the digestion is complete remove the vessels from the oven and place in a fume hood to cool to room temperature. Add 5.0 mL of DI water. For ICP-OES analysis, also add 1.0 mL concentrated Hydrochloric acid. Put the vessels back into the oven at 105ºC for 1 hour. After cooling open the vessels and transfer the digestates to 50 mL centrifuge tubes and dilute to 20 mL with de ionized water. (CAUTION: Perform this step in a fume hood as toxic nitrogen oxide fumes may be released when the vessels are opened.) The samples are now ready for analysis by the appropriate analytical method being sure that standards are matrix matched.

12) QA/QC Requirements

12.1 This method shall operate under the formal Quality Assurance Program established at ALS and must maintain records that define the quality of data that is generated. Data shall be compared to established criteria in order to determine if the results of the analyses meet the performance characteristics of the method. It is required that an initial demonstration of capability and periodic analysis of laboratory reagent blanks, laboratory fortified blanks, and other QC solutions as a continuing check on performance. The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made.

12.2 Method Detection Limits and Method Reporting Limits

12.2.1 If reporting to the MDL, a method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 8 to digest the samples:

12.2.2 Calculate the average concentration found (x) in µg/mL, and the standard deviation of the concentrations (s) in µg/mL for each analyte. Calculate the MDL for each analyte. Refer to, *Performing Method Detection Limit Studies and Establishing Limits of detection and Quantification.* The MDL study must be verified annually.

12.2.3 The Method Reporting Limits (MRLs) used at ALS - Kelso are the routinely reported lower limits of quantitation which take into account day-to-day

fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS - Kelso routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches*. Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DOD ELAP must follow requirements defined in the DoD *Quality Systems Manual for Environmental Laboratories.* General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management (ADM-DOD/ADMDOD5).* General QC Samples are:

12.3.1 Lab Control Sample (LCS)

12.3.1.1 The laboratory control sample is composed of analyte-free water or solid matrix into which is spiked a number of appropriate target analytes. The LCS is designed to monitor the accuracy of the procedure. The concentration of the spike in the LCS matrix should be at 5 to 10 times the MRL or at levels specified by a project analysis plan.

12.3.1.2 A lab control sample (LCS) must be prepared and analyzed with every batch of 20 (or fewer) samples. Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

12.3.1.3 The acceptance criteria are given in the ALS Kelso DQO Table. If the recovery is within control limits, the analysis is in control and results may be reported. If not, this indicates that the analysis is not in control. Samples associated with the 'out of control' LCS, shall be considered suspect and corrective action is taken. The samples are re-extracted or re-analyzed or the data reported with the appropriate qualifiers.

12.4 Digest one laboratory control sample with each batch. Use the appropriate oil reference material if available or alternatively use 0.4 mL of spiking solutions (Appendix A) for blank spike.

12.5 Digest one preparation blank (with each samples matrix). Prepare one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent.

12.6 One duplicate and matrix spiked sample must be prepared and analyzed with every batch of 20 (or fewer) samples or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements. Spikes are prepared by adding 0.4 mL of spiking solutions to the designated spike sample.

12.7 When available, a Standard Reference Material (SRM) should be analyzed with each batch of samples. The SRM should match as closely as possible the matrix of the samples being analyzed. (Note: finding an SRM of the correct matrix with certified values for the analytes of interest is often not possible.

13) Data Reduction and Reporting

13.1 Digestion data sheets including weights and volumes used and reagents/acids are completed and a prep run number or batch lot number is assigned and attached to the data sheet. The lot numbers for the reagents used are added to the digestion data sheet (see Attachments).

13.2 Metals Spiking Solutions Concentration Form(s) (spike sheets) accompany the benchsheets (digestion data sheets).

13.3 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the *SOP for Laboratory Data Review Process* (ADM-DREV) for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Manager to inclusion in the report narrative..

14) Method Performance

14.1 Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as in the determinative procedure. The method detection limit(s) and method reporting limit(s) are established for the determinative procedure. See *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* (CE-QA011/ADM-MDL).

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. Refer to the ALS Kelso Lab Waste Management Plan.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformance and Corrective Action Procedure* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.
- Customer inquiries concerning data quality or services (when applicable). NCAR not required for simple corrections with no impact to the client.
- Data errors reported to clients, non-conforming re-checks.
- Deficiencies found during internal or external audits.
- Login errors or shipping errors.
- IT issues if there is a significant impact to a client.
- Turnaround time complaints.
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Training outline

17.1.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to TNI's Initial Demonstration of Capability.

17.2 Training is documented following *Employee Training and Orientation* (ADM-TRAIN).

17.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 A conventional oven able to maintain 105˚C has been substituted for a microwave oven as the heating source for the digestion.

19) References

19.1 Method 3051A *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils,* Revision 1 February 2007.

19.2 DoD Quality Systems Manual for Environmental Laboratories, current version.

19.3 TNI Standard, Volume 1- 2009.

20) Changes Since the Last Revision

Summary of Revision Changes			
Revision Number	Effective Date	Document Editor	Description of Changes
6.0	12/17/19	T. Caron	Reformatted SOP to current ALS SOP branding. Minor typographical, grammatical, and formatting revisions to improve readability. Section 9.4 - new. Sections 7and 11 – Numerous revisions to match current spiking and procedural techniques. Tables A - Updated.

21) Attachments, Tables, and Appendices

21.1 Table A: Metals Spiking Solutions Concentrations Form.

Table A
Metals Spiking Solutions Concentrations Form

Solution		mL of 1000ppm	Final	Solution	Enter mL	
Name	Element	Solution	Volume	Conc. mg/L	Added	
K-MET SS1	HNO3	50.0	1000 mL	-		
	Al	100*	1000 mL	200		
	Ag	100*	1000 mL	5		
	Ba	100*	1000 mL	100		
	Be	100*	1000 mL	5		
	Cd	100*	1000 mL	5		
	Co	100*	1000 mL	50		
	Cr	100*	1000 mL	20		
	Cu	100*	1000 mL	25		
	Fe	100*	1000 mL	100		
	Pb	100*	1000 mL	50		
*** Add after HNO3	Mn	100*	1000 mL	50		
and before ALS-89	Ni	100*	1000 mL	50		
when making the	Sb***	50.0	1000 mL	50		
solution	V	100*	1000 mL	50		
	Zn	100*	1000 mL	50		
K-MET SS2	HNO3	25.0	500 mL	-		
	As	2.00	500 mL	4		
	Cd	2.00	500 mL	4		
	Pb	2.00	500 mL	4		
	Se	2.00	500 mL	4		
	Tl	2.00	500 mL	4		
	Cu	2.00	500 mL	4		
K-MET SS3	HNO3	25.0	500 mL	-		
	As	50.0	500 mL	100		
	Se	50.0	500 mL	100		
	Tl	10.0	500 mL	20		
	Hg	6.00	500 mL	12		
	HNO3	25.0	500 mL	-		
	Mo	50.0	500 mL	100		
	U	10.0	500 mL	20		
K-MET SS5	HNO3	25.0	500 mL	-		
	K**	50.0	500 mL	1000		
	Na**	50.0	500 mL	1000		

	Mg**	50.0	500 mL	1000		
	Ca**	50.0	500 mL	1000		
K-MET Hydride	HNO3	1.0	100 mL	-		
	As, Se	0.25	100 mL	2.5		
K-MET QCP-CICV-1	Ca, Mg, Na, K	no dilution	-	2500		
	Al, Ba	no dilution	-	1000		
	Fe	no dilution	-	500		
	Co, Mn, Ni, V, Zn	no dilution	-	250		
	Cu, Ag	no dilution	-	125		
	Cr	no dilution	-	100		
	Be	no dilution	-	25		
K-MET QCP-CICV-3	As, Pb, Se, Tl	no dilution	-	500		
	Cd	no dilution	-	250		
		* Denotes volume of mixed stock standard.				
		** Denotes 10,000 ppm individual stock standards.				
	mL of					
Standard	standard	ppm	Logbook #			Exp. Date

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

DOCUMENT I.D. MET-6020

Approved By: _____ Date: 10/19/18
Technical Director, Jeff Coronado

Prepared By: _____ Date: 10/19/18
Quality Assurance Manager, Carl Degner

Prepared By: _____ Date: 10/22/18
General Manager, Ambrose Hughey

Doc Control ID:	_____	Archived Date:	_____

ALS-Kelso SOP Annual Review Statement

SOP Code: MET-6020
Revision: 18

An annual review of the SOP listed was completed on (date): **2/28/2020**

☒ The SOP reflects current practices and requires no procedural changes.

Supervisor: RRM Date: 2/28/2020

☐ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision

ALS-Kelso SOP Annual Review Statement

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SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision
11.4.4 (new section)	Water samples with silver concentations greater than 100 ug/L require confrimation from the original sample container to ensure silver has not been lost through precipitation in the digestate.	03/21/19	JC

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DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

1) Scope & Applicability

1.1 This procedure is used to determine the concentrations of certain elements in water, soil, tissues, aqueous and non-aqueous wastes, and sediment samples using EPA Method 6020B. The Kelso DQO table indicates analytes that are typically determined by this procedure and lists the standard Method Reporting Limits (MRLs) for each analyte in water and soil. Project-specific MRLs may apply, and if lower than standard MRLs, it is demonstrated through method detection limit determinations and analysis of MRL standards that the MRL is achievable. Method Detection Limits are referenced in the laboratory DQO tables and may change as new studies are performed.

1.2 The complexity of the technique generally requires outside study of appropriate literature as well as specialized training by a qualified spectroscopist. The scope of this document does not allow for the in-depth descriptions of the relevant spectroscopic principles required for gaining a complete level of competence in this scientific discipline.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD5) may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 Prior to analysis, samples must be digested using appropriate sample preparation methods. The digestate is analyzed for the elements of interest using ICP-mass spectrometry (ICP-MS).

2.2 Methods 6020B describe the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The matrix of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Nonaqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8 Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.9 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. The CCV is used to verify that the initial calibration curve is still valid for quantitative purposes.

3.10 Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.11 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4) Interferences

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system

must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Attention should be given to circumstances where very high ion currents at adjacent masses may contribute to ion signals at the mass of interest. Matrices exhibiting a significant problem of this type may require resolution improvement, matrix separation, or analysis using another isotope.

4.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Refer to Method 6020B for further discussion.

5) Safety

5.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

5.3 Hydrochloric and/or Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

5.4 High Voltage - The RF generator supplies up to 2000 watts to maintain an ICP. The power is transferred through the load coil located in the torch box. Contact with the load coil while generator is in operation will likely result in death. When performing maintenance on the RF generator, appropriate grounding of all HV capacitors must be performed as per manufacturer.

5.5 UV Light - The plasma is an intense source of UV emission, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available when direct viewing of the plasma is necessary.

6) Sample Collection, Containers, Preservation, and Storage

6.1 Aqueous samples are typically collected in plastic containers. Aqueous samples are preserved with nitric acid (pH<2), then stored at room temperature from receipt until digestion. Soil or solid samples may be collected in plastic or glass jars. Non-aqueous samples are refrigerated at 4 ± 2°C from receipt until digestion.

6.2 Samples are prepared via procedures in SOPs MET-DIG, MET-3020A, MET-3050, MET-3051M, MET-3052M, or MET-TDIG depending on matrix and project specifications.

6.3 Digestates are stored in the appropriate containers. Following analysis, digestates are stored until all results have been reviewed. Digestates are neutralized prior to disposal through the sewer system, 2 weeks after data is reviewed.

7) Standards, Reagents, and Consumable Materials

7.1 All standards are prepared from NIST traceable standards. The expiration dates are assigned according to the EPA method and the vendor's assigned expiration dates.

7.1.1 1000 ppm Single Element Stock Standard Solutions: Each stock standard is stored at room temperature on shelves located in room 113 of the metals lab. The manufacturer, lot number, and expiration date of each stock standard is recorded in a bound logbook also located in room 113. Additionally each stock standard is given a unique, identifying name.

7.1.2 Intermediate Standard Solutions: Intermediate mixed stock solutions are made from the individual stock standards described above. The individual component of each mixed solution is recorded in a bound logbook located in the ICP-MS laboratory and mixed solution is given a unique, identifying name. The expiration date for the intermediate standard is the earlier of any one of its stock components.

7.1.3 Calibration Standards: Calibration standards are made fresh daily from the intermediate standard solutions. Each individual intermediate standard used in the calibration standard is recorded in a bound logbook located in the ICP-MS laboratory, and the calibration standard solution is given a unique, identifying name. The calibration standards unique name is used on the raw data to link the data to the subsequent prepared standards and ultimately the original purchased stock standard.

7.2 Standards Preparation

7.2.1 Expiration of all standard solutions defaults to the earliest expiration date of an individual component unless otherwise specified.

7.2.2 Calibration Standards

The calibration standard is prepared from two intermediate stock solutions. These solutions are prepared in acid rinsed 1000 mL Class A volumetric flasks following the formulations laid out on the attached example standard sheet (see Attachments). The working calibration standard is made daily by aliquoting 2.5 mL of each of the intermediate solutions in to a 100 mL Class A volumetric flask and diluting to volume with DI water and the appropriate acid(s). This standard is also used as the Continuing Calibration Verification (CCV).

7.2.3 Initial Calibration Verification (ICV)

7.2.3.1 The ICV intermediate stock solution is prepared in an acid rinsed 100 mL Class A volumetric flask. The solution is prepared by adding 2.0 mL of Inorganic Ventures QCP-CICV-1, 1.0 mL of QCP-CICV-3, 0.5 mL of 1000 ppm Boron, Bismuth, Molybdenum, Strontium, Titanium, an

Uranium stock solutions, 0.25 mL of 1000 ppm Antimony stock solution and diluting to volume with the appropriate acid matrix.

7.2.3.2 The working ICV solution is prepared by aliquoting 0.5 mL of the mixed ICV intermediate solution and 0.25 mL of 10 ppm Tin standard into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with the appropriate acid matrix.

NOTE: The ICV solution is not at the midpoint of the linear range which may be as high as 1000 µg/L for some elements. The ICV solution used is a premixed standard purchased from Inorganic Ventures and contains the elements of interest between 2.5 and 100 µg/L. This solution provides calibration confirmation at more representative levels, given that most ICP-MS analyses are quantifying analytes in the low-ppb to sub-ppb range.

7.2.4 Interference Check Solutions (ICSA and ICSAB)

7.2.4.1 The ICSA is prepared in an acid rinsed 50 mL Class B volumetric flask by aliquoting 1.0 mL of Elements ICSAm (CS-CAK02) and 0.250 mL of 10 ppm molybdenum solutions and diluting to volume with the appropriate acid matrix.

7.2.4.2 The ICSAB is prepared in an acid rinsed 50 mL Class B volumetric flask by aliquoting 1.0 mL of Elements ICSAm (CS-CAK02), 0.125 mL of Inorganic Ventures 6020ICS-9B, and 0.250 mL of 10 ppm Molybdenum solutions and diluting to volume with the appropriate acid matrix.

7.2.5 Post-digestion spikes are performed by adding appropriate amounts of the calibration intermediate solutions to aliquots of the sample digestate. The volumes of each standard used vary based on the native concentrations found in the field samples. Refer to the post-digestion spike in Section 12 for details.

7.2.6 Refer to the appropriate digestion SOP for details of LCSW and matrix spike solution composition and preparation.

7.2.7 Tuning / Mass Calibration Solution

7.2.7.1 A 1ppm intermediate solution containing Be, Bi, Ce, Co, In, Li, Pb, Mg, and U is prepared by adding 1.0 mL of each from 1000 ppm stock standards to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid. The expiration date for the intermediate solution is the earlier of any one of its stock components.

7.2.7.2 The working solution is prepared in depending upon the instrument:

- For the Agilent: a 10 ppb tune/mass calibration solution is prepared by adding 10 mL of intermediate solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with the appropriate acid matrix.

- For the NexION (K-ICP-MS-04) instrument a 2.0 ppb tune/mass calibration solution is prepared by adding 2.0 mL of intermediate solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with the appropriate acid matrix.

  The expiration date for this solution is taken from the intermediate stock above.

7.3 Internal Standards Stock Solution – Prepare solutions by adding appropriate amounts of each 1000 ppm single element stock solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric. The internal standard solution is teed in by the peristaltic pump and used for the entire analytical sequence. The typical solutions are:

- Agilent Instrument: 1 ppm, Sc, Y, Ge, Ce, Tm, In, Lu, Th; 0.2 ppm ^{6}Li.
- NexION instrument: 30 ppb In, Tm, Lu, Th; 60 ppb ^{6}Li, Rh, Au; 75 ppb Sc; 100 ppb Ga, Y; 500 ppb Ge.

7.4 Additional Reagents

7.4.1 Reagent water, ASTM Type II.

7.4.2 All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

7.4.3 "OmniTrace Ultra" Concentrated Nitric Acid (EM Science # NX0408-2).

7.4.4 Argon (Airgas Industrial Grade – 99.999% pure, bulk delivered).

8) Apparatus and Equipment

8.1 ICP/MS Instruments

8.1.1

Instrument:	NexION 300D
Nebulizer:	PFA-ST Microflow
Spray Chamber:	Cyclonic, Peltier-cooled
Cones:	Nickel Sampler (1.0 mm orifice)
	Nickel Skimmer (0.75 mm orifice)

8.1.2

Instrument:	Agilent 7700
Nebulizer:	MicroMist
Spray Chamber:	Double Pass quartz spray chamber
Cones:	Nickel Sampler (1.0 mm orifice)
	Nickel Skimmer (0.75 mm orifice)

8.1.3

Instrument:	Agilent 7800
Nebulizer:	MicroMist
Spray Chamber:	Cyclonic, Peltier-cooled
Cones:	Nickel Sampler (1.0 mm orifice)
	Nickel Skimmer (0.75 mm orifice)

9) Preventative Maintenance

9.1 All maintenance is documented in the instrument logbook. ALS/Kelso maintains a service contract with the instrument manufacturer that allows for an unlimited number of service calls and full reimbursement of all parts and labor.

9.2 Most routine maintenance and troubleshooting is performed by ALS staff. Preventive maintenance activities listed below should be performed when needed as determined by instrument performance (i.e. stability, sensitivity, etc.) or by visual inspection. Other maintenance or repairs may, or may not require factory service, depending on the nature of the task.

- cone removal and cleaning
- removal and cleaning of ICP glassware and fittings
- checking and cleaning RF contact strips
- checking air filters and cleaning if necessary
- checking the oil mist filters and cleaning if necessary
- checking the rotary pump oil and adding or changing if necessary
- removal and cleaning of extraction lens
- removal and cleaning of ion lens stack
- replace the electron multiplier as necessary

10) Responsibilities

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the SOP for Documentation of Training, is also the responsibility of the department supervisor/manager.

11) Procedure

11.1 Refer to method 6020B and the instrument manuals for detailed instruction on implementation of the following daily procedures preceding an analytical run.

11.2 The following parameters are monitored to assure awareness of changes in the instrumentation that serve as signals that optimum performance is not being achieved, or as indicators of the physical condition of certain consumable components (i.e. EMT and cones).

11.2.1 Multiplier Voltages

11.2.2 Gas Flows - Coolant Ar

11.2.3 The nebulizer and auxiliary flows are adjusted later as part of the optimizing procedure.

11.3 Optimization

11.3.1 Gas Flows

11.3.1.1 Allow a period of not less than 30 minutes for the instrument to warm up.

11.3.1.2 Aspirate a mixed tune solution into the plasma and monitor the instrument output signal at mass 115 on the rate meter. Adjust the nebulizer and auxiliary flows to obtain maximum signal. Adjust the tension screw on the peristaltic pump to obtain minimum noise in the analytical signal. Record flow rates and note any large variances.

Note: Significant differences in flow rates will be observed for different torches and cones.

11.3.2 Tuning

11.3.2.1 Ion Lens Setting - While monitoring the output signal of a mixed tune solution at mass 115 on the ratemeter, adjust the ion lenses to obtain maximum sensitivity. Refer to the instrument manual for details on performing the adjustments.

11.3.2.2 Mass Calibration - Aspirate the tune / mass calibration solution described in section 7.2 and perform the mass calibration using the instrument's Mass Calibration program. (Refer to the instrument manual for details pertaining to the mass calibration procedure.) The acceptance criteria for the mass calibration is <0.1 amu from the true value. If the mass calibration fails criteria re-tune the instrument and perform the mass calibration procedure again.

11.3.2.3 Resolution Check - Using the spectra created during the mass calibration procedure; perform the resolution check to assure the resolution is less than 0.9 AMU at 5% peak height. If the resolution does not pass criteria adjust the instrument's resolution settings, run a new scan of the mass calibration solution and recheck.

11.3.2.4 Stability Check - Using the tune / mass calibration solution, perform a short-term stability check as per EPA Method 6020B. The relative standard deviations of five scans for each element in the tune solution must be < 5%. If the test does not pass criteria determine the cause (i.e. dirty cones, improper tune, etc.) correct the problem and re-run the test.

11.4 Analytical Run

11.4.1 Calibrate the instrument using a calibration blank (Standard 0), composed of reagent water, the appropriate acid matrix, and the working calibration standard (7.2.2). The masses typically monitored and those used for quantification are listed in Table 2. These masses are set as defaults in the instrument's analytical procedures. To begin select the correct method. Nebulize Standard 0 (Blank) into the plasma. Allow 1-2 minutes for system to equilibrate prior to establishing baseline. Follow directions on computer screen to perform standardization. Nebulize the working calibration standard into the

plasma. The operator must sign and date the first page of standardization.

11.4.2 After the first CCB and before the ICS standards a LLCCV standard, at or below the LOQ, is analyzed. The LLCCV must recover between ±20%.

11.4.3 Perform the analysis in the order listed below.

Initial Calibration Verification (ICV)
Continuing Calibration Verification (CCV)
Initial Calibration Blank (ICB)
Continuing Calibration Blank (CCB)
LLCCV
ICSA
ICSAB
Analyze 10 Samples
CCV
CCB
Analyze 10 Samples
CCV
CCB

Repeat sequence as required to complete analytical run, analyzing CCVs/CCBs every 10 analyses and at the end of the run.

12) Quality Assurance/Quality Control Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery of for each analyte must be 85-115% (for water, and within the LCS limits for soils) and the RSD <20%.

12.2 Method Detection Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. Refer to *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL) for details of performing the MDL study.

12.2.2 Calculate the average concentration found (x) and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. MDL's must be verified annually or whenever there is a significant change in the background or instrument response.

12.3 The LLQC is verified initially by the analysis of at least 7 replicate samples, spiked at the LLOQ. In most cases, the mean recovery should be ±35% of the true value and the RSD should be <20%.

12.4 IDLs should be determined at least once using new equipment, or after major instrument maintenance. The IDL is determined as the mean of the blank results + three times the standard deviation of 10 replicate analyses of the reagent blank solution.

12.5 Method 6020B requires that the linear range for each wavelength be verified on a daily basis. The linear range verification must recover within 10% of the true value and can be analyzed anywhere within a particular run. If a linear range verification is not analyzed for a specific element, the highest calibration range becomes the linear range. All reporting sample measurements must fall within the linear range.

12.6 The Initial Calibration Verification (ICV) standard is analyzed immediately after calibration. The results of the ICV must agree within ±10% of the expected value. If the control limits are exceeded, the problem will be identified and the instrument recalibrated.

12.7 A Continuing Calibration Verification (CCV) is analyzed after calibration then every 10 samples thereafter with a final CCV closing the final samples of the analytical run.

12.7.1 The results of the CCV must agree within ±10% of the expected value.

12.7.2 If the control limits are exceeded, the problem will be identified and corrective action taken. The instrument recalibrated. The previous 10 samples must be reanalyzed.

12.8 A Continuing Calibration Blank (CCB) is analyzed after calibration then every 10 samples thereafter with a final CCB closing the final samples of the analytical run.

12.8.1 The CCB measured values must be less than the MRL / LOQ for each element for standard applications. Other project-specific criteria may apply (for DoD QSM projects CCB can have no analytes > the LOD).

12.9 The ICSA and ICSAB solutions are analyzed after calibration and before any field samples. The solutions are then reanalyzed every 12 hours. Results of the ICSA are used by the analyst to identify the impact of potential interferences on the quality of the data. Based on these results appropriate action should be taken when interferences are suspected in an field sample including, but not limited to, selecting and alternative isotope for quantification, manual correction of the data, elevating the MRL, selection of an alternative method (e.g. optical ICP) or flagging the result as estimated when no other action is possible. Results for the spiked analytes in the ICSAB solution must agree with ± 20% of the expected value.

INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

	Solution A Concentrations (mg/L)	**Solution B** Concentrations (mg/L)
Al	20.0	20.0
Ca	60.0	60.0
Fe	50.0	50.0
Mg	20.0	20.0

Na	50.0	50.0
P	20.0	20.0
K	20.0	20.0
S	20.0	20.0
C	40.0	40.0
Cl	424	424
Mo	0.05	0.05
Ti	0.40	0.40
As	0.0	0.025
Cd	0.0	0.025
Cr	0.0	0.050
Co	0.0	0.050
Cu	0.0	0.050
Mn	0.0	0.050
Ni	0.0	0.050
Se	0.0	0.025
Ag	0.0	0.0125
V	0.0	0.050
Zn	0.0	0.025

NOTE: The concentration of interfering elements in the ICSA and ICSAB solutions are spiked at levels 5 times lower than recommended in Table 1 of Method 6020B. Running the full strength solutions as described in 6020B introduces too much material approximately 0.35 % dissolved solids into the ICP-MS system when trying to conduct low level analysis. Since the ICP-MS instrumentation is able to handle a maximum of 0.2% solids, the 6020B ICSA solution is higher in interfering components than any sample that would run through the instrument. However, the ICS solutions will be analyzed at levels that will provide approximately 0.1% dissolved solids.

12.10 Internal standards are used to correct for physical interferences. Masses used as internal standards include; ^{71}Ga, ^{72}Ge, ^{115}In, ^{6}Li, ^{175}Lu, ^{103}Rh, ^{45}Sc, ^{232}Th, and ^{89}Y. These internal standards are used in combination to cover the appropriate mass ranges. Internal standard correction is applied to the analytical isotopes by direct correlation of analyte to IS (Agilent), (NexION). This function is performed in real-time by the instruments operating system. Internal standards must be run within 50 AMU of the masses that are analyzed. Internal standard recoveries must fall between 30% and 125%. If not, then the sample must be reanalyzed after a fivefold or greater dilution has been performed.

12.11 A method blank is digested and analyzed with every batch of 20 (or fewer) samples to demonstrate that there are no method interferences. If the method blank shows any hits above the MRL for standard applications, or >½ the LOQ for DoD projects or > 1/10 the sample result, corrective action must be taken. The MB can only be rerun once. Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction and re-analysis.

12.12 Laboratory Control Samples are analyzed at a frequency of 5% or one per batch, whichever is greater. Refer to the current ALS-Kelso DQO spreadsheets for the LCS limits. For method 6020B, the LCS recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range. Project, QAPP, or client-specific control

limits may supersede the limits listed, but laboratory limits should be consistent with specified limits in order to establish that the specified limits can be achieved. If the control limits are exceeded, the associated batch of samples will be re-digested and reanalyzed.

12.13 A duplicate is digested one per batch, or per 20 samples (i.e. 5%). The duplicate RPD limits is ≤20%. Project, QAPP, or client-specific control limits may supersede the limits listed. If the control limits are exceeded, the samples will be re-digested and reanalyzed, unless sample non-homogeneity is established as the cause. In these instances, the data and the report will be flagged accordingly.

12.14 A Matrix Spike sample is digested one per batch, or per 20 samples (i.e. 5%). Default spike concentrations are listed in the sample digestion SOPs. Spike concentrations may be adjusted to meet project requirements. The matrix spike recovery will be calculated while the job is in progress. Where specified by project requirements, a matrix spike duplicate may be required. Matrix spike recovery criteria are derived from lab data. For Method 6020B, the recovery limits are 75-125%. If statistical in-house limits are used, they must fall within the 75-125% range. In some cases, project-specific QC limits may be required. Unless specified otherwise, for DoD QSM projects the project LCS criteria will be used for evaluation of matrix spikes. If an analyte recovery is outside acceptance limits proceed with the additional quality control tests described in sections 12.13 and 12.14. Based on results of these tests, the physical nature of the sample (e.g. homogeneity), and any specific project requirements, a determination can then be made as to appropriate corrective action (e.g. re-digestion, reporting with a qualifier, alternative methodologies, etc.). If the analyte concentration is >4x the spike level the spike control limit is no longer applicable and no action is required. For specifics on the preparation and composition of matrix spike solutions refer to the appropriate digestion SOP.

Note: For DoD projects a MS/MSD is required with every extraction batch. The %RSD should be < 20%.

12.15 Post Digestion Spike Test: The post digestion spike test is performed whenever matrix spike or replicate criteria are exceeded. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 75% to 125% of the known value. If this spike fails, then the dilution test should be run on this sample. If both the matrix spike and the post digestion spike fail, then matrix effects are confirmed. For DOD QSM 5.0 the post digestion spike shall be recovered to within 80-120% of the known value.

12.16 Dilution Test: The dilution test is performed whenever matrix spike or replicate criteria and post digestion spike criteria are exceeded. For sample concentrations that are sufficiently high (minimally, a factor of 25 times greater than the LOQ), the analysis of a fivefold (1+4) dilution must agree within ± 20% of the original determination. If the dilution test fails then a chemical or physical effect should be suspected. Corrective action can include additional dilution of the sample, the use of alternate methodologies, etc. or the data can be flagged and reported. The exact course of action will be dependent on the nature of the samples and project requirements and should be discussed with the project manager.

12.17 Instrument blanks should be evaluated for potential carryover and rinse times need to bring the analyte signal to within the CCB criteria. Results from instrument blanks run after standards or control samples should be used to establish levels at which carryover in samples may occur. Samples exhibiting similar effects of carryover should be reanalyzed.

13) Data Reduction and Reporting (or Documentation and Records)

13.1 Calculations

Calculate sample results using the data system printouts and digestion information. The digestion and dilution information is entered into the data system. The data system then uses the calculations below to generate a sample result.

Aqueous samples are reported in µg/L:

µg/L (Sample) = C* x Digestion Dilution Factor x Post Digestion Dilution Factor.

C*= Concentration of analyte as measured at the instrument in µg/L (in digestate).

Solid samples are reported in mg/Kg:

$$mg/Kg\ (Sample) = C^{*}\ x\ Post\ Digestion\ Dilution\ Factor\ x\ \frac{Digestion\ Vol.(ml)}{Sample\ wt.(g)}\ x\ \frac{1mg}{1000ug}\ x\ \frac{1L}{1000ml}\ x\ \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in µg/L (in digestate).

NOTE: If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the SOP for Total Solids.

13.2 Common isobaric interferences are corrected using equations equivalent to those listed in EPA Methods 6020B and 200.8. Monitoring of multiple isotopes for a single element provides a mechanism for identifying isobaric interferences. Refer to the Interferences section of EPA methods for additional descriptions of possible interferences and the mechanisms required for adequately compensating for their effects.

13.3 Data Review and Reporting

13.3.1 The ICP-MS operator reviews the MS data and signs and dates the Data Review Form. A qualified senior staff spectroscopist performs a secondary review of the data and the Data Review Form is signed and dated. The data is scanned for later compiling.

13.3.2 The data is saved on the local hard drive and is also copied to the appropriate directory on the network. The data directories are located at r:\icp\wip\data. The data is kept on the local directory for 1 month. The network files are periodically backed up on disc or network tape.

13.3.3 For "non-production" work (such as method development or research/development studies) the analyses are performed under the direction of a senior spectroscopist. All associated data is scrutinized by the senior spectroscopist. Original raw data and associated records are archived in the analytical project file.

13.3.4 The final review and approval of all data is performed by qualified spectroscopists.

14) Method Performance

14.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional available method performance data.

14.2 The method detection limit (MDL), limit of detection (LOD) and limit of quantitation (LOQ) are established using procedures described in *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS, Kelso Quality Assurance Manual.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 5-9 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS Lab Waste Management Plan for details.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformance and Corrective Action Procedure* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a

Nonconformity and Corrective Action Report (NCAR):

- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Refer to the SOP *ALS-Kelso Training Procedure* (ADM-TRAIN) for standard procedures.

17.2 A minimum of two senior level spectroscopists are to be maintained on staff at all times. Senior spectroscopists are defined as individuals with a minimum of ten years combined education and experience in, or related to atomic spectroscopy. Of those ten years, a minimum of two years of ICP-MS experience is required.

17.3 On-the-job-training occurs daily with the senior spectroscopists providing direction to new operators. The physical operation of the equipment is relatively simple. The data reduction and troubleshooting requires extensive experience that can only be gained by hands-on operation of the instrument and assisted evaluation of raw data.

17.4 Training outline

17.4.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.4.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.4.3 Perform initial precision and recovery (IPR) study as described above for water or soil samples. Summaries of the IPRs are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.5 Training and proficiency is documented in accordance with the *ALS-Kelso Training Procedure* (ADM-TRAIN).

18) Method Modifications

18.1 There are no known modifications in this laboratory standard operating procedure from the reference method.

19) Summary of Changes Since Last Revision

19.1 Updated to latest ALS format.
19.2 Minor typographical, grammatical, and formatting revisions.
19.3 Updated SOP references were necessary.
19.4 All references to 6020 and 6020A revised to reflect 6020B requirements.
19.5 Removed Thermo Electron instrument from SOP.
19.6 Section 1.1 – Removed MDLs and added reference to DQO tables.
19.7 Section 3.6 (old) – Deleted reference to surrogate.
19.8 Section 6 – Updated storage conditions and prep methods used.
19.9 Section 7 - Significant changes to standard makeup.
19.10 Section 7.2.4.2 and 7.2.7.2 – replaced 1% HNO3 with "the appropriate acid matrix".
19.11 Section 7.3 – Replaced second sentence to reflect automatic addition of IS by instrument.
19.12 Section 8.1.4 – Added additional instrument.
19.13 Section 11.4 – Replaced CRA with LLICV.
19.14 Section 11.4.1 – updated section reference.
19.15 Section 12.2 – Removed sentence referring to old MDL procedure.
19.16 Section 12.3-5 – New for 6020B.
19.17 Section 12.7 and 12.7 – Split up CCV and CCB.
19.18 Section 12.9 – Removed reference to GFAA and added Agilent to the direct correlation of analyte to IS statement.
19.19 Section 12.10 – Added additional IS elements.
19.20 Section 12.17 – deleted.
19.21 Section 13 - Restored missing information Aqueous (µg/L (Sample) lost in transfer between document versions.
19.22 Section 13.1 – Replaced last sentence.
19.23 Section 17.3 (old) – Removed.
19.24 Tables 1A, 1B, 1C – Removed MDLs and updated where necessary.

20) References and Related Documents

20.1 USEPA, Test Methods for Evaluation Solid Waste, SW-846, Update V, Method 6020B, Revision 2, July 2014.

20.2 Agilent and Thermo Elemental Instrument Manuals

20.3 Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories, Current Version.

21) Attachments/Appendices

21.1 Tables 1A, 1B, and 1C – MRLs for analyte matrix combinations.

21.2 Attachment A – Example Standard Sheets.

TABLE 1A
Target Analyte MRLs - Soil

METHOD	PREP METHOD	ANALYTE	MATRIX	MRL mg/kg
6020B	EPA 3050B	Aluminum	Soil	2
6020B	EPA 3050B	Antimony	Soil	0.05
6020B	EPA 3050B	Arsenic	Soil	0.5
6020B	EPA 3050B	Barium	Soil	0.05
6020B	EPA 3050B	Beryllium	Soil	0.02
6020B	EPA 3050B	Bismuth	Soil	0.05
6020B	EPA 3050B	Boron	Soil	0.5
6020B	EPA 3050B	Cadmium	Soil	0.02
6020B	EPA 3050B	Chromium	Soil	0.2
6020B	EPA 3050B	Cobalt	Soil	0.02
6020B	EPA 3050B	Copper	Soil	0.1
6020B	EPA 3050B	Lead	Soil	0.05
6020B	EPA 3050B	Manganese	Soil	0.05
6020B	EPA 3050B	Molybdenum	Soil	0.05
6020B	EPA 3050B	Nickel	Soil	0.2
6020B	EPA 3050B	Selenium	Soil	1
6020B	EPA 3050B	Silver	Soil	0.02
6020B	EPA 3050B	Thallium	Soil	0.02
6020B	EPA 3050B	Tin	Soil	0.1
6020B	EPA 3050B	Uranium	Soil	0.02
6020B	EPA 3050B	Vanadium	Soil	0.2
6020B	EPA 3050B	Zinc	Soil	0.5

TABLE 1B
Target Analyte MRLs – Water

METHOD	PREP METHOD	ANALYTE	MATRIX	MRL µg/L
6020B	MET-DIG (CLP)	Aluminum	Water	4
6020B	MET-DIG (CLP)	Antimony	Water	0.05
6020B	MET-DIG (CLP)	Arsenic	Water	0.5
6020B	MET-DIG (CLP)	Barium	Water	0.05
6020B	MET-DIG (CLP)	Beryllium	Water	0.02
6020B	MET-DIG (CLP)	Bismuth	Water	0.05
6020B	MET-DIG (CLP)	Boron	Water	2
6020B	MET-DIG (CLP)	Cadmium	Water	0.02
6020B	MET-DIG (CLP)	Chromium	Water	0.2
6020B	MET-DIG (CLP)	Cobalt	Water	0.02
6020B	MET-DIG (CLP)	Copper	Water	0.1
6020B	MET-DIG (CLP)	Iron	Water	2
6020B	MET-DIG (CLP)	Lead	Water	0.02
6020B	MET-DIG (CLP)	Manganese	Water	0.2
6020B	MET-DIG (CLP)	Molybdenum	Water	0.1
6020B	MET-DIG (CLP)	Nickel	Water	0.2
6020B	MET-DIG (CLP)	Selenium	Water	1
6020B	MET-DIG (CLP)	Silver	Water	0.02
6020B	MET-DIG (CLP)	Thallium	Water	0.02
6020B	MET-DIG (CLP)	Tin	Water	0.1
6020B	MET-DIG (CLP)	Uranium	Water	0.02
6020B	MET-DIG (CLP)	Vanadium	Water	0.2
6020B	MET-DIG (CLP)	Zinc	Water	2

TABLE 1C
Target Analyte MRLs – Tissue

METHOD	PREP METHOD	ANALYTE	MATRIX	MRL mg/kg
6020B	PSEP TISSUE	Aluminum	Tissue	2
6020B	PSEP TISSUE	Antimony	Tissue	0.05
6020B	PSEP TISSUE	Arsenic	Tissue	0.5
6020B	PSEP TISSUE	Barium	Tissue	0.05
6020B	PSEP TISSUE	Beryllium	Tissue	0.02
6020B	PSEP TISSUE	Bismuth	Tissue	0.05
6020B	PSEP TISSUE	Boron	Tissue	2
6020B	PSEP TISSUE	Cadmium	Tissue	0.02
6020B	PSEP TISSUE	Chromium	Tissue	0.2
6020B	PSEP TISSUE	Cobalt	Tissue	0.02
6020B	PSEP TISSUE	Copper	Tissue	0.1
6020B	PSEP TISSUE	Iron	Tissue	1
6020B	PSEP TISSUE	Lead	Tissue	0.02
6020B	PSEP TISSUE	Manganese	Tissue	0.05
6020B	PSEP TISSUE	Molybdenum	Tissue	0.05
6020B	PSEP TISSUE	Nickel	Tissue	0.2
6020B	PSEP TISSUE	Selenium	Tissue	1
6020B	PSEP TISSUE	Silver	Tissue	0.02
6020B	PSEP TISSUE	Thallium	Tissue	0.02
6020B	PSEP TISSUE	Tin	Tissue	0.05
6020B	PSEP TISSUE	Uranium	Tissue	0.02
6020B	PSEP TISSUE	Vanadium	Tissue	0.2
6020B	PSEP TISSUE	Zinc	Tissue	0.5

TABLE 2
Target Element Masses

ANALYTE	ISOTOPES ANALYZED	ISOTOPE REPORTED
Aluminum	27	27
Antimony	121, 123	123
Arsenic	75	75
Barium	135, 137, 138	137
Beryllium	9	9
Cadmium	111, 112, 114	111
Chromium	52, 53	52
Cobalt	59	59
Copper	63, 65	65
Lead	206, 207, 208	208
Manganese	55	55
Molybdenum	95, 97, 98	98
Nickel	60, 61, 62	60
Selenium*	77, 78, 82	82
Silver	107, 109	107
Thallium	203, 205	205
Uranium	238	238
Vanadium	51	51
Zinc	66, 67, 68	66

*Se 78 Is the default isotope on the NexION and The Agilent instruments.

ATTACHMENT A
Example Standard Sheets

Solution: ICP-MS, 200.8 Intermediate Stock
Matrix: 2% HNO_3

Element	Aliquot of 1000 ppm Std/1000 mL	Concentration (µg/L)
HNO_3	50.0 mL	5%
Al	1.0 mL	1000
Sb	1.0 mL	1000
As	1.0 mL	1000
Ba	1.0 mL	1000
Be	1.0 mL	1000
Cd	1.0 mL	1000
Cr	1.0 mL	1000
Co	1.0 mL	1000
Cu	1.0 mL	1000
Fe	1.0 mL	1000
Pb	1.0 mL	1000
Mn	1.0 mL	1000
Mo	1.0 mL	1000
Ni	1.0 mL	1000
Se	1.0 mL	1000
Tl	1.0 mL	1000
V	1.0 mL	1000
U	1.0 mL	1000
Zn	1.0 mL	1000

Solution: **ICP-MS, 200.8 Silver Intermediate Stock**
Matrix: **5% HNO_3**

Element	Aliquot of 500 ppm Std/1000 mL	Concentration (µg/L)
HNO_3	50.0 mL	5%
Ag	0.5 mL	500

Solution: **ICP-MS 25 ppb Calibration Standard and CCV**
Matrix: **As required**

Source	Aliquot per 100 mL	Concentration (µg/L)
HNO_3 (Ultrex)	As Required	As Required
Intermediate Stock	2.5 mL	25.0
Silver Intermediate Stock	2.5 mL	12.5

Metals and Semi-Volatiles SPLP Extraction

DOCUMENT ID: MET-SPLP, REV 3.0

Approved By: _____ Date: 12/5/19
Inorganics Manager, Jeff Coronado

Approved By _____ Date: 12/5/19
Quality Assurance Manager, Carl Degner

Approved By: _____ Date: 12/9/19
General Manager, Ambrose Hughey

1) Scope & Applicability

1.1 This Standard Operating Procedure (SOP) describes procedures for performing the extraction (excluding zero headspace extraction) of samples requiring (SPLP) analysis. This procedure is based upon EPA Method 1312, Synthetic Precipitation Leachate Procedure. The SPLP-ZHE procedure is described in *Zero Headspace Extraction* (EXT-ZHE). The SPLP procedure is designed to determine the mobility of organic and inorganic analytes present in liquid, soils and waste matrices. The results of a "total" analysis of the waste may be used to evaluate if the SPLP needs to be performed.

1.2 The determinative procedures for SPLP analysis, with the exception of a few special considerations, will be referenced in the appropriate determinative method.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DOD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD/ADM-DOD5)* may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 The sample is characterized as to its moisture content, size, physical state and miscibility in water (in cases of liquid samples). The flowchart found in Attachment A should be used to aid in determination of these sample characteristics.

2.2 Liquid waste (those containing less than 0.5% solid material) is defined as the SPLP extract after passing through a 0.6 to 0.8 µm filter. For samples containing greater than or equal to 0.5% dry solids, the liquid, if any, is separated from the solid phase and stored for later analysis. The solid phase is extracted and subsequently analyzed. If compatible, the initial liquid phase of the sample is added to the liquid extract and these are analyzed together. If incompatible, the liquids are analyzed separately.

2.3 The extraction fluid used is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid is a pH 4.2 solution.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The matrix of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.3 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.4 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not previously described. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.5 Miscellaneous matrices - These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix

3.4 Method Blank (MB) - An artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.5 Laboratory Control Samples (LCS) – An aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.6 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.7 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the

ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

4.2 It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in the SOP *Employee Training and Orientation,* (ADM-TRAIN).

5) Interferences

5.1 Some samples such as paints, thick oils or fine particulates may cause problems due to their physical characteristics. Potential interferences that may be encountered during analysis are discussed in the determinative methods.

5.2 Filters used in various stages of the procedure should be pre-washed to reduce interferences. This may include acid washing to reduce metals contaminants.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and gloves appropriate for the solvent being used. .

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDS where available. Refer to the ALS Kelso Chemical Hygiene Plan and the appropriate SDS prior to beginning this method.

6.3 Sulfuric and Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Samples should be collected (received) in glass jars with a minimum of headspace. Samples may be refrigerated at 4 ± 2ºC until analysis, unless damage to the physical characteristics of the sample will result. Preservatives shall not be added to samples prior to extraction.

7.2 The amount of extract need for each method is listed below:

Volume →		**mL of Sample Extract Needed**		**mL of Blank Solution Needed**	
ANALYSIS	**Sample**	**MS/DUP**	**MS/MSD**	**Method Blank**	**LCS/DLCS**
Pesticides	100		200	100	200
PCB	100		200	100	200
Herbicides	10		20	10	20

SVO	100		200	100	200
Metals& Hg	45	90		45	90

8) Apparatus and Equipment

8.1 Balance: accurate to within ± 0.1 gram.

8.2 Beaker or Erlenmeyer flask (various sizes ranging from 100 ml to 500 ml).

8.3 Extraction Bottles: Teflon, or plastic. Plastic bottles should not be used when organics are being determined.

8.4 Graduated Cylinders: various sizes 250 ml to 2000 ml.

8.5 Drying Oven: capable of maintaining a constant temperature of 100 ± 20°C.

8.6 Magnetic Stirrer and Stir Bar.

8.7 pH Meter: accurate to ± 0.05 units at 25°C.

8.8 Filtration Apparatus and filters suitable for filtration (vendors may sell filters designed specifically for the method). Filters are acid-washed borosilicate glass fiber and have an effective pore size of 0.6 to 0.8 µm. Glass fiber filters are fragile and should be handled with care.

8.9 Tumbler: Must be capable of rotating the extraction vessel end-over-end at 30 ± 2 rpm.

8.10 Stopwatch, preferably digital for tumbler rotation checks

9) Standards, Reagents, and Consumable Materials

9.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking (ADM-RTL)* for the complete procedure and documentation requirements.

9.2 All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

9.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3

9.4 Extraction Fluid (#1): This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05. The fluid is used to determine the leach ability of soil from the site that is east of the Mississippi River, and the leach ability of wastes and wastewaters.

9.5 Extraction Fluid (#2): This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. The fluid is used to determine the leach ability of soil from a site that is west of the Mississippi River.

9.6 Extraction Fluid (#3): For Cyanide-containing wastes and/or soils reagent water must be used because leaching of cyanide – containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

9.7 pH buffers, 1.68, 4.00, and 7.00. Expiration dates for the buffers are listed on the container. Buffers are replaced and disposed of before the expiration date passes. Portions poured into other containers for daily use are discarded daily

9.8 pH buffers 2.00 and 5.00 are used to verify the validity of the initial calibration. If the calibration falls between between 4.00 and 7.00, a 5.00 pH standard is used. If the calibration falls between 1.68 and 4.00, a 2.00 pH standard is used.

10) Preventative Maintenance

10.1 Maintenance activities are generally limited to performance checks of balances, monitoring of extraction room temperature, and verification of tumbler rotation speed. Documentation is maintained in an associated logbook or onto an analytical record.

11) Procedure

11.1 Preliminary Evaluations: These procedures should be performed in cases where the waste is not obviously solid (contains a liquid phase that cannot be completely mixed into the solid phase without a phase separation occurring) and/or when the waste cannot be extracted without size reduction.

11.1.1 Determine the percent solids.

11.1.1.1 If the sample contains moisture that which may produce liquids when subjected to pressure filtration, the following steps are taken. If not, proceed to the particle size reduction section.

11.1.1.2 Pre-weigh the filter and the container that will receive the filtrate. Record the weight.

11.1.1.3 Assemble the filter holder and filter as per manufacturer's instructions.

11.1.1.4 Weigh out a minimum of 100 g of the sample and record the weight.

11.1.1.5 Allow slurries to settle prior to filtration, centrifuge to aid in filtration if necessary.

11.1.1.6 Quantitatively transfer the waste to the filter (both the liquid and the solid). Apply gentle pressure (<10 psi) to the filter holder, if no solution has passed through the filter for two minutes, increase the pressure in increments of 10 psi until air passes through the filter or 50 psi is reached. Use only one filter. The portion remaining on the filter is considered the solid phase.

11.1.1.7 Determine the weight of the liquid phase by weighing the filtrate container and subtracting the initial weight of the container.

11.1.1.8 Subtract the weight of the liquid from the weight of sample filtered to get the weight of the solid phase.

11.1.1.9 Calculate the percent solids as follows:

$$\text{Percent Solids} = \frac{\text{Weight of solid}}{\text{Total weight of waste}} \times 100$$

11.1.2 If the percent solids is <0.5%, then the filtered sample is considered to be the SPLP extract and further manipulation of the sample is unnecessary. If the sample is ≥0.5% solids go to the next step.

11.1.2.1 In standard cases (i.e. liquids which will not pass through the filter are not present) remove the solid phase and the filter from the filtration apparatus; else continue to the particle size reduction section (11.1.4).

11.1.2.2 Dry the solid phase with the filter at 100 ± 20ºC until two successive weightings yield the same value within ± 1%. Record the final mass.

Note: If the amount of material remaining on the filter will obviously yield solids >0.5% note this on the extraction bench sheet, skip the drying step, and proceed to section 11.1.4 and subsequent extraction with this aliquot of waste.

11.1.2.3 Calculate the percent dry solids.

$$\text{Percent Dry Solids} = \frac{\text{(Weight of dry sample + filter) – tared weight of filter}}{\text{Initial weight of sample}} \text{ x100}$$

11.1.3 If the percent dry solids are < 0.5%, the filtrate is considered the SPLP extract and further manipulation of the sample is unnecessary. If the percent dry solids is ≥ 0.5%, then continue with a fresh portion of waste.

11.1.4 Does the solid portion of the waste require particle size reduction?

Using the solid portion of the sample, see if all of the sample will pass through a 9.5 mm sieve (the surface area is > 3.1 cm^2 per gram). If these criteria are not met, the sample must be ground, cut, or crushed to fulfill the requirements. For samples that are pieces of wire, cloth, wire mesh, etc., the analyst must prepare the sample to reduce the size as describe above.

11.1.5 Determine the extraction fluid to be used.

11.1.5.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 is used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 is used.

11.1.5.2 For wastes and wastewater, extraction fluid #1 is used.

11.1.5.3 For cyanide containing wastes and/or soils, extraction fluid #3 is used since leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas and the loss of cyanide from the sample.

11.2 Extraction procedure

11.2.1 If the sample was determined to be 100% solids and the sample did not require particle size reduction, weigh out a 100 g aliquot of the sample and quantitatively transfer to the extraction vessel.

11.2.2 If the sample is liquid and contains <0.5% solids, the filtered sample is considered the SPLP extract. Record the pH of the extract.

11.2.3 Extractions for 100% solids when only organics or metals are requested:

11.2.3.1 Determine if particle size reduction is required. If so, refer to section 11.1.4.

11.2.3.2 Weigh the sample into the extraction vessel and add the appropriate extraction fluid.

11.2.3.3 Extract the sample by rotating the tumbler for 18 ± 2 hours at 30 ± 2 rpm. Check for pressure in the bottle after 15 minutes and release if necessary. If pressure is present, subsequently check for pressure at 15 minute intervals until pressure buildup is minimized. Measure and record on the bench sheet the tumbler rotation (RPM) and room temperature (ºC) when the tumbling is in process. Room temperature must be maintained at 23 ± 2ºC.

11.2.3.4 Filter the sample and record the pH of the extract.

11.2.3.5 For metals analysis, take a small portion of the extract (~5 mL) and add some nitric acid. If a precipitate forms, do nothing further with the extract and analyze as soon as possible.

Note: For metals analyses, the aliquot of SPLP extract that is to be used for the matrix spike analysis must be spiked prior to preservation.

11.2.3.6 Acidify the extract to a pH of <2 and store until time of analysis. For organics, the extract is ready for preparation for analysis, do not acidify.

11.2.4 Extractions for 100 % solids when both organics and metals are requested.

11.2.4.1 Determine if particle size reduction is required. If so, refer to section 11.1.4.

11.2.4.2 Weigh the sample into the Teflon extraction vessel and add the appropriate extraction fluid.

11.2.4.3 Extract the sample by rotating the tumbler for 18 ± 2 hours at 30 ± 2 rpm. Check for pressure in the bottle after 15 minutes, release if necessary. If pressure is present, subsequently check for pressure at 15 minute intervals until pressure buildup is minimized. Measure and record on the bench sheet the tumbler rotation (RPM) and room temperature (ºC) when the tumbling is in process. Room temperature must be maintained at 23 ± 2ºC.

11.2.4.4 Filter the sample and record the pH of the extract. Separate the samples, an aliquot for organics and an aliquot for metals. For metals fraction, take a small portion of the extract (~5 mL) and add some nitric acid. If a precipitate forms, do nothing further with the extract and analyze as soon as possible. If no precipitate forms, acidify the extract to a pH of <2 and store until analysis. For organics, the extract is ready for preparation for analysis.

Note: For metals analyses, the aliquot of SPLP extract that is to be used for the matrix spike analysis must be spiked prior to preservation.

11.2.5 Less than 0.5% solids (liquids only) when metals and/or organics are requested.

11.2.5.1 Measure out the required amount of sample.

11.2.5.2 Assemble the filtration apparatus, rinse, and filter the measured aliquot of waste into an amber bottle.

11.2.5.3 Separate the fractions, if necessary. Take a small portion of the metals fraction (5 mL) and add some nitric acid. If a precipitate forms, do nothing further with the extract and analyze as soon as possible. If no

precipitation occurs, acidify the metals fraction to a pH of <2 and store until time of analysis.

Note: For metals analyses, the aliquot of SPLP extract that is to be used for the matrix spike analysis must be spiked prior to preservation.

11.2.5.4 The samples are ready for preparation for analysis.

11.2.6 For 0.5 % to <100 % solids when either organics or metals, or both, are requested.

11.2.6.1 Pre-weigh the container that will receive the filtrate. If a fresh portion of the waste is to be used (section 11.1.3) weigh out a subsample of the waste and record the mass and go to 11.2.6.2, else go to 11.2.6.3. Determine the sample size and amount of extraction fluid as specified in the method.

11.2.6.2 Assemble the filtration apparatus, rinse, and filter. Allow slurries to settle prior to filtration, centrifuge to aid in filtration if necessary. Quantitatively transfer the waste to the filter (both the liquid and the solid). Apply gentle pressure (<10 psi) to the filter holder, if no solution has passed through the filter for two minutes, increase the pressure in increments of ten psi until air passes through the filter or 50 psi is reached. Use only one filter.

11.2.6.3 The portion remaining on the filter is considered the solid phase. If a significant amount of waste remains in the transfer vessel, this should be taken into account by subtracting the amount left behind from the total amount of waste.

11.2.6.4 Collect the filtrate and determine if it will be miscible with the extraction fluid. If not, separate it into two fractions of ratio 1:5 (one part for metals and five parts for organics), preserve the metals fraction and analyze. If the filtrate will be miscible with the extractant, store the filtrate until the two portions can be mixed.

11.2.6.5 Reduce particle size of the solid portion if necessary.

11.2.6.6 Quantitatively transfer the solid portion of the waste to a Plastic or Teflon bottles.

11.2.6.7 Slowly add the determined amount of the appropriate extraction fluid and seal the extraction vessel.

11.2.6.8 Extract the sample by rotating the tumbler for 18 ± 2 hours at 30 ± 2 rpm. Check for pressure in the bottle after 15 minutes and release if necessary. If pressure is present, subsequently check for pressure at 15 minute intervals until pressure buildup is minimized. Measure and record on the bench sheet the tumbler rotation (RPM) and room temperature (ºC) when the tumbling is in process. Room temperature must be maintained at 23 ± 2ºC.

11.2.6.9 Filter the sample and record the pH of the extract.

11.2.6.10 If applicable, mix the extract with the filtrate from section 11.2.5.3.

11.2.6.11 If both metals and organics are requested, separate the fractions. Acidify the extract to a pH of <2 and analyze. For organics, the extract is ready for further preparation for analysis.

Note: For metals analyses, the aliquot of SPLP extract that is to be used for the matrix spike analysis must be spiked prior to preservation.

11.2.6.12 If only organics is requested, the extract is now ready for further preparation for analysis.

11.2.6.13 For metals analysis, take a small portion of the extract (~5 mLs) and add some nitric acid. If a precipitate forms, do nothing further with the extract and analyze as soon as possible.

Note: For metals analyses, the aliquot of SPLP extract that is to be used for the matrix spike analysis must be spiked prior to preservation.

11.2.7 If the liquid portion of the waste and the extraction fluid are not miscible, the results from the analysis of the two fractions must be mathematically combined to give the final SPLP result for the waste.

12) QA/QC Requirements

12.1 This method shall operate under the formal Quality Assurance Program established at ALS and must maintain records that define the quality of data that is generated. Data shall be compared to established criteria in order to determine if the results of the analyses meet the performance characteristics of the method. It is required that an initial demonstration of capability and periodic analysis of laboratory reagent blanks, laboratory fortified blanks, and other QC solutions as a continuing check on performance. The accuracy and precision of the procedure must be validated *before* analyses of samples begin, or whenever significant changes to the procedures have been made.

12.2 Method Blank: A minimum of one Method Blank must be prepared with each batch or with every 20 samples processed (if batch size is greater than 20 samples). Do not designate specific extraction bottles for method blanks, randomly select the extraction bottles to obtain a representative cross-section. If a method blank contains a positively identified target analyte above the MRL, all samples that contain that analyte will be re extracted, unless the sample results are greater than 20x the level detected in the method blank.

12.3 Matrix Spike: A matrix spike shall be performed for each waste type unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. At a minimum, use the guidelines for addition of matrix spikes found in the determinative methods.

12.4 Matrix spikes are added after filtration of the 1312 extract and before preservation.

Note: For metals analyses, the aliquot of SPLP extract that is to be used for the matrix spike analysis must be spiked prior to preservation.

12.5 All quality control measures described in the determinative methods shall be followed.

12.6 Refer to section 9.0 of the SPLP method for method performance information...

13) Data Reduction and Reporting

13.1 See analytical Method SOPs...

14) Method Performance

14.1 Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as in the determinative procedure. The method detection limit(s) and method reporting limit(s) are established for the determinative procedure. See *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* (CE-QA011/ADM-MDL).

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. Refer to the ALS Kelso Lab Waste Management Plan.

15.4 This method uses a base. Waste base is hazardous to the sewer system and to the environment. All waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS Lab Waste Management Plan for more details.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformance and Corrective Action Procedure* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).

- Sample preservation or handling discrepancies due to laboratory or operations error.
- Customer inquiries concerning data quality or services (when applicable). NCAR not required for simple corrections with no impact to the client.
- Data errors reported to clients, non-conforming re-checks.
- Deficiencies found during internal or external audits.
- Login errors or shipping errors.
- IT issues if there is a significant impact to a client.
- Turnaround time complaints.
- Sample preservation or handling discrepancies due to laboratory operations error.

17) Training

17.1 Training outline

17.1.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to TNI's Initial Demonstration of Capability.

17.2 Training is documented following *Employee Training and Orientation* (ADM-TRAIN).

17.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 There are no known modifications in this laboratory standard operating procedure from the reference method

19) References

19.1 US Environmental Protection Agency, Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, September 1994

19.2 USEPA Region 10 Document Number ESAT-10A-210, February, 1991

19.3 DoD Quality Systems Manual for Environmental Laboratories, current version.

19.4 TNI Standard, Volume 1, 2009 & 2016.

19.5 SPLP EXTRACTION WORKSHEET

R:\ICP\MISC\DIGFORMS\TCLP Bench Sheets\TCLP Extraction Benchsheet 10-10-17.xltx.

20) Changes since the Last Revision

Summary of Revision Changes			
Revision Number	Effective Date	Document Editor	Description of Changes
3.0	12/17/19	T. Caron	Reformatted SOP to current ALS SOP format. Minor typographical, grammatical and formatting changes to improve readability. Section 8 - Updated filtration apparatus. Section 9.8 – New. Section 11.2.5.3 - Updated metals sample fraction preparation. Replaced obsolete benchsheet hyperlinks. Attachment B, section 1.20 – New.

21) Attachments, Tables, and Appendices

21.1 Attachment A - Preliminary Determination flowchart.

21.2 Table 1 - TCLP/SPLP Rotational Tumbler Diagram.

21.3 Attachment B – pH Calibration Procedure and Maintenance.

Attachment A

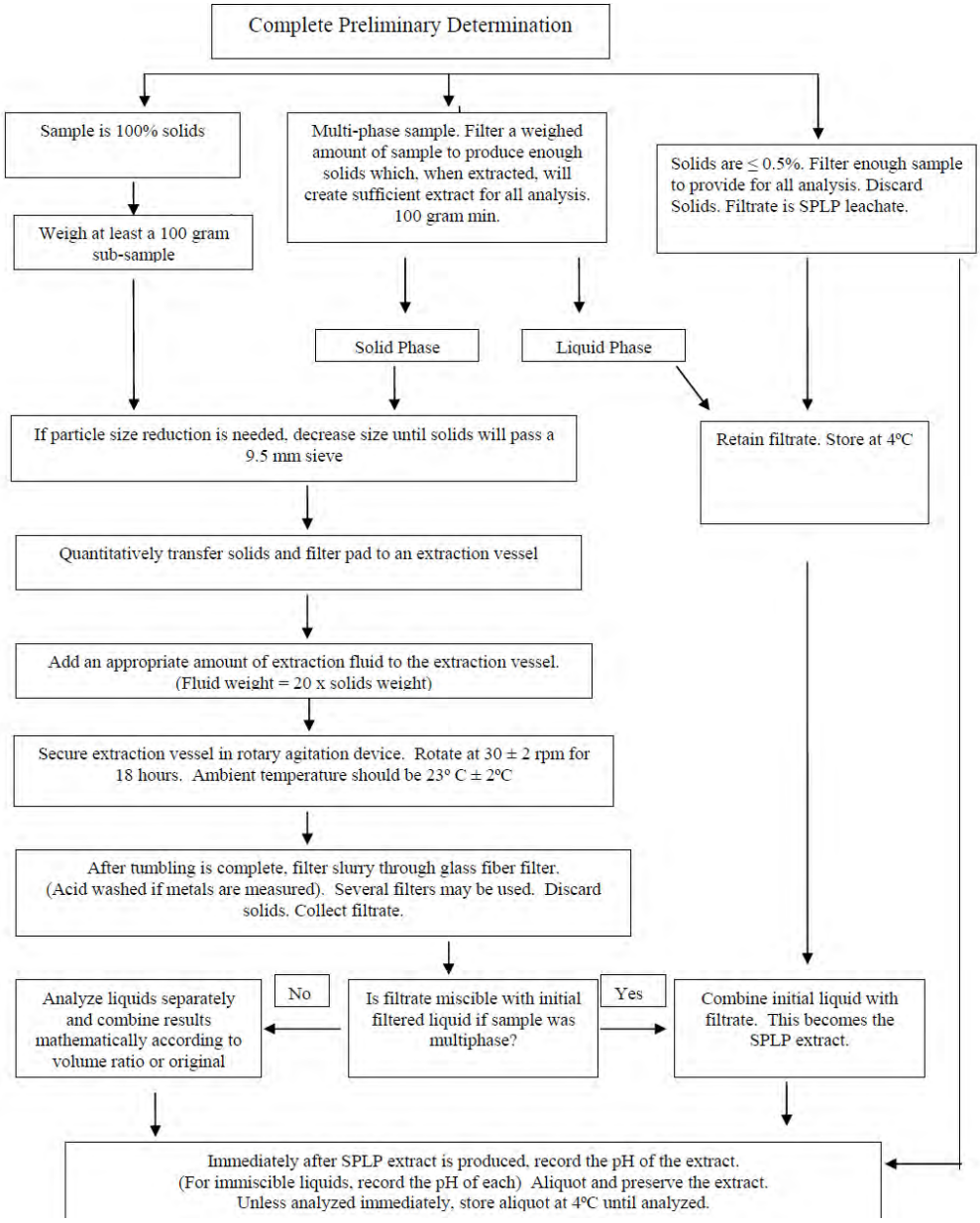
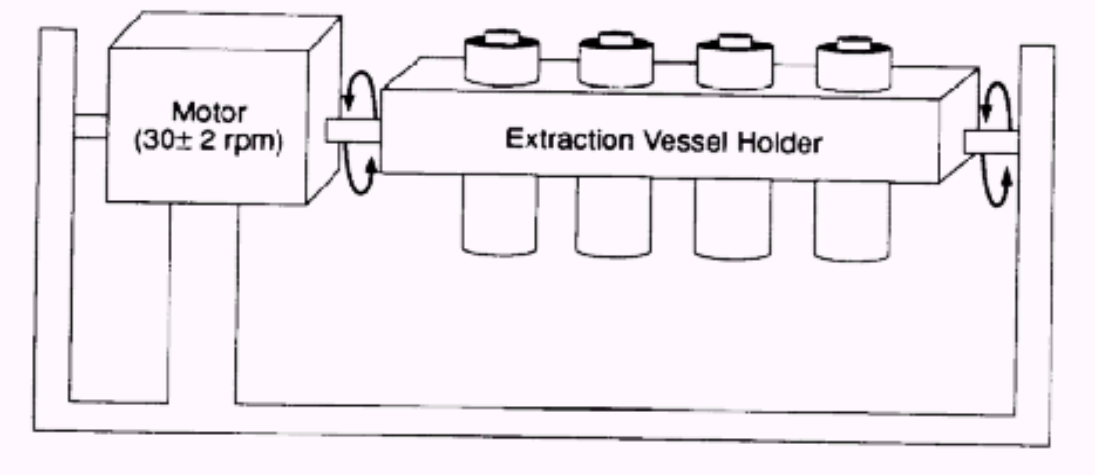


Table 1
TCLP/SPLP Rotational Tumbler



Attachment B
pH Calibration Procedure and Maintenance

Standard pH buffers: 1.68, 2.00, 4.00, 5.00 and 7.00

1. pH Calibration Procedure

1.1. Buffers in 50 mL plastic centrifuge tubes need to be replaced with buffer from the primary container daily.

1.2. Once a manufacture's cubitainer is open it is good for three months.

1.3. Perform calibration daily. Record calibration; buffer checks and buffer temperatures in instrument logbook or bench sheet with date and analyst's initials.

1.4. The slope percentage of the calibration points should be between 95 and 105%, the meter displays the slope of calibration.

1.5. If the slope exceeds the above end points either the buffer(s) is contaminated or the probe is no longer functioning properly.

1.6. Replace buffers, and then re calibrate.

1.7. If after replacing the buffer solutions slope percentage of the calibration points is not between 95 and 105% follow the directions for cleaning the probe and re calibrate.

1.8. If cleaning the probe does not correct the calibration slope percentage error the probe needs to be replaced.

1.9. Pour the buffer calibration solutions into labeled calibration vessel. The label must have the date and pH buffer solution name, pH buffer solution lot #.

1.10. Rinse the probe with deionized water and put the probe into the first calibration vessel. Make sure that there are no air bubbles under the probe tip.

1.11. From the standby screen press CALIBRATE.

1.12. Press READ to measure the first calibration solution. Record the measurement in the pH calibration logbook 2001-MET-pH. When the measurement is stable, the instrument will request the next calibration solution.

1.13. Rinse the probe with deionized water and put the probe into the second calibration vessel. Make sure that there are no air bubbles under the probe tip.

1.14. Press READ to measure the second calibration solution. Record the measurement in the pH calibration logbook 2001-MET-pH.

1.15. If the calibration is correct the meter will display the message CALIBRATION OK and will save the calibration data.

1.16. From the standby screen press CALIBRATE.

1.17. Press CAL.DATA

1.18. Select CURRENT CALIBRATION option. The data from the last calibration is shown.

1.19. Record the slope percentage of the calibration points in the pH calibration logbook 2001-MET-pH.

1.20. Following the instrument calibration, a pH check standard is analyzed. The check stnandard or buffer verifies the validity of the initial calibration and must be from a different lot

number or manoufacturer. If the calibraiton is between 4.00 and 7.00, a 5.00 pH standard is used. If the calibration is between 1.68 and 4.00, a 2.00 pH standard is used. The acceptance criterion is ± 0.05 pH units of the true value. If the standard is outside of these acceptance limits, the buffer is rechecked once. If it is still outside the ± 0.05 pH unit limit, the instrument is recalibrated.

2. pH Probe Cleaning and Maintenance

2.1. The glass bulb should be cleaned every other week, or more, by placing it in a centrifuge tube with approximately 30 mL of 0.1N HCL. (The 0.1N HCL is made by adding 250 µL of concentrated acid to 20 mL of de ionized water in a graduated centrifuge tube. Dilute to 30 mL with deionized water in the graduated centrifuge tube and allow to sit while stirring for approximately 5 minutes. Then rinse the probe with DI water 3 times and blot with a Kimwipe®.

APPENDIX D

EXAMPLES OF FIELD FORMS

CHAIN OF CUSTODY FORM

Project: _____

Samplers: _____

Example

Project Contact:

Office _____

Phone _____

Ship to:

Lab Name _____

Address _____

_____

_____

Contact _____

Phone _____

Soil Sample No.	Date	Time	Matrix	Preservative (if any)	ANALYSES REQUESTED					Extra Container	Archive	Comments

Analysis Turn Time: Normal Rush Rush Results Needed By:

Shipped by: Shipping Tracking No.:

Condition of Samples Upon Receipt: Custody Seal Intact?

Matrix Code:

SO - Soil

Other:

Relinquished by: _____ **Date/Time:** _____ **Received by:** _____ **Date/Time:** _____

(signature) *(signature)*

Relinquished by: _____ **Date/Time:** _____ **Received by:** _____ **Date/Time:** _____

(signature) *(signature)*

Special Intructions:

CHAIN OF CUSTODY FORM

Page ____ of ____

Project: TAI UCR Soil Sampling

Samplers: Field S. Ampler, Helper S. Amplers

Example

Project Contact: Project Manager

Office: Bellevue, Wa

Phone: 555-555-5555

Ship to:

Lab Name: Analytical Laboratory

Address: 111 Laboratory Lane

Seattle, WA 55555

Contact: Lab Mananger

Phone: 555-555-5555

Soil Sample No.	Date	Time	Matrix	Preservative (if any)	ANALYSES REQUESTED: Conventional Parameters	EPA TAL Metals	All Metal COIs	All Organic COIs		Extra Container	Archive	Comments
RF1-001	2010-06-01	1300	SO	None	x	x				N	N	None
RF1-002					x	x				N	N	None
RF1-003					x	x				N	N	None
RF1-004					x	x				N	N	None
RF1-005					x	x				N	N	None
RF1-006					x		x	x		N	N	None
RF1-007					x		x	x		N	N	None
RF1-008					x		x	x		N	N	None
RF1-009					x		x	x		N	N	None
RF1-010					x		x	x		N	N	None

Analysis Turn Time: (Normal) Rush Rush Results Needed By:

Matrix Code:
SO - Soil
Other:

Shipped by: F. Sampler Shipping Tracking No.: 123456787463

Condition of Samples Upon Receipt: Custody Seal Intact?

Relinquished by: Field S. Ampler *(signature)* **Date/Time:** 2010-06-01 1644 **Received by:** UPS *(signature)* **Date/Time:** 2010-06-01 1644

Relinquished by: *(signature)* **Date/Time:** **Received by:** *(signature)* **Date/Time:**

Special Intructions:

Custody Seal

CUSTODY SEAL

Example

Date: _____ Time: _____

Sampler Signature: _____

Sample Label

Example

Soil

Sample No: _____ Date: _____

Sampler: _____ Time: _____

Preservative: _____

Custody Seal

CUSTODY SEAL

Example

Date: 2010-06-01 Time: 1630

Sampler Signature: *Field S. Ampler*

Sample Label

Example

Soil

Sample No: RF1-005 Date: 2010-06-01

Sampler: FSA Time: 0912

Preservative: None

	Field Change Request	

Field Change No.:_____
Page _____ to _____

Project number:
Project name:

CHANGE REQUEST
Applicable Reference:
Description of Change:

Reason for Change:

Impact on Present and Completed Work:

Requested by:
Date: ____/____/____
(Field Scientist)

Acknowledged by:
Date: ____/____/____
(Field Coordinator)

FIELD COORDINATOR RECOMMENDATION

Recommended Disposition:

Recommended by:
Date: ____/____/____

PROJECT MANAGER APPROVAL

Final Disposition:

Approved/Disapproved by:
Date: ____/____/____

CORRECTIVE ACTION RECORD

Page ___ of ___

Audit Report No. : _____ Date: _____

Report Originator:

Person Responsible for Response:

DESCRIPTION OF THE PROBLEM:

Date and Time Problem Recognized: _____ By: _____

Date of Actual Occurrence: _____ By: _____

Analyte: _____ Analytical Method:

Cause of Problem:

CORRECTIVE ACTION PLANNED:

Person Responsible for Corrective Action:

Date of Corrective Action:

Corrective Action Plan Approval: _____ Date:

DESCRIPTION OF FOLLOW-UP ACTIVITIES:

Person Responsible for Follow-up Activities:

Date of Follow-up Activity:

Final Corrective Action Approval: _____ Date:

SOIL COLLECTION FIELD FORM

Project Name:_______________ Project No.:_______________ Page: ____of____

Date:__________ Sampling Crew: _______________

Weather: _______________Sampling Equipment_______________

Time:________ Station No.:________ Elevation: ________

Latitude:________ Longitude: ________ Accuracy: ________

Sample ID: _______________ Depth: ________

Sample analysis: _______________ No. sample containers:____

Soil Volume: _______________

Vegetation: _______________

Photograph numbers: _______________

Comments: _______________

Time:________ Station No.:________ Elevation: ________

Latitude:________ Longitude: ________ Accuracy: ________

Sample ID: _______________ Depth: ________

Sample analysis: _______________ No. sample containers:____

Soil Volume:_______________

Vegetation: _______________

Photograph numbers: _______________

Comments: _______________

Time:________ Station No.:________ Elevation: ________

Latitude:________ Longitude: ________ Accuracy: ________

Sample ID: _______________ Depth: ________

Sample analysis: _______________ No. sample containers:____

Soil Volume: _______________

Vegetation: _______________

Photograph numbers: _______________

Comments: _______________

APPENDIX E

HEALTH AND SAFETY PLAN ADDENDUM

CONTENTS

LIST OF TABLES

ACRONYMS AND ABBREVIATIONS

COPC	chemical of potential concern
PPE	personal protective equipment
RI/FS	remedial investigation and feasibility study
SHSP	site health and safety plan
Site	Upper Columbia River site
SATES	Soil Amendment Technology Evaluation Study
TAI	Teck American Incorporated
UCR	Upper Columbia River

SITE HEALTH AND SAFETY PLAN ADDENDUM APPROVAL

This addendum to the general site health and safety plan (SHSP) has been reviewed and approved by Teck American Incorporated's (TAI) technical consultant (Ramboll) for the Soil Amendment Technology Evaluation Study (SATES) program field-scale soil treatment pilot test and related soil sampling activities to be conducted at the Upper Columbia River (UCR) site (Site) in support of the remedial investigation and feasibility study (RI/FS) for the Site.

Ramboll Task Manager Date

Ramboll Corporate Health and Safety Officer Date

SITE HEALTH AND SAFETY PLAN ADDENDUM ACKNOWLEDGEMENT

This addendum to the general SHSP (TCAI 2009) is approved for use at the Site. The general SHSP and addendum are the minimum health and safety standard for the Site and will be strictly enforced for all personnel conducting the SATES program field-scale soil treatability testing and monitoring (soil sampling) activities at the Site. Contracted personnel may request to adopt a project-specific plan in lieu of this addendum but must obtain prior written approval from TAI and provide written concurrence that the contractor will assume direct responsibility and liability for administering the plan to its employees.

I have reviewed this addendum to the general SHSP for the SATES program tasks. I have had an opportunity to ask any questions I may have and have been provided with satisfactory responses. I understand the purpose of the plan, and I consent to adhere to its policies, procedures, and guidelines.

Employee signature	Company	Date
Employee signature	Company	Date
Employee signature	Company	Date
Employee signature	Company	Date
Employee signature	Company	Date
Employee signature	Company	Date
Employee signature	Company	Date

1 INTRODUCTION

This addendum to the general site health and safety plan (SHSP) for the Upper Columbia River (UCR) site (Site) remedial investigation and feasibility study (RI/FS) provides specific Site information and health and safety provisions to protect workers from potential hazards during the SATES field test implementation and subsequent soil sampling at the designated SATES test plots, located near Northport, Washington.

Site background information and general health and safety provisions to protect workers from potential hazards during work at the Site are presented in the general SHSP (TCAI 2009).

Subcontractors that are contracted to perform field work associated with the RI/FS may adopt this SHSP or develop and follow their own SHSPs. However, subcontractor SHSPs must be consistent with the provisions outlined in this addendum and the general SHSP, and any discrepancies will follow the most protective practices.

It is Ramboll's policy to provide a safe and healthful work environment. No aspect of the work is more important than protecting the health and safety of all workers.

Ramboll cannot guarantee the health or safety of any person entering the Site. Because of the potentially hazardous nature of the Site and the activity occurring thereon, it is not possible to regulate personal diligence or to discover, evaluate, and provide protection for all possible hazards that may be encountered. Adherence to the health and safety guidelines set forth herein will reduce, but not eliminate, the potential for injury and illness at the Site. The health and safety guidelines in this SHSP addendum were prepared specifically for the UCR Site and should not be used on any other site without prior evaluation by trained health and safety personnel.

A copy of this addendum and the general SHSP must be in the custody of the field team during field activities. All individuals performing field work must read, understand, and comply with this plan before undertaking field activities. Once the information has been read and understood, the individual must sign the Site Health and Safety Acknowledgment Form provided with this addendum to the general plan. Any changes to the plan will be written in the plan and initialed by all potentially affected field personnel. The signed form and any initialed changes will become part of Ramboll's project file. A copy of the form will be provided to Teck American Incorporated (TAI).

This addendum may be modified at any time based on the judgment of the site safety officer in consultation with Ramboll's corporate health and safety officer and project manager or

designee. Any modification will be presented to the on-site team during a safety briefing and will be recorded in the field logbook.

1.1 ORGANIZATION

Task-specific safety procedures associated with soil sampling are presented in this addendum to the general SHSP. In addition, this addendum provides detailed field site and hospital location maps, air monitoring requirements, specific requirements for personal protective equipment (PPE), work zone definitions, and key emergency contact information.

The general SHSP (TCAI 2009) provides background site information and general health and safety provisions to protect workers from potential hazards during field activities. The information includes general safety guidelines for physical hazards, a chemical hazard evaluation, health and safety training requirements, general PPE requirements, emergency planning, general decontamination procedures, vehicle safety, and spill containment.

1.2 SCOPE OF WORK

The SATES field testing activities will be performed entirely on Colville tribal allotments (see Figure E-1).

1.3 DEFINITIONS

Contamination reduction zone:	Area between the exclusion and support zones that provides a transition between contaminated and clean zones
Exclusion zone:	Any area of the Site where hazardous substances are present, or are reasonably suspected to be present, and pose an exposure hazard to personnel
HAZWOPER:	Hazardous Waste Operations and Emergency Response standard, as described in 29 Code of Federal Regulations (CFR) Part 1910.120
OSHA:	Occupational Safety and Health Administration
Support zone:	Any area of the Site, so designated, that is outside the exclusion and contamination reduction zones
WISHA:	Washington Industrial Safety and Health Act, as described in Chapter 49.17 Revised Code of Washington

2 SAFETY GUIDELINES FOR PHYSICAL HAZARDS

Potential physical hazards posed by the proposed field test implementation and soil sampling activities include uneven walking surfaces, fallen trees, exposed tree roots, cold weather/hypothermia, hot weather/heat stress, material handling, heavy equipment operation, including the use of tractors, lifts, or other types of equipment, adverse weather conditions, working in remote areas. Table E-2-1 summarizes potential physical hazards that may be present during sediment sampling activities. TAI's

contractor and site personnel may identify additional potential hazards and proposed safety procedures applicable to the tasks they will be performing in the execution of the work plan for SATES field-scale soil treatment pilot testing and monitoring.

All work will be done using the buddy system.

Depending upon the time of year and the location of work, biting insects, wildlife encounters, or weather-related hazards may be experienced during any of the field activities proposed for the SATE field study.

Table E-2-1. Potential Physical Hazards and Proposed Safety Procedures

Potential Hazard	Yes	No	Proposed Safety Procedure
Slippery surfaces	X		Use caution; wear properly fitting shoes or boots with good gripping capacity; keep work area orderly.
Cold/hypothermia	X		Keep warm and dry, bring changes of clothes; do not work in extreme conditions without proper equipment and training; follow cold stress information (Attachment E-2); potential for cold/hypothermia will depend on season.
Heat stress	X		Drink water frequently in hot weather; take work breaks; follow the heat-related illness information (Attachment E-3); potential for heat stress will depend on season.
Material handling	X		Lift properly; seek assistance if necessary; do not overfill coolers or boxes.
Adverse weather	X		Seek shelter during storms; work in adverse weather conditions only with proper training, clothing, and equipment.
Work in remote areas	X		Use the buddy system; carry radio and/or cellular phone; bring sufficient equipment in case of accident or injury (first aid kit, shelter if appropriate).
Wildlife encounters	X		Wear snake chaps when in areas that snakes may be present and difficult to see, such as tall grass. Make noise and stay in groups to frighten away predators.
Biting insects	X		Use repellents, as needed.

3 CHEMICAL HAZARD EVALUATION

A chemical hazard evaluation is presented in the general SHSP (TCAI 2009) and incorporated herein by reference.

4 DISEASE MANAGEMENT

All contractors, field personnel, and visitors to the Site to conduct or observe field operations must be familiar with requirements and restrictions enacted by the State of Washington, local governments, and the Confederated Tribes of the Colville Reservation to reduce the risk of spreading pathogens, including viruses, bacterium, or other microorganism that can cause a disease outbreak. Importantly, this includes measures to prevent the spread of the novel coronavirus (COVID-19) and/or similar pathogens. TAI's contractor(s) will be required to include specific provisions to prevent the spread of pathogens while conducting work at the Site in a project-specific health and safety plan, and shall implement the same plan as guests of local accommodations, restaurants, shops, and other businesses in the local area during the execution of project-related field activities. The contractor's field personnel, TAI's staff and technical consultants, and visitors to the Site will be required to be familiar with the contractor's plan for disease management.

5 PERSONAL PROTECTIVE EQUIPMENT AND SAFETY EQUIPMENT

The following sections address the minimum personal protective equipment (PPE) and safety equipment required for completing the SATES field-scale testing implementation and monitoring (soil sampling) activities. Contractors may provide additional PPE, as needed, to respond to changing weather, disease management requirements, or smoke from seasonal wildfires that may occur in the region.

5.1 PERSONAL PROTECTIVE EQUIPMENT

Based on chemical and physical hazards associated with the soil sampling activities, Tables E-5-1 and E-5-2 identify the minimum PPE requirements for sampling.

Table E-5-1. Level of Protection Required for Site Activities

	Level of Protection	
Site Activity	Initial[a]	Contingency[b]
Soil sampling	MD	Leave Site, reassess situation
Sample handling	D	Leave Site, reassess situation

[a] See Table E-4-2 for definitions

[b] Based on unexpected change in Site conditions

Table E-5-2. Levels of Protection and Personal Protective Equipment

Protection Level	Required	Personal Protective Equipment
Level MD	X	Same as Level D with modification (M) of addition of rain gear, if necessary.
Level D	X	Long pants and shirt or work coveralls; safety glasses or goggles (as appropriate); and nitrile, neoprene, or Barrier® 5 layer laminate gloves (as appropriate). Hard hat and hearing protection as needed.

Is there potential for a respirator to be donned during field work? Yes _____ No X

5.2 SAFETY EQUIPMENT

The following safety equipment will be on site during the proposed field activities.

Air Monitoring (Check the items required for this project)

- ☐ Photoionization Detector
- ☐ Lower Explosive Limit/Oxygen meter
- ☐ Hydrogen sulfide meter
- ☐ Air sampling pumps
- ☐ Miniram aerosol monitor
- ☐ Radiation meter

☐ Detector pump and tubes ☐ Other _____

First Aid Kit (mandatory, including adhesive band-aids, gauze, tape, gloves, cardiopulmonary resuscitation shield, triangle bandage)

X	Emergency blanket	X	Sunscreen
X	Insect repellent	☐	Other _____

Other (Check the items required for this project)

X	Eyewash	☐	Fit test supplies
X	Drinking water	X	Fire extinguisher (boat)
☐	Stop watch for monitoring heart rate	☐	Windsock
☐	Thermoscan® thermometer (or equivalent) for heat stress monitoring	X	Cellular phone
		☐	Radio sets
X	Survival kit	X	Global positioning system
☐	Personal flotation device	X	Other: Satellite phone
☐	Cool vests		

6 AIR MONITORING

The principal chemicals of potential concern (COPCs) at the Site are metals/metalloids, and not volatile. There is a small chance for the COPCs to become airborne in dust form if the soil being sampled is dry; however, the chemical hazard evaluation presented in the general SHSP (TCAI 2009) concluded that, based on previous evaluations, the soil COPCs are not expected to pose a threat to field personnel during soil sampling activities. If windblown dust becomes problematic, field activities may be suspended. Tables E-5-1 and E-5-2 provide air monitoring requirements and action levels to be used during sampling activities.

Table E-6-1. Site-specific Air Monitoring Requirements

Monitoring Instrument	Calibration Frequency	Parameters of Interest	Monitoring Frequency
Visual	N/A	Dust	Continuous

Table E-6-2. Action Levels Established to Determine the Appropriate Level of Personal Protection

Instrument	Reading	Action	Comments
Visual	Visual Dust	Leave Site, if necessary	

7 EMERGENCY PLANNING

In case of any emergency affecting the Site, all affected personnel must immediately evacuate the work area and report to the Site safety officer at the following predetermined location:

DESIGNATED ASSEMBLY LOCATION: Field vehicle

In case of injury, field personnel should take precautions to protect the victim from further harm and notify local or facility emergency services. In remote areas, it will be necessary to have first aid-trained personnel on the field team. The victim may require decontamination prior to treatment—requirements will vary based on Site conditions.

Emergency medical care will be provided by:

- [X] Local emergency medical provider (i.e., fire department; see Table E-6-1 for local contact information)
- [X] Facility emergency medical provider
- [X] First aid-trained field staff (for remote areas only)

Table E-7-1. Local Emergency Telephone Numbers

Local Resources	Name	Telephone	Notified Prior to Work (Yes/No)?
Fire	Varies by location	911	Yes. Notify the E911 coordinator for Stevens County (Debby McCanna; 509-684-2555) of the schedule and location of work.
Police	Varies by location	911	Yes (see above)
Ambulance	Varies by location	911	Yes (see above)
Main Hospital	Mount Carmel Hospital, Colville, WA	(509) 684-2561	No
Alternative Hospitals	Coulee Community Hospital, Grand Coulee, WA	(509) 633-1753	No
	Ferry County Memorial Hospital, Republic, WA	(509) 775-3333	No
	Lincoln Hospital, Davenport, WA	(509) 725-7101	No
	St Joseph's Hospital, Chewelah, WA	(509) 935-8211	No
	Deer Park Hospital, Deer Park, WA	(509) 276-5061	No
	Deaconess Medical Center-Spokane, Spokane, WA	(509) 473-7178	No
	Holy Family Hospital, Spokane, WA	(509) 482-0111	No
	Sacred Heart Medical Center, Spokane, WA	(509) 474-3131	No
	Veterans Affairs Medical Center, Spokane, WA	(509) 434-7032	No
Site phone	Field cellular phone. Cellular phone coverage is spotty in the vicinity of the sampling areas. If cellular phone coverage is lost due to a mountain or hill, drive a little farther to get coverage. If cellular phone coverage is available, the 911 system will work. A	(503) 320-1796	NA

Local Resources	Name	Telephone	Notified Prior to Work (Yes/No)?
	satellite phone may be necessary for areas with limited cellular phone coverage.		
Directions to Mount Carmel Hospital (from Highway 395)	Begin traveling SE on Highway 395. Highway 395 becomes Main Street in Colville. Turn LEFT on E. Columbia Ave. Go 0.6 mile. Arrive at 982 E. Columbia Ave. Hospital is on right. (See detailed hospital location maps in Attachment E-1)		

In case of serious injuries, death, or other emergency, the TAI Project Coordinator and TAI Principal Investigator must be notified immediately. Contact numbers are listed in Table E-6-2.

Table E-7-2. Corporate Emergency Telephone Numbers

Corporate Resources	Name	Work/Cellular Telephone
TAI Project Coordinator	Kris McCaig	Work: (509) 623-4501 Cellular: (509) 434-8542
TAI Principal Investigator	Rosalind Schoof	Work: (206) 336-1653 Cellular: (206) 713-5449

Table E-7-3 provides local hospital contact and location information. See Attachment E-1 for a detailed hospital location map.

Table E-7-3. Project Area Hospital Information

Facility Name	Hours of Operation	Phone Number	Address	City
Coulee Community Hospital	24 hours/ emergency	509-633-1753	411 Fortuyn Road	Grand Coulee
Ferry County Memorial Hospital	24 hours/ emergency	509-775-3333	36 Klondike Road	Republic
Lincoln Hospital	24 hours/ emergency	509-725-7101	10 Nichols Street	Davenport
St Joseph's Hospital	24 hours/ emergency	509-935-8211	500 East Webster Street	Chewelah
Mount Carmel Hospital	24 hours/ emergency	509-684-2561	982 East Columbia Street	Colville
Deer Park Hospital	24 hours/ emergency	509-276-5061	East 1015 'D' Street	Deer Park
Deaconess Medical Center-Spokane	24 hours/ emergency	509-473-7178	West Fifth Avenue	Spokane
Holy Family Hospital	Dependent on case	509-482-0111	North 5633 Lidgerwood Avenue	Spokane
Sacred Heart Medical Center	24 hours/ emergency	509-474-3131	West 101 Eighth Avenue	Spokane

Facility Name	Hours of Operation	Phone Number	Address	City
Veterans Affairs Medical Center	7:30 am to 4:00 pm	509-434-7032	North 4815 Assembly Street	Spokane

In the event any health or safety issue arises, after the victim(s) receive appropriate medical treatment, the relevant field crew member(s) will be interviewed to formally document the incident by, at a minimum, the field supervisor and TAI Project Coordinator. All incidents will be reported as soon as reasonably possible and will be documented in the field logbook. If applicable, a corrective action record form will be filled out (see Appendix D of the work plan) so the circumstances leading to the incident can be considered and, if appropriate, integrated into future health and safety plan addenda.

8 WORK ZONES

The following work zones are defined for the SATES field-scale soil treatment testing work plan implementation, including the application of soil treatment amendments to designated SATES test plots and periodic sampling that will be conducted on those plots in accordance with the field-scale testing work plan (Ramboll 2020).

Exclusion zone. The area immediately around the sampling activities will be designated as the exclusion zone. Traffic cones and/or caution tape will be used to delineate the specific area(s).

Contamination reduction zone. Not applicable. All work plan activities will occur within the exclusion zone.

Support zone. Not applicable. All sampling activities will occur within the exclusion zone.

Controls to be used to prevent entry by unauthorized persons. Sampling staff will remain cognizant of people approaching the exclusion zone. All unauthorized persons will be instructed to remain outside of the sampling area.

9 DECONTAMINATION

The field team will decontaminate all sampling equipment that comes into contact with soil prior to the commencement of sampling at each location and upon completion of the study. This will include equipment such as trowels, mixing bowls, and utensils. The decontamination will consist of thoroughly rinsing all of the equipment with potable water, then with soap (i.e., Alconox®) and rinsed with potable water after each use.

Clean gloves will be worn at each sampling location to avoid transfer of potential contaminants among samples. Otherwise, decontamination procedures will follow those presented in the general SHSP (TCAI 2009) and are incorporated herein.

10 VEHICLE SAFETY, SPILL CONTAINMENT, AND SHIPPING INSTRUCTIONS

Vehicle safety, spill containment, and shipping instructions are presented in the general SHSP (TCAI 2009) and are incorporated herein.

11 TASK-SPECIFIC SAFETY PROCEDURES

Slips, trips, and falls are anticipated to be the greatest hazards to field personnel during the soil sampling event, as well as unexpected contact with the sampling equipment. Wear properly fitting shoes or boots with non-slip soles and good ankle support.

The Site is located in a remote region but typically has adequate cellular phone coverage. The field crews will coordinate departure and expected return times for all field activities with the field supervisor. Field crews will provide the field supervisor with status updates at least every 4 hours while performing field collection activities.

The areas that will be sampled are accessible to the public. Always be aware of your surroundings. Use the buddy system and keep in line-of-sight contact with other sampling personnel at all times. Do not leave samples or sampling equipment unattended. If you feel threatened, or if the situation feels unpredictable, leave the area immediately.

Always wear nitrile gloves and safety glasses or goggles when handling sampling equipment, samples, or preservative chemicals (if required). Keep a 1-L eye wash bottle accessible during all field work. If handling preservatives or sample containers with preservatives added, field personnel should avoid getting preservatives on their skin or clothes. If contact with skin or clothes occurs, immediately rinse the affected area with potable water and get medical attention, if warranted. If a preservative is splashed in the eye, flush the eye with the eye wash solution and get immediate medical attention.

12 REFERENCES

Ramboll. 2020. Soil Amendment Technology Evaluation Study Phase III & IV Work Plan: Test Plot Field-scale Implementation & Test Plot Monitoring. Prepared for Teck American Incorporated. Ramboll, Seattle, Washington.

TCAI. 2009. Upper Columbia River general site health and safety plan for the remedial investigation and feasibility study. Prepared for Teck American Incorporated. Integral Consulting Inc., Mercer Island, Washington, and Parametrix, Bellevue, WA.

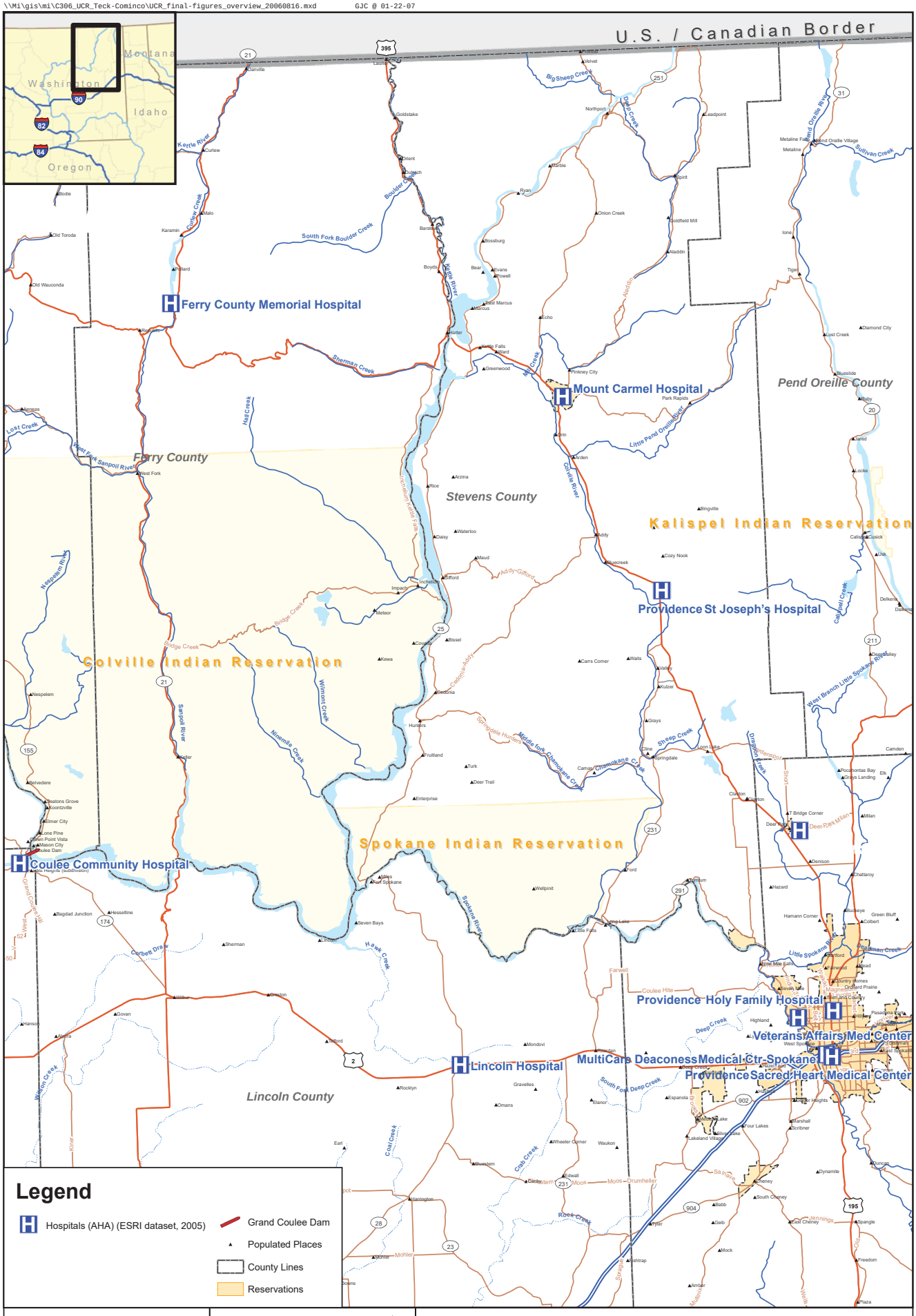
APPENDIX E-1

LOCATIONS OF SATES TEST PLOTS AND HOSPITAL LOCATION MAPS

RAMBOLL

Figure E-1
Location of Decision Units with SATES Test Plots
Upper Columbia River SATES Program

\\Mi\gis\mi\C306_UCR_Teck-Cominco\UCR_final-figures_overview_20060816.mxd GJC @ 01-22-07



ATTACHMENT E-2

COLD-STRESS FACT SHEET

FROSTBITE

What happens to the body:

Freezing in deep layers of skin and tissue; pale, waxy-white skin color; skin becomes hard and numb; usually affects fingers, hands, toes, feet, ears, and nose.

What to do: (land temperatures)

- Move the person to a warm, dry area. Don't leave the person alone.
- Remove wet or tight clothing that may cut off blood flow to the affected area.
- **Do not** rub the affected area because rubbing damaged the skin and tissue.
- Gently place the affected area in a warm water bath (105°) and monitor the water temperature to **slowly** warm the tissue. Don't pour warm water directly on the affected area because it will warm the tissue too fast, causing tissue damage. Warming takes 25-40 minutes.
- After the affected area has been warmed, it may become puffy and blister. The affected area may have a burning feeling or numbness. When normal feeling, movement, and skin color have returned, the affected area should be dried and wrapped to keep it warm. **Note:** If there is a chance the affected area may get cold again, do not warm the skin. If the skin is warmed and then becomes cold again, it will cause severe tissue damage.
- Seek medical attention as soon as possible.

How to Protect Workers

- Recognize the environmental and workplace conditions that lead to potential cold-induced illnesses and injuries.
- Learn the signs and symptoms of cold-induced illnesses/injuries and what to do to help the worker.
- Train workers about cold-induced illnesses and injuries.
- Select proper clothing for cold, wet, and windy conditions. Layer clothing to adjust to changing environmental temperatures. Wear a hat and gloves, in addition to underwear that will keep water away from the skin (polypropylene.)
- Take frequent short breaks in warm, dry shelters to allow the body to warm up.
- Perform work during the warmest part of the day.
- Avoid exhaustion or fatigue because energy is needed to keep muscles warm.
- Use the buddy system (work in pairs.)
- Drink warm, sweet beverages (sugar water, sports-type drinks.) **Avoid drinks with caffeine** (coffee, tea, or hot chocolate) **or alcohol**.
- Eat warm, high-calorie foods like hot pasta dishes.

Workers are at increased risk when…

- They have predisposing health conditions such as cardiovascular disease, diabetes, and hypertension.
- They take certain medications. Check with your doctor, nurse, or pharmacy and ask if medicines you take affect you while working in cold environments.
- They are in poor physical condition, have a poor diet, or are older.

HYPOTHERMIA - (Medical Emergency)

What happens to the body:

Normal body temperature (98.6°F/37°C) drops to or below 95°F/35°C; fatigue or drowsiness; uncontrolled shivering; cool, bluish skin; slurred speech; clumsy movements; irritable, irrational, or confused behavior.

What to do: (land temperatures)

- Call for emergency help (i.e., ambulance or 911).
- Move the person to a warm, dry area. Don't leave the person alone.
- Remove wet clothing and replace with warm, dry clothing or wrap the person in blankets.
- Have the person drink warm, sweet drinks (sugar water or sports-type drinks) if he is alert. **Avoid drinks with caffeine** (coffee, tea, or hot chocolate) **or alcohol**.
- Have the person move his arms and legs to create muscle heat. If he is unable to do this, place warm bottles or hot packs in the armpits, groin, neck, and head areas. **Do not** rub the person's body or place him in a warm water bath. This may stop his heart.

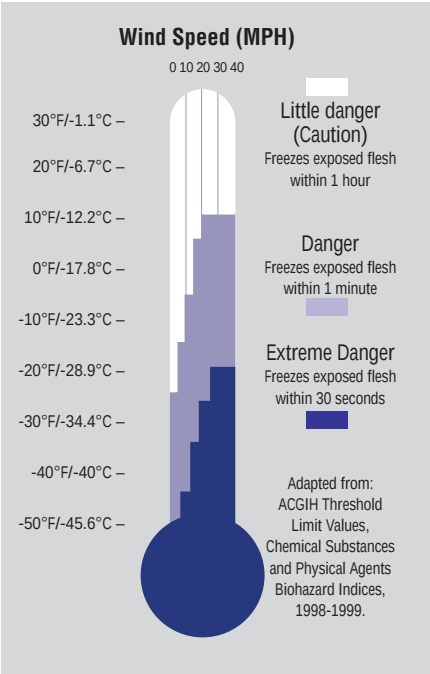
What to do: (water temperatures)

- Call for emergency help (i.e., ambulance or 911). Body heat is lost up to 25 times faster in water.
- **Do not** remove any clothing. Button, buckle, zip, and tighten any collars, cuffs, shoes, and hoods because the layer of trapped water closest to the body provides a layer of insulation that slows the loss of heat. Keep the head out of the water and put on a hat or hood.
- Get out of the water as quickly as possible or climb on anything floating. **Do not** attempt to swim unless a floating object or another person can be reached because swimming or other physical activity uses body heat and reduces survival time by about 50 percent.
- If getting out of the water is not possible, wait quietly and conserve body heat by folding arms across the chest, keeping thighs together, bending knees, and crossing ankles. If another person is in the water, huddle together with chests held closely.

THE COLD STRESS EQUATION

LOW TEMPERATURE + WIND SPEED + WETNESS = INJURIES & ILLNESS

When the body is unable to warm itself, serious cold-related illnesses and injuries may occur, and permanent tissue damage and death may result. **Hypothermia** can occur when *land temperatures* are **above** freezing or *water temperatures* are below 98.6°F/37°C. Cold-related illnesses can slowly overcome a person who has been chilled by low temperatures, brisk winds, or wet clothing.



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ATTACHMENT E-3

HEAT-RELATED ILLNESS FACT SHEET

HEAT EXHAUSTION

What happens to the body:

Headaches, dizziness, or light-headedness, weakness, mood changes, irritability or confusion, feeling sick to your stomach, vomiting, fainting, decreased and dark-colored urine, and pale, clammy skin.

What should be done:

- Move the person to a cool shaded area. Don't leave the person alone. If the person is dizzy or light-headed, lay him on his back and raise his legs about 6-8 inches. If the person is sick to his stomach, lay him on his side.
- Loosen and remove heavy clothing.
- Have the person drink some cool water (a small cup every 15 minutes) if he is not feeling sick to his stomach.
- Try to cool the person by fanning him. Cool the skin with a cool spray mist of water or wet cloth.
- If the person does not feel better in a few minutes call for emergency help (ambulance or call 911.)

(If heat exhaustion is not treated, the illness may advance to heat stroke.)

HEAT STROKE - A Medical Emergency

What happens to the body:

Dry, pale skin (no sweating); hot red skin (looks like a sunburn); mood changes; irritability, confusion, and not making any sense; seizures or fits, and collapse (will not respond).

What should be done:

- Call for emergency help (i.e., ambulance or 911.)
- Move the person to a cool, shaded area. Don't leave the person alone. Lay him on his back and if the person is having seizures, remove objects close to him so he won't hit them. If the person is sick to his stomach, lay him on his side.
- Remove heavy and outer clothing.
- Have the person drink some cool water (a small cup every 15 minutes) if he is alert enough to drink anything and not feeling sick to his stomach.
- Try to cool the person by fanning him or her. Cool the skin with a cool spray mist of water, wet cloth, or wet sheet.
- If ice is available, place ice packs in armpits and groin area.

How to Protect Workers

- Learn the signs and symptoms of heat-induced illnesses and what to do to help the worker.
- Train workers about heat-induced illnesses.
- Perform the heaviest work during the coolest part of the day.
- Slowly build up tolerance to the heat and the work activity (usually takes up to 2 weeks.)
- Use the buddy system (work in pairs.)
- Drink plenty of cool water (one small cup every 15-20 minutes.)
- Wear light, loose-fitting, breathable (like cotton) clothing.
- Take frequent short breaks in cool, shaded areas (allow your body to cool down.)
- Avoid eating large meals before working in hot environments.
- Avoid caffeine and alcoholic beverages (these beverages make the body lose water and increase the risk of heat illnesses.)

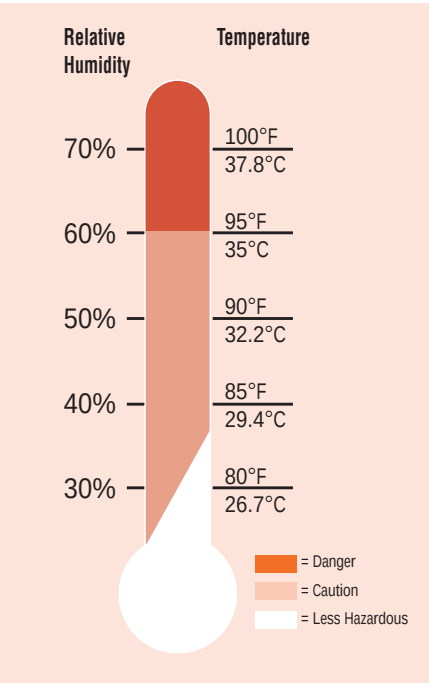
Workers are at increased risk when…

- They take certain medications. Check with your doctor, nurse, or pharmacy to see if medicines you take affect you when working in hot environments.
- They have had a heat-induced illness in the past.
- They wear personal protective equipment.

THE HEAT EQUATION

HIGH TEMPERATURE + HIGH HUMIDITY + PHYSICAL WORK = HEAT ILLNESS

When the body is unable to cool itself through sweating, **serious** heat illnesses may occur. The most severe heat-induced illnesses are **heat exhaustion** and **heat stroke**. If actions are not taken to treat heat exhaustion, the illness could progress to heat stroke and **death**.



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APPENDIX F

WORK PLAN FOR THE SOIL AMENDMENT TECHNOLOGY EVALUATION STUDY PHASE I: TEST PLOT CHARACTERIZATION AND INITIAL AMENDMENT ALTERNATIVES EVALUATION