UPPER COLUMBIA RIVER

FINAL
Soil Amendment Technology Evaluation Study Phase II: Bench-Scale Treatability Testing Work Plan

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May, 2019

TITLE AND APPROVAL SHEET

SOIL AMENDMENT TECHNOLOGY EVALUATION STUDY
PHASE II: BENCH-SCALE TREATABILITY STUDY WORK PLAN

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ACRONYMS AND ABBREVIATIONS

ANOVA	analysis of variance
C0	Cochran's test statistic
CCT	Confederated Tribes of the Colville Reservation
DQO	data quality objective
DU	decision unit
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
IVBA	*in vitro* bioaccessibility
MAP	monoammonium phosphate
NRMRL QMP	National Risk Management Research Laboratory Quality Management Plan
OSU	Ohio State University
P_{sat}	phosphorus saturation
QA	quality assurance
QC	quality control
RI/FS	remedial investigation and feasibility study
RPD	relative percent difference
SATES	Soil Amendment Technology Evaluation Study
SOP	standard operating procedure
SPLP	synthetic precipitation leaching procedure
t	time point
TAI	Teck American Incorporated
TAL	target analyte list
TSP	triple super phosphate
UCR	Upper Columbia River
WTR	water treatment residual(s)
XRF	x-ray fluorescence

UNITS OF MEASURE

ft	foot or feet
gal	gallon(s)
g	gram(s)
g/kg	gram(s) per kilogram
in.	inch(es)
kg	kilogram(s)
kg/ha/yr	kilogram(s) per hectare per year
kg/ha	kilogram(s) per hectare
mil	one thousandth of an inch (0.001 in.)
μm	micrometer(s)
mg/kg	milligram(s) per kilogram
mm	millimeter(s)
mol/kg	mole(s) per kilogram
lb	pound(s)
tons/ac	dry U.S. tons per acre

1 INTRODUCTION

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 part of the ongoing UCR remedial investigation and feasibility study 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 background, purpose, and description of SATES and the participants 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.

Phase II will involve a series of laboratory bench-scale treatability tests designed to evaluate soil amendment options. The work plan for the Phase II bench-scale treatability study is presented two parts: 1) the EPA-approved soil sample collection work plan (Ramboll 2018b) and 2) the bench-scale testing work plan described in this document.

[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.

The objectives of the Phase II bench-scale treatability study are to: 1) evaluate whether soil amendments show potential to reduce the bioaccessibility of lead in Site soils; 2) evaluate the impact of amendments on key soil chemical and physical properties; and 3) develop data that can be used to reduce uncertainty about selection of amendment technologies for application in Phase III. Soil amendments to be evaluated in the Phase II bench-scale treatability study are soluble phosphate, biosolids, wood ash, biochar, and compost (Ramboll 2018a). The results will be used to identify the soil amendment options that most effectively meet the SATES data quality objectives (DQOs) and select which amendment technologies to carry forward for further evaluation in Phases III and IV – the field-scale pilot implementation and test plot monitoring.

Field testing of the selected soil treatment or treatments will occur within decision units (DUs) 258, 401, and 441 (see Map 4-1), located on Confederated Tribes of the Colville Reservation (CCT) tribal allotments characterized during the 2014 residential soil sampling study (CH2M HILL 2016). Six test plots within these DUs were selected for initial soil screening (SATES Phase IA Part 1) and, based on the screening results, four test plots (258-3, 401-1, 401-2, and 441-1) were selected for more detailed baseline soil characterization (SATES Phase IA Part 2), consistent with the Phase I Work Plan (Ramboll 2017a).

This Phase II work plan is organized into ten sections:

- Section 1 – Introduction
- Section 2 – Soil collection and processing
- Section 3 – Amendment prescreening and selection
- Section 4 – Amendment rate rationale
- Section 5 – Bench-scale testing design
- Section 6 – Monitoring and analysis program
- Section 7 – Data evaluation and interpretation
- Section 8 – Quality assurance and quality control
- Section 9 – Data verification and validation
- Section 10 – References.

2 SOIL COLLECTION AND PROCESSING

2.1 SOIL COLLECTION

The bulk soil sampling for Phase II bench-scale testing was performed in accordance with the EPA-approved Phase II soil collection work plan (Ramboll 2018b). Note that the soil samples were collected from the buffer areas in the test plot that will not be sampled as part of the as part of Phase IV test plot monitoring. The sampling strategy that preserves the integrity of the soil sampling conditions as part of Phase IV is discussed in the Phase I Work Plan (Ramboll 2018).

The soil samples were collected from test plot 401-2 (Map 1-1) on October 18, 2018, and the samples were received at The Ohio State University (OSU) on October 23, 2018. The objective was to collect soil that is representative of test plot conditions for the laboratory bench-scale treatability tests. With a mean soil lead concentration greater than 500 mg/kg, test plot 401-2 was selected to supply the soils for bench-scale testing (see Map 2-1). Following approval from the landowner's representative (CCT) and EPA, 16 soil samples were collected from the 4-foot (ft) buffer zones inside test plot 401-2, between the treatment sub-plots. Samples were collected from beneath vegetation and surface debris (e.g., undecomposed vegetation litter and surficial rocks) over a 2-by 2-ft area to a depth of 3 in. below the surficial debris. Final sample locations were selected in the field using a hand-held x-ray fluorescence (XRF) meter to ensure that lead screening concentrations met study criteria. XRF readings were taken from the surface (after clearing vegetation and surface debris) and approximately 1 in. below that.

Soil from each sample location was placed into three separate 5-gallon (gal) polyethylene buckets lined with two 3-mil (0.003 in.) thick food-grade plastic bags. A total of 48 buckets of soil were collected, with approximately 2.5 gal of soil in each bucket. The buckets were delivered by the field sampling team to Anatek Labs in Spokane, Washington. Anatek Labs then shipped the buckets to OSU.

2.2 SOIL PROCESSING PROCEDURE

The OSU laboratory processed the soil collected for the Phase II bench testing in accordance with the procedures described in the following subsections.

2.2.1 Lead Screening

Lead screening was conducted on the soil in each bucket to verify that, once combined into a single composite sample, the soil for the bench testing would have elevated lead concentrations. Soil in each bucket was homogenized by mixing in a 50-gal drum cement mixer, and the mixed soil was

screened for total lead concentration using an XRF unit, following the procedure described in Standard Operating Procedure 1 (SOP 1) (see Appendix A). If the homogenized soil in a bucket had a lead concentration less than 800 mg/kg, that soil was not used in the composite soil sample for the laboratory bench tests. Based on the screening results, soil in three buckets (bucket numbers 17, 33, and 41) was not used. The XRF screening results are summarized in Table 2-1 and may be obtained from the secure UCR web tool, accessible to registered users at: http://teck-ucr.exponent.com.

Note duplicate samples were not collected during the lead screening, which is a deviation from the procedure outlined in SOP 1. The impact of this deviation on project quality control is negligible.

2.2.2 Soil Homogenization

To create the composite soil sample for the bench-scale treatability tests, soil from buckets with lead concentrations greater than 800 mg/kg was combined and homogenized in an approximately 200-gal cement mixer for 2 hours. It was then sieved, consistent with SOP 2 (adapted from McClure [2001]) (Appendix A), to develop a sample grain size fraction less than 2 mm in diameter.

The homogenized soil was divided equally into 16 containers. Eight containers were randomly selected by numbering the 16 containers then using an Excel formula to generate eight random numbers from 1 to 16 for the container selection. Three soil samples were collected from the top, middle, and bottom of soil in each of the 8 containers, resulting in 24 soil sub-samples. The soil sub-samples were analyzed for total lead using an XRF unit as described in SOP 1 (Appendix A), and the range of lead concentrations measured in individual containers and among the 8 containers was evaluated statistically.[2] The results of the XRF screening of the post-homogenization soils are included in Appendix B (Table B-1 and B-2), along with the laboratory quality control data (Table B-3 and B-4). There was no statistical difference in total lead concentrations at a probability level less than 0.1 ($P < 0.1$), indicating that the lead in the soils was uniformly distributed in and among the containers, and therefore deemed to be representative of a single homogeneous sample suitable for use in the bench-scale treatability tests.

[2] Variance within each container was evaluated using Cochran's test statistic (C0). This analysis divides the largest variance between samples in the same container by the sum of all variances within each container. The soil is deemed homogenous in the containers if the test statistic (C0) is not significant at a 95 percent probability level, which is determined with (n-1) degrees of freedom, where n is three (i.e., the number of sub-samples for a single container). Variance between containers is evaluated using a one-way analysis of variance (ANOVA) with a calculated probability of $P < 0.01$. An ANOVA compares the means between groups and determines whether any of those means are statistically significantly different from each other.

After processing, 430 lb of soil with grain sizes < 2 mm was available for use in the bench tests.

3 AMENDMENT PRESCREENING AND SELECTION

3.1 SOIL AMENDMENT REVIEW

Candidate soil amendments were selected for potential evaluation in the bench-scale testing based on their properties and test plot soil characteristics from Phase IA, as described in the Phase IB amendment screening and design memorandum dated January 11, 2019 (Ramboll 2018a).[3] The soil amendment technology options selected for evaluation in Phase II (candidate amendments) and the rationale for selecting these amendments are summarized below.

3.1.1 Soluble Phosphate

Phosphorus is the most extensively studied proposed amendment with proven efficacy to reduce lead bioaccessibility. A clear link between lead pyromorphite formation and bioaccessibility reduction has been demonstrated in several studies (Scheckel et al. 2013), and reductions in bioaccessibility associated with chloropyromorphite formation are considered to be permanent unless extreme changes in soil conditions occur. Chloropyromorphite is the least bioaccessible and most stable form of lead pyromorphite; it is considered to be a permanent, stable form unless extreme changes in soil conditions occur (Basta et al. 2016).

For the bench testing, soluble phosphate will be applied using a phosphate-based fertilizer product that contains phosphorus as either monoammonium phosphate (MAP), triple super phosphate (TSP) or both. For each case where soluble phosphate is applied, potassium chloride fertilizer will be added as an adjunct amendment to the phosphorus. The presence of potassium chloride can promote the formation of chloropyromorphite (N. L. Basta personal communication 2019).

The soluble phosphate is also expected to nourish vegetative growth in a manner that could reduce the potential for human exposure to lead-impacted soil by acting as a barrier to prevent direct contact with surface soil.

3.1.2 Biosolids

High-iron biosolids have been shown to reduce lead bioaccessibility (Brown et al. 2012) in association with lead sorption to iron oxide and manganese oxide surfaces, and through pyromorphite formation related to phosphorus content. The relatively high organic carbon content

[3] The Phase IA Data Summary Report (Ramboll 2019) presents a detailed discussion of the Phase IA test plot screening and characterization procedures and results.

in biosolids may also reduce lead bioaccessibility by sorption of lead through chelation. Biosolids are also expected to nourish vegetative growth in a manner that could reduce the potential for human exposure to lead-impacted soil, again by reducing the potential for direct contact with surface soil.

3.1.3 Wood Ash

Wood ash has not been thoroughly tested for its ability to reduce lead bioaccessibility; however, it often contains phosphorus, which may play a role in pyromorphite formation. Additionally, the presence of iron and manganese may reduce lead bioaccessibility through lead sorption. Wood ash commonly contains chloride, which would promote reduction of lead bioaccessibility by contributing to the formation of chloropyromorphite. Wood ash may also nourish vegetative growth in a manner that could reduce the potential for human exposure to lead-impacted soils.

3.1.4 Biochar

Similar to wood ash, biochar has not been thoroughly tested for its ability to reduce lead bioaccessibility; however, it has the advantage of being a tailored product so that a specific variety could be developed to reduce lead bioaccessibility in soil. The relatively high organic carbon content of biochar may reduce lead bioaccessibility by sorption of lead through chelation. Biochar may provide nutrients and improve soil conditions, which could increase vegetative growth in a manner that could reduce the potential for human exposure to lead-impacted soil.

3.1.5 Compost

Composts are a good source of organic matter and soil nutrients, and they can contain significant levels of phosphorus. The relatively high organic carbon content in compost may also reduce lead bioaccessibility by sorption of lead through chelation. Compost with reactive forms of iron and manganese may also reduce lead bioaccessibility through lead sorption. Compost is expected to nourish vegetative growth in a manner that could reduce the potential for human exposure to lead-impacted soil.

3.1.6 Combined and Secondary Amendments

Each of the amendments described above may be used in combination with another amendment to enhance the efficacy for reducing lead bioaccessibility in soil. Several combinations, such as a mixture of soluble phosphate and biosolids, have been shown to be very effective in reducing lead bioaccessibility (Brown et al. 2007; Obrycki et al. 2017a; Sieblec et al. 2013). As discussed in Section 3.1.1, potassium chloride will be combined with soluble phosphate in the bench-scale treatability tests.

Aluminum-based water treatment residual (WTR), also referred to as alum-based WTR material has been considered as a potential secondary amendment because of the potential for reactive aluminum in the material to sorb lead and thereby reduce lead bioavailability in soil. A sample of alum-based WTR was evaluated as part of the amendment prescreening, as described below.

3.2 AMENDMENT PRESCREENING

Laboratory prescreening was conducted on samples of each candidate amendment to preliminarily assess their composition and effectiveness in reducing lead bioaccessibility in lead-contaminated soil. Properties of these amendments important for preserving or enhancing soil quality and reducing lead bioaccessibility were also evaluated, including total carbon, total nitrogen, select toxic metals, and reactive iron and aluminum oxide determined by acid ammonium oxalate.

The prescreening results and publicly-available performance data from other studies (Brown et al. 2007; Obrycki et al. 2017a; Sieblec et al. 2013) were used to identify the amendment alternatives (individual and combined) for further evaluation in Phase II. The prescreening criteria and methods used, the results, and the amendment combinations selected for the bench tests are described below.

3.2.1 Soil Amendment Prescreening Analyses and Methods

To aid the design of the bench-scale tests and selection of soil amendments, samples of the amendments identified in Section 3.1 were obtained and analyzed for the following parameters using methods summarized in the referenced SOPs, provided in Appendix A:

- Lead sorption capability (see SOP 3)
- Total lead, arsenic, zinc, cadmium, copper, and nickel by XRF (see SOP 1)
- Total carbon and nitrogen (see SOP 4)
- Oxalate-extractable aluminum, iron, manganese, and phosphorus (see SOP 5)
- Phosphorus saturation (P_{sat}) (calculated to evaluate the amount of phosphorus available to react with lead, which may indicate a good candidate for remediation via pyromorphite formation)[4]

[4] For materials with P_{sat} less than 25 percent, the phosphorus is not likely to be available to react with lead or result in pyromorphite formation. For the purposes of this bench-scale testing, calculations of available phosphorus assume a 25% inefficiency rate.

- Available phosphorus (the sum of the soluble phosphorus and easily released phosphorus from the amendment that is available to react with lead in soil).

The methods used for these analyses are summarized in Tables 3-1a and 3-1b.

The lead sorption test method, provided in Appendix C, was developed by EPA Research Soil Scientist Dr. Mark Johnson and used by the OSU soil laboratory team for amendment prescreening. The method evaluates amendment sorption potential and the reversibility of lead sorption. To evaluate sorption potential, the method involves combining a synthetic precipitation leaching procedure (SPLP) extract (from test plot soil with a known lead concentration) with a small amount of the amendment material being analyzed. The lead concentration remaining in the solution after the extract is mixed with the amendment is measured to determine the lead reduction potential of the material. To evaluate the reversibility of lead sorption, the amended extract is challenged with calcium chloride ($CaCl_2$) to determine if the lead sorbed to the amendment is weakly bound.[5] The lead sorption test method was used in advance of the bench tests to screen and rank materials for the potential to reduce soluble lead in Site soils.[6] The percent reduction of soluble lead is calculated as follows:

$$Pb\ reduction = 100\ x\ \frac{soil\ SPLP\ [Pb] - amended\ soil\ SPLP\ [Pb]}{soil\ SPLP\ [Pb]}$$

Where:

soil SPLP [Pb]	=	lead concentration in SPLP extract from test plot soil
amended soil SPLP [Pb]	=	residual lead concentration in extract after adding amendment material
Pb reduction	=	reduction in lead concentration, percent

Total metals, 0.2 molar acid ammonium oxalate at pH 3.0-extracted metals, and total carbon and nitrogen were obtained using the following analysis methods, respectively: EPA Method 6010 (USEPA 2007a), McKeague and Day (1966), and Nelson and Sommers (1996) (see SOPs 10, 4, and 5 in Appendix A).

The P_{sat} values are calculated as follows:

$$\text{Psat} = 100\ x\ \left(\frac{oxalate\ [P]}{oxalate\ [Al] + oxalate\ [Fe] + oxalate\ [Mn]}\right)$$

[5] Prescreening results of the amendment extraction with 0.01 molar $CaCl_2$ solution were below analytical instrument detection limits, and thus, are not included in the percent lead reduction.

[6] The percent reduction in soluble lead in the prescreening tests will likely be much higher than bioaccessible lead reductions tested with gastric fluid extraction standards.

Where:

oxalate [P]	=	phosphorus concentration extracted by oxalate extraction, moles per kilogram (mol/kg)
oxalate [Al]	=	aluminum concentration extracted by oxalate extraction, mol/kg
oxalate [Fe]	=	iron concentration extracted by oxalate extraction, mol/kg
oxalate [Mn]	=	manganese concentration extracted by oxalate extraction, mol/kg
P_{sat}	=	phosphorus saturation

Available phosphorus is calculated as follows:

$$\text{Available P} = oxalate\ [P] - \left\{[0.25 \times (oxalate\ [Fe] + oxalate[Al] + oxalate[Mn])] \times 30.97_{g\ P/mol}\right\}$$

Where:

Available P	=	available phosphorus, g/kg
P	=	phosphorus concentration extracted by oxalate extraction, g/kg
Fe	=	iron concentration extracted by oxalate extraction, mol/kg
Al	=	aluminum concentration extracted by oxalate extraction, mol/kg
Mn	=	manganese concentration extracted by oxalate extraction, mol/kg
30.97	=	molar conversion factor based on atomic mass of phosphorus, grams phosphorus per mole (g P/mol)

3.2.2 Soil Amendment Prescreening Results

The soil prescreening results are summarized in Tables 3-1a through 3-1b. Notable results are summarized below. Phosphorus, P_{sat}, and oxalate-extractable metals analyses provided the most useful information relating to the expected treatment efficacy.

Soluble Phosphate

A commercially available general purpose fertilizer (16-16-16 blend) was used for the prescreening evaluation. The available phosphorus content of the tested fertilizer was 77.5 g/kg, which was within the range of expected concentrations. The phosphorus in this brand was MAP, according to the product label. This fertilizer also contained cadmium at a concentration of 54.7 mg/kg which could limit the amount of fertilizer application in our study. The fertilizer rule in the state of Washington is based on limiting cadmium application to 0.089 kg/ha/yr for 45 years. The maximum cumulative addition of cadmium is 4 kg/ha based on Canadian Food Inspection Agency international trade standards (CFIA, 1993). Alternative phosphorus fertilizers locally available to the UCR area will be identified and analyzed for metals prior to use in bench-scale testing; only

those with lower heavy metals concentrations will be used. The fertilizers that may be used in the bench tests have not yet been determined.

Based on the results of the lead sorption test, the soluble phosphate application demonstrated one of the largest reductions in soluble lead (greater than 97 percent reduction in soluble lead). This reduction was likely due to lead pyromorphite formation using available phosphorus.

Biosolids

The biosolids used for the prescreening were obtained from a municipal wastewater treatment facility. (The public entity that is supplying the biosolids for the bench tests requested that the source information remain confidential.) The biosolids sample contained a relatively high concentration of iron (28 g/kg) as well as 18 g/kg of available phosphorus. The lead sorption test on this sample resulted in a 93 percent reduction in soluble lead, demonstrating the potential to reduce lead bioaccessibility in Site soils. The reductions in soluble lead were likely due to a combination of phosphorus potentially available for reaction with lead, iron and/or manganese present in a form that may provide lead sorption as a potential binding mechanism, and a total carbon content (36.8 percent) at a level where the carbon may adsorb lead through surface chelation.

Wood Ash

The wood ash used for the prescreening was obtained from Avista's Kettle Falls Biomass Generating Station, in Kettle Falls, Washington, where wood ash is a byproduct of biomass-based power generation. The wood ash sample contained a moderate amount of phosphorus (4.5 g/kg), with 0.82 g/kg potentially available to react with lead, which is relatively low. The wood ash also contained the highest reactive manganese content of the amendments tested. Reactive manganese has the potential to tightly bind to lead in a manner that reduces lead bioaccessibility. The lead sorption test results produced one of the largest reductions in lead bioaccessibility among the tested amendments (greater than 97 percent reduction of soluble lead), which could be the result of reactivity with both the reactive phosphorus and manganese fractions.

Biochar

The biochar that was prescreened is a locally-available commercial product called Black Owl Environmental Ultra. This product has a low phosphorus content (0.558 g/kg), with 0.354 g/kg potentially available phosphorus to react with lead. This biochar showed 100 percent reduction of soluble lead in the sorption test, which is likely the result of lead adsorption onto organic surfaces of the biochar or chelation with organic carbon.

Compost

The compost material selected for the prescreening evaluation is a commercially available, compost-based potting soil product (G&B Organics Potting Soil). The tested compost had low to moderate phosphorus content (1.4 g/kg), with 0.95 g/kg potentially available phosphorus to react with lead. The material tested had a P_{sat} value of 74 percent, and it demonstrated a 95 percent reduction of soluble lead in the sorption test. The soluble lead reduction was likely due to a combination of phosphorus potentially available for reaction with lead and a sufficiently high total carbon content (35.2 percent) where the carbon may adsorb lead through surface chelation.

Water Treatment Residuals

The WTR used for the prescreening was obtained from a municipal water treatment facility. The WTR had essentially no potentially available phosphorus for treatment due to a low phosphorus content and high aluminum content. The lead sorption test results indicated that WTR yielded a 79 percent reduction of soluble lead and therefore showed the lowest potential to reduce lead bioaccessibility. Notably, when compared to other proposed amendments, the WTR contains fewer ions (phosphorus, iron, and manganese) necessary to reduce lead bioaccessibility in soil.

3.3 AMENDMENT SELECTION FOR BENCH-SCALE TESTING

Bench testing will be conducted with both individual amendments and combinations of two amendments. Individual amendments will be selected based on their potential to reduce lead bioaccessibility and to promote vegetative growth. Amendment combinations will be selected based on these same criteria and on the expected potential for the combinations to mitigate possible undesirable effects of applications of single amendments (e.g., addition of biosolids to reduce the potential for arsenic mobilization that could result from phosphate application).

Based on the results of test plot field characterization (Ramboll 2018a, 2019), available amendment performance data from other studies, and the results of the amendment prescreening analyses, a total of 12 amendments have been selected for bench-scale testing as follows:

Individual Amendments

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

Combination Amendments

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

- Biochar + compost

The rationale for selection of these amendments is summarized in Tables 3-2. The combination amendments identified will allow for the evaluation of more than one potential lead binding mechanism and the potential for augmenting soil quality to foster plant growth. For example, a combination of soluble phosphate and biosolids will allow evaluation of the potentially compounding effect of lead pyromorphite formation from the soluble phosphate and lead sorption effects from iron in the biosolids.

WTR was eliminated from consideration as an individual or secondary amendment for bench testing because the material performed the poorest in the lead sorption test compared with the other amendments. In addition, this material is composed primarily of aluminum and is unlikely to benefit soil quality in a manner that would boost plant growth.

4 AMENDMENT APPLICATION RATES

The bench-scale testing will include evaluation of two volumetric application rates for each amendment: a low rate and a high rate. This section summarizes the rationale for the two application rates that will be considered for each amendment in the development of the bench test design described in Section 5.

The selected application rates and an estimate of the amounts of amendment needed for each experimental unit (a prepared pot) to be tested are summarized in Tables 4-1 respectively. The rates are based on the use of 400 g of homogenized soil per pot. Based on the bulk density assumptions (see Table 4-1) and the study design presented in this work plan, the estimated minimum quantities of amendments and accessory application materials needed for soil treatability testing are as follows: 1 kg of MAP or 0.7 kg of TSP, 0.5 kg of potassium chloride fertilizer (0-0-60), 60 kg of biosolids, 1.5 kg of wood ash, 60 kg of compost, and 5 kg of biochar. Additional details are discussed in the following sections.

4.1 SOLUBLE PHOSPHATE

The primary mechanism for reducing lead bioaccessibility by using soluble phosphorus is pyromorphite formation. Chloropyromorphite, $Pb_5(PO_4)_3Cl$, has a lead-to-phosphorus molar ratio of 5:3. Based on the XRF results for the soil collected for bench testing (Table 2-1) and the phosphorus content in phosphorus fertilizers (MAP and TSP), molar ratios of applied phosphorus can be calculated. While only 150 mg/kg of phosphorus in soil is required to satisfy the stoichiometric conversion of 1,500 mg/kg of lead in soil to pyromorphite, studies show that a large molar excess of phosphorus is needed to ensure the reaction that creates pyromorphite occurs (Basta and McGowen 2004; Obrycki et al. 2017b). As a result, the low application rate of phosphorus (0.75 g of phosphorus per kg of soil) is 5 times the molar balance of phosphorus needed for pyromorphite formation, assuming a baseline lead concentration of 1,500 mg/kg in soil. The high application rate of 2.25 g of phosphorus per kilogram of soil is 15 times the phosphorus mass needed for pyromorphite formation.

Previous studies have shown that concentrations higher than 10 g of phosphorus per kg of soil can result in saline soil that inhibits plant growth (Brown et al. 2007), and there is a greater risk that bioaccessible arsenic concentrations will increase as the application rate of phosphorus increases (Scheckel et al. 2009).

Previous research shows additional chloride may be necessary to add to soil to form chloropyromorphite. Because chloride is highly mobile and easily leached out of soil, potassium chloride will be added to each soluble phosphate application to ensure a source of chloride is

present. Potassium chloride is readily available as a commercial fertilizer. The fertilizer analysis for potassium chloride, or the nitrogen-phosphorus-potassium percent content (N-P-K), is 0-0-60 (i.e., 60 percent as potassium oxide [K_2O]). The bench testing application will include a 2:1 chloride-to-lead molar ratio application rate to promote formation of chloropyromorphite.

The final phosphorus application rates will be determined as follows: site soil (100 g) will be treated with phosphorous amendment (using five application rates: 0.30, 0.75, 1.50, 2.25, and 5.0 g phosphorus per kilogram of soil) and incubated for two weeks under temperature and moisture conditions described in Section 5.3 below. Treated soil will be analyzed for bioaccessible lead (Method 1340 at pH 2.5) and soluble phosphorus (0.01 molar calcium chloride [$CaCl_2$] extraction). Bioaccessible lead and soluble phosphorus results will be plotted against the phosphorous amendment application rate, as described in Osborne et al. (2015). All treatments will be performed with four replications. The optimum low and high phosphorus application rates for the Phase II bench-scale testing will be those that effectively reduce bioaccessible lead with minimal mobilization of soluble phosphorus from the treated soil.

4.2 BIOSOLIDS

The reductions in bioaccessibility expected for biosolid amendments are associated with lead sorption to iron oxide surfaces and/or pyromorphite formation with available phosphorus, and lead chelation may also occur because of the high organic carbon content. The main consideration for establishing the bench test application rates was practical application volumes. It is anticipated that applications greater than approximately ¼-in. thickness to the soil surface would be impractical over large areas of the field test plots, but applications of ¼-in. thickness or less may not provide sufficient material to reduce lead bioaccessibility. As a result, a ¼-in. thickness was chosen as the low rate, and a 1-in. thickness was selected as the high rate. These rates translate to approximately 22 dry tons per acre (tons/ac) and 89 tons/ac for the low and high rates, respectively. Although the lower rate may not provide sufficient material to maximize reductions in lead bioaccessibility, it is expected to result in appropriate nutrient provision to promote robust plant growth. The high rate was selected based on the projected volume of material necessary to optimize lead bioaccessibility reduction.

4.3 WOOD ASH

The wood ash tested in the prescreening evaluation had a relatively low amount of potentially available phosphorus and did contain a significant amount of reactive manganese that is likely available for lead sorption. The low application rate for wood ash was established at 10 g/kg of soil (1 percent by weight or 5 tons/ac, based on the lowest volumetric amount of the amendment

that is expected to effectively reduce lead bioaccessibility. The high application rate was established at 30 g/kg of soil (3 percent by weight or 15 tons/ac, which is the maximum amount that could be applied without the potential for increasing soil salinity and pH to levels that could limit the growth of existing vegetation.

4.4 BIOCHAR

The reductions in bioaccessibility expected for biochar amendments will likely be due to adsorption onto organic surfaces of the biochar, and lead chelation may also occur because of the high organic carbon content. The low application rate for biochar was established at 10 g/kg of soil (1 percent by weight or 5 tons/ac), based on the lowest volumetric amount that is expected to effectively reduce lead bioaccessibility. This amount is also expected to result in soil conditioning and nutrient provision (e.g., nitrogen and phosphorus) benefits to promote robust plant growth. The high application rate was established at 25 g/kg of soil (2.5 percent by weight or 12.5 tons/ac, which is the maximum amount that could be applied at the Site based on the projected volume of material necessary to optimize lead bioaccessibility reduction.

4.5 COMPOST

The reductions in bioaccessibility expected for compost amendments are likely due to lead chelation related to the high organic carbon content. The same application rates are proposed for compost as described for biosolids in Section 4.2 because field-scale application methods are assumed to be similar. Although the lower application rate for compost may not provide sufficient material to maximize reductions in lead bioaccessibility, it is expected to result in appropriate nutritional and soil conditioning benefits to promote plant growth. The high application rate was selected based on the projected volume of material necessary to maximize effective lead bioaccessibility reduction.

4.6 AMENDMENT COMBINATIONS

The same low and high rates established for the individual amendments will be used for the combination amendments, except for the low application rate of the biochar-compost combination (Amendment 12 on Table 3-2). When combined, the low rate established for each of these amendments individually will be halved (to 1/8 in. or 11 tons/ac each) to yield a combined application thickness of approximately ¼ in. or 22 tons/ac as established for biosolids, biochar, and compost, which are included in each of the seven combinations (see Table 3-2).

5 BENCH-SCALE TESTING DESIGN

5.1 SOIL TREATABILITY EXPERIMENT DESIGN

The experiment design developed to address the key decision points during the bench-scale testing and amendment recommendations are summarized in Table 5-1, and reflects the consensus of the SATES Technical Team, as discussed on a phone call on November 1, 2018 (SATES Technical Team 2018). The following information will be developed for each amendment in this study:

- Lead bioaccessibility reduction
- Changes in the leachability of metals and phosphorus from soil
- Changes in general soil chemistry (pH, available phosphorus, available and total nitrogen, total carbon, and organic carbon).

Based on the results, the different amendments tested will be evaluated for changes in lead and arsenic mineralogy to provide additional information on the quality of the lead transformation from more bioaccessible species into less bioaccessible forms. This evaluation will provide insight into the efficacy of the amendment applications and information related to maintaining reduced lead bioaccessibility conditions after initial treatment is complete.

To obtain this information, the effects of each of the 12 amendments will be evaluated using two application methods: surficial application of the amendment onto soil and full incorporation of the amendment into the soil. The surficial application method will be evaluated to approximate anticipated application conditions in the field. Incorporation into the soil will allow evaluation of the potential maximum effectiveness of the amendments in reducing lead bioaccessibility and improving soil characteristics (i.e., pH, available phosphorus, available and total nitrogen, total carbon, and organic carbon). Surficial application will be done by placing the amendment material on the soil surface in the target pots. Incorporation will be completed by fully mixing the amendment with the soil in each target pot.

For each amendment and each application method, the low and high application rates described in Section 4 will be applied and evaluated. The bench-scale test development, duration, and processes are summarized below.

5.2 BENCH-SCALE TESTING POT SET PREPARATION

The fundamental experimental units (pots) will be prepared using polyethylene plastic containers that are 5½ in. high and have a top diameter of 4½ in. and a bottom diameter of 3½ in. The bottom of each container will be perforated and lined with fine polyethylene mesh to allow drainage of

excess water without soil or solid amendment loss. A total of 400 g of the homogenized soil will be added to each container to establish the pots. The set of pots to be developed for each amendment is depicted in Figure 5-1, with further details provided in Appendix D.

The pots will be used to evaluate 12 different soil amendments (see Table 3-2) by applying the application rates and methods described previously.[7] The total number of pots prepared for each amendment is called an "amendment pot set." Control pots will be prepared the same way, but with the homogenized soil and no amendment. These will be evaluated in a separate "control pot set" (Figure 5-1) in the same manner as the amendment pot sets. The specific elements of each amendment pot set and the associated control pot set are detailed below.

During the bench tests, soil samples will be collected from each pot set at three time points (t_1 = 1 month after amendment application, t_2 = 4 months, and t_3 = 6 months) for laboratory analysis. To evaluate variability, for each combination of amendment application rate and method, four pots will be designated for sampling at each time point and a fifth pot will be developed and used for measurement of soil moisture conditions (Figure 5-1).

A total of 437 pots will be prepared for bench-scale testing (see Appendix D), as follows:

- Surface application – 312 pots
- Incorporated application – 120 pots
- Control pot set – 5 pots.

A summary of the pot preparation methods, pot sampling procedures, and pot counts for each of these subsets is described in Sections 5.2.1 through 5.2.3.

5.2.1 Surface Application Pot Subset

For the evaluation of surface applications, the specific volumes of each amendment will be placed on a single layer of cheese cloth then applied to the surface of each pot at the corresponding high and low application rates, without mixing.

Sample collection from these pots will disturb the pot soil and may cause mixing and displacement of the surface-applied amendment material. To maintain the integrity of the pot soil, pots from which soil samples are collected during the bench testing will be eliminated from further use in the study. Because samples will be collected at each of the three sample time points, 3 sets of 4 pots (12 pots) will be prepared for both the high and low amendment application rates to be able to collect a full set of samples at each time point. One additional pot will be developed in each of the pot subsets for soil moisture monitoring. Therefore, for the surface-applied amendments, 13 pots

[7] A single treatment is the combination of an amendment with an application method and rate of application.

will be prepared for each amendment and for each application rate (26 pots total), as illustrated in Figure 5-1.

Since there are 12 amendments to be tested, a total of 312 pots will be developed for the surface application pot subset, with 24 of these designated for soil moisture monitoring.

5.2.2 Incorporated Application Pot Subset

Pot sets to evaluate amendments incorporated into the soil will be prepared by thoroughly blending the volumes of each amendment that correspond to the high and low application rates into the soil in each pot.

Four pots will be prepared for the high and low application rates for each amendment, plus 1 additional pot for soil moisture monitoring for each application rate. Unlike the surface application pots, each sample set can be collected at each time point (t_1, t_2, and t_3) from the pots for the high and low application rates. Therefore, a total of 10 pots will be prepared for each incorporated amendment pot set, with 5 pots for both the high and low application rates, as illustrated in Figure 5-1. Since there are 12 amendments to be tested, a total of 120 pots will be developed for the incorporated application pot subset, with 24 of these designated for soil moisture monitoring.

5.2.3 Control Pot Set

Control pots will be prepared using the same method described in Sections 5.2.1 and 5.2.2, except no treatments will be applied. The control pot set will be monitored during testing for comparison to the pots with the 12 amendment applications. Four control pots will be developed for soil sample collection and one for soil moisture monitoring, for a total of 5 pots in the control pot subset (see Figure 5-1).

5.3 BENCH-SCALE TESTING DURATION AND SETTING

The pot sets will be incubated in a greenhouse with the temperature controlled to remain between 50 and 75 degrees Fahrenheit at ambient humidity for a period of 6 months. To provide optimal and realistic conditions for reactions to occur, the soil moisture content in the pots will be maintained at 90 percent of soil water holding capacity (i.e., amount of water that remains in the soil after it is gravity drained). This will be accomplished by adding water to achieve a known mass of the soil, pot weight, and water weight. The pot weight relative to moisture content will be determined for each moisture monitoring pot by using the water holding capacity measured for the soil and amendments as discussed in Section 6.1. Laboratory technicians will evaluate pot moisture regularly by weighing the pots at least once a week. To ensure the soil moisture content

is maintained at the correct level, pot weight measurements will be compared to the predicted pot weights calculated at 90% moisture content. Appropriate soil moisture conditions will be defined as those pot weight measurements that are within a relative percent difference of 20% as compared to the predicted pot weights at 90 percent water holding capacity.

The 6-month testing duration in combination with the setting described above were selected to provide sufficient time for reactions to occur within a reasonable timeframe for beneficial effect in the field. However, it is acknowledged that this may not provide sufficient time to appropriately observe and quantify potential longer-term effects on soil conditions. During the bench-scale testing, soil samples will be collected and analyzed from the treatment and control pots at each time point to monitor the effect and progress of the amendment applications on the treatment pot sets (see monitoring and analysis as described in Section 6.) At the conclusion of the second time point (t_2), data from the first two time points (t_1 and t_2) will be reviewed to evaluate whether the initially projected 6-month duration is sufficient or if longer testing is warranted. This decision will be made in collaboration with the SATES technical team.

6 MONITORING AND ANALYSIS PROGRAM

The monitoring and analysis program for the study is described in this section. Data that will be collected and the rationale for their selection are presented in Table 6-1. The sampling and analysis plan for the bench tests is summarized in Table 6-2, followed by target laboratory reporting limits in Table 6-3. SOP 4 and SOPs 6 through 13, included in Appendix A, describe the specific sample collection methods, analytical methods, and monitoring methods that will be used.

To establish baseline conditions (time zero, t_0), four soil samples will be collected from the homogenized soil that will be used to construct the bench-test pots. To evaluate progress of the bench testing, soil samples will be collected from all of the pot sets, including the control pots, will occur at the three predetermined time points after amendment application: 1 month (t_1), 4 months (t_2), and 6 months (t_3). Approximately 50 g of soil will be collected for each sample.

6.1 AMENDMENT CONDITIONS

To confirm the quality of the amendments prior to use in the bench testing, one sample of each individual amendment will be collected and analyzed for the following parameters:

- Total target analyte list (TAL) metals, by EPA Method 6010 (except mercury), and mercury by 7471B
- Volatile organic compounds by EPA Method 8260
- Semi-volatile organic compounds by EPA Method 8270
- Oxalate extraction by McKeague and Day (1966)
- Total carbon and nitrogen by Nelson and Sommers (1996).

6.2 PRE-TREATMENT BASELINE SOIL CONDITIONS

Baseline soil conditions (t_0) will be measured prior to the preparation of the pot sets by collecting four soil samples from the homogenized soil prepared for the pots for bench-scale testing. The baseline sample analyses will be the same as for the treated pots later in the study. Baseline soil samples will be analyzed for the following parameters:

- Bioaccessible lead and arsenic by EPA Method 1340, with sample aliquots extracted at pH 1.5 (USEPA 2013)
- Bioaccessible lead and arsenic by EPA Method 1340 (USEPA 2013), modified with sample aliquots extracted at pH 2.5

- Mehlich III extractable lead and phosphorus by the Mehlich (1984) method and EPA Method 6010
- Total TAL metals, by EPA Method 6010 (except mercury), and mercury by 7471B
- SPLP TAL metals and phosphorus, by EPA Method 1312 Western U.S. (pH 5.00)/6010 (USEPA 2007b), followed by EPA Method 6010 (USEPA 2007a)
- Soil pH by the Thomas (1996) method
- Total carbon and nitrogen by the Bremner and Mulvany (1982) and Nelson and Sommers (1996) methods
- Mineralizable nitrogen by the Waring and Bremner (1964) method
- Total organic carbon by the Heanes (1984) method
- Soil water holding capacity by the Cassel and Nielsen (1986) method.

Additionally, for one of the baseline (t_0) soil samples, lead and arsenic mineralogy will be evaluated by synchrotron analysis using EPA National Risk Management Research Laboratory Quality Management Plan (NRMRL QMP) Method L18735 with Athena software data analysis. Additional baseline samples may be evaluated for mineralogy at the discretion of the SATES technical team.

One sample each of the individual amendments (except soluble phosphate) and combination amendments will be collected and analyzed for water holding capacity by the American Society for Testing and Materials Method D2216 and the Cassel and Nielsen (1986) method. Soluble phosphate is excluded from analysis, because, as a soluble material, water holding capacity analysis would not be relevant.

The soil sample aliquots collected for the lead and arsenic bioaccessibility and total metals analyses will be sieved so that the analyzed sample aliquot consists of the soil grains less than 150 μm in diameter. Concentration and name of standard reference materials (SRMs) used as part of laboratory QA/QC will be documented in laboratory bench-sheets for use during third-party data validation.

6.3 TREATMENT PROGRESS SOIL CONDITIONS

To monitor the effect and progress of the amendment applications on the treatment pot sets, soil samples will be collected and analyzed from the treatment and control pots during the study, as described below.

6.3.1 Progress and Control Sample Collection

Treated Pot Sets. A total of 576 soil samples will be collected and analyzed from treatment pot sets during the bench testing period at time points t_1, t_2, and t_3 after the selected amendments have been applied to the pots. At each time point, four soil samples ("progress samples") will be collected from each treatment pot set developed for the high and low application rates. At each time point, 192 soil samples will be collected during the bench-scale testing (4 samples x 12 amendments x 2 application methods x 2 application rates = 192 samples). Soil samples will be collected at 3 time points (t_1, t_2, and t_3) for a total of 576 samples (192 x 3 time points = 576 samples). For surface applied treatments, treatment that did not infiltrate into soil will be removed by removing the cheese cloth and exposing the soil beneath. The soil will be homogenized by end over end mixing and then sampled for analysis. For incorporated treatments, the entire pot (soil plus amendment) will be re-homogenized by end over end mixing and then sampled for analysis. End over end mixing will be conducted by placing a lid on the soil containers and inverting them multiple times to mix.

Control Pot Set. A total of 16 samples will be collected from the control pot set during the bench testing period at each of the three time points (1 control sample x 4 samples x 3 time points = 12 samples). Control pot soils will be homogenized immediately before sample collection.

6.3.2 Progress and Control Pot Sample Analyses

The progress samples and control pot set samples will be analyzed for the following parameters:

- Bioaccessible lead and arsenic by EPA Method 1340, with sample aliquots extracted at pH 1.5
- Bioaccessible lead and arsenic by EPA Method 1340, modified with sample aliquots extracted at pH 2.5
- Mehlich III extractable lead and phosphorus by the Mehlich (1984) method and EPA Method 6010
- SPLP TAL metals and phosphorus, by EPA Method 1312 Western U.S. (pH 5.00)/6010
- Soil pH by the Thomas (1996) method
- Total carbon and nitrogen by the Bremner and Mulvany (1982) and Nelson and Sommers (1996) methods
- Mineralizable nitrogen by the Waring and Bremner (1964) method
- Total organic carbon by the Heanes (1984) method.

The sample analysis plan is summarized in Table 6.2. Additionally, lead and arsenic mineralogy may be evaluated in two or more samples by synchrotron analysis using EPA NRMRL QMP Method L18735 with Athena software data analysis. Samples to be evaluated for mineralogy will

be selected at the discretion of the technical team based on the analytical results for the baseline samples and progress samples.

For the bioaccessibility and total metals analyses, the soil sample aliquots will be sieved so that the analyzed sample aliquot consists of the soil grains less than 150 μm in diameter.

Moisture content for the control pot set will be evaluated by calculating the weight of water required to establish a 90 percent moisture content in each pot, based on the water holding capacity of the soil. The water holding capacity will be measured by analyzing the control soil samples. The control pot designated for moisture monitoring will be weighed at each time point to confirm the water content for comparison to the predicted moisture content capacity calculated from the baseline water holding capacity sample results.

7 DATA EVALUATION AND INTERPRETATION

The measurements collected during the bench tests for each soil treatment will be reviewed and synthesized in a statistical analysis that will be used to rank treatments based on efficacy, and that will help select the amendments that should be advanced to the Phase III field-scale pilot testing on the SATES test plots. The project data and the ranking results will be used to design and develop a plan for the field pilot study.

7.1 DATA REPORTING AND ANALYSIS

At the conclusion of the bench-scale testing, the analytical data will be summarized and reported in standard electronic data deliverable (EDD) format (see Section 8.4).

The results will be analyzed based on the effectiveness and applicability of each amendment, and the amendments will be ranked from least effective to most effective with regard to the program objectives and the evaluation elements listed below. Results of the analyses outlined in Section 6 will be reviewed to quantitatively and qualitatively evaluate changes in arsenic bioaccessibility, metal leachability, and soil quality associated with the amendments at varying application rates and methods. The following information will be evaluated:

- Total 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 lead and arsenic mineralogy.

The evaluation methods are described further in the following subsections.

7.1.1 Lead and Arsenic Bioaccessibility Changes

Variations in percent bioaccessible lead and arsenic between soil treatments will be evaluated using a one-way analysis of variance (ANOVA[8]) to determine statistical differences in percent bioaccessible lead and arsenic between the treatments and the control pot set for time points t_1 and t_3. Results of this evaluation will be used to rank the soil treatments from the least effective at reducing bioaccessibility to the most effective. Measurements that will be used for this analysis include the following: 1) total lead and arsenic concentrations; 2) lead and arsenic bioaccessibility

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

(*in vitro* bioaccessibility or IVBA) using the EPA 1340 protocol with a pH 1.5 for extraction; and 3) lead and arsenic bioaccessibility using a modified EPA 1340 protocol with a pH 2.5 for extraction.

Total lead and arsenic will be determined for each treatment based on the baseline sample results. These results and the results of bioaccessible lead and arsenic analyses run at pH 1.5 and pH 2.5 for the baseline (t_0) and final sampling time point (t_3) 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 in glycine extraction at pH 1.5 or 2.5
total [As]	=	arsenic concentration in glycine extraction at pH 1.5 or 2.5

A comparison of the baseline and the final progress sample results will be used to calculate the change in percent bioavailability of lead and arsenic for each amendment application. Using percent change in bioavailability normalizes for differences in total lead and arsenic content after dilution due to the addition of treatments.

7.1.2 Completeness of Bioaccessibility Reduction Reactions

A one-way ANOVA will be performed for lead and arsenic bioaccessibility results for each amendment type, application rate, and application method at each time point. This will allow a determination of whether there is a statistical difference between the baseline conditions and soil conditions at the three progress time points for each amendment application. For example, a result showing initial reaction at the first time point but no significant statistical difference between the two following time points would indicate the bioaccessibility reduction reaction, has slowed or stopped. A result showing a significant difference between the second and third time points would indicate that at least at four months since amendment application to the treatment pot sets, the reactions associated with the amendment application are continuing.

7.1.3 Leachability of Other Metals

The leachability of other metals and phosphorus in the soils tested will be determined 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 pot set at time point three (t_3) to determine if any of the soil treatments caused an increase in the leachability of metals in any of the pot sets. To account for dilution of total metals and phosphorus

content related to amendment applications, 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 treatment and each application method for time point t_1 in each set of four soil samples (replicates). The average total metals and phosphorus from the four soil samples (replicates) will be used to calculate the percent SPLP. The total metals and phosphorus results from the baseline (t_0) samples will be considered during data evaluation.

7.1.4 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 pot sets by using the data from the baseline and progress sampling time points. 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, as described above.

7.1.5 Lead and Arsenic Mineralogy

Samples for lead and arsenic mineralogy will be selected based on the results of the bioaccessibility analysis results. Samples from both soil treatments that produce significant reductions (in comparison to the control pots and baseline) and the control will be selected to test for changes in lead and arsenic mineralogy.

8 QUALITY ASSURANCE AND QUALITY CONTROL

8.1 QUALITY CONTROL REQUIREMENTS

Quality control requirements for the Phase II bench-scale testing are described in Section 10 of the SATES Phase IA Work Plan (Ramboll 2017a) and incorporated by reference into this Phase II Work Plan. These include quality assurance objectives and criteria (Section 10.2), analytical laboratory quality control 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).

8.2 INSTRUMENT AND EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

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

8.3 INSTRUMENT CALIBRATION FREQUENCY

Laboratory equipment calibration procedures and frequency requirements are described in Section 12.2 of the Phase I 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 laboratory SOP for the required calibration procedures and frequencies. Records of calibrations will be filed and maintained by the laboratory and will be subject to quality assurance (QA) auditing. Special care will be taken to verify the correct concentration, use, and documentation of reference media and materials.

8.4 DOCUMENTATION AND RECORDS

Procedures for laboratory documentation and records are described in Section 6.2 of the Phase I Work Plan. 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 quality control (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
- 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
- Matrix spike and matrix spike duplicate recoveries and relative percent difference (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. Final data packages in EDD format, as well as the results report sheets in a PDF or electronic spreadsheet format, will be provided within 30 working days from the end date of the bench-scale testing. SOP 2, provided in Appendix A of the Phase I Work Plan (Ramboll 2017a), specifies the EDD formatting requirements.

Sampling and analysis subcontractors will transfer all project documentation to Ramboll. Project files will be stored according to Ramboll and TAI requirements.

8.5 DATA MANAGEMENT

Procedures for data management are described in Section 14 of the Phase I Work Plan. The data management plan and its draft amendment (Exponent 2010) establish standard procedures for the management of all documents and environmental data (field and laboratory) generated during

the UCR remedial investigation and feasibility study. 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.

8.6 ASSESSMENT AND RESPONSE ACTIONS

Procedures for assessment and response actions are described in Section 15 of the Phase I Work Plan. 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 (see Section 6/Table 6-3). 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:

- Protocols as 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.

Corrective action will be initiated upon identification of the problem. At whatever level this occurs (analyst, supervisor, data review, or QC), it will be brought to the attention of the analytical laboratory QA manager and, ultimately, the laboratory director. Final approval of any action deemed necessary is subject to the approval of the laboratory director. Corrective action may include sample re-extraction, re-preparation, reanalysis, cleanup, dilution, matrix modification, or other activities.

8.7 REPORTS TO MANAGEMENT

Reports to management are described in Section 16 of the Phase I Work Plan. The laboratory will maintain QA records related to analyses, 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.

8.8 DATA REDUCTION AND REVIEW

Procedures for data reduction and review are described in Section 17 of the Phase I Work Plan. The calculations used for data reduction will be in accordance with the analytical methods. Any deficiencies discovered as a result of internal data review, as well as the corrective actions implemented to rectify the situation, will be documented on a corrective action form (Appendix E).

9 DATA VERIFICATION AND VALIDATION

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

9.1 DATA VALIDATION PROCESS

Data validation will be performed as outlined in Section 18 of the Phase I Work Plan. For Phase II, a third-party validator will be used. Soil data generated will be validated using the EPA's National Functional Guidelines (USEPA 2017) for data validation available at the time of project initiation, where appropriate. 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 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).

It should be noted that 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. The third-party validator will provide definitions of qualifiers applied by the laboratory and the data validator. As is the case with laboratory data and information, data qualifier entries into the database will be discussed between the laboratory validator and the laboratory and verified. Any discrepancies will be resolved before the final database is released for use.

Non-conforming data may be qualified as estimated (i.e., a "J" qualifier will be applied to the result) or rejected as unusable (i.e., an "R" qualifier will be applied to the result) during data validation if criteria for data quality are not met. Data may also be qualified as undetected during validation based on laboratory blank results. Rejected data will not be used for any purpose other than corrective action development. A summary of the qualified data and the reasons for qualification will be included in the data validation report.

Resolution of any issues regarding laboratory performance or deliverables will be handled between the laboratory and the data validator. Suggestions for reanalysis may be made by the quality assurance 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 kept in the UCR project database maintained by Exponent.

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MAPS

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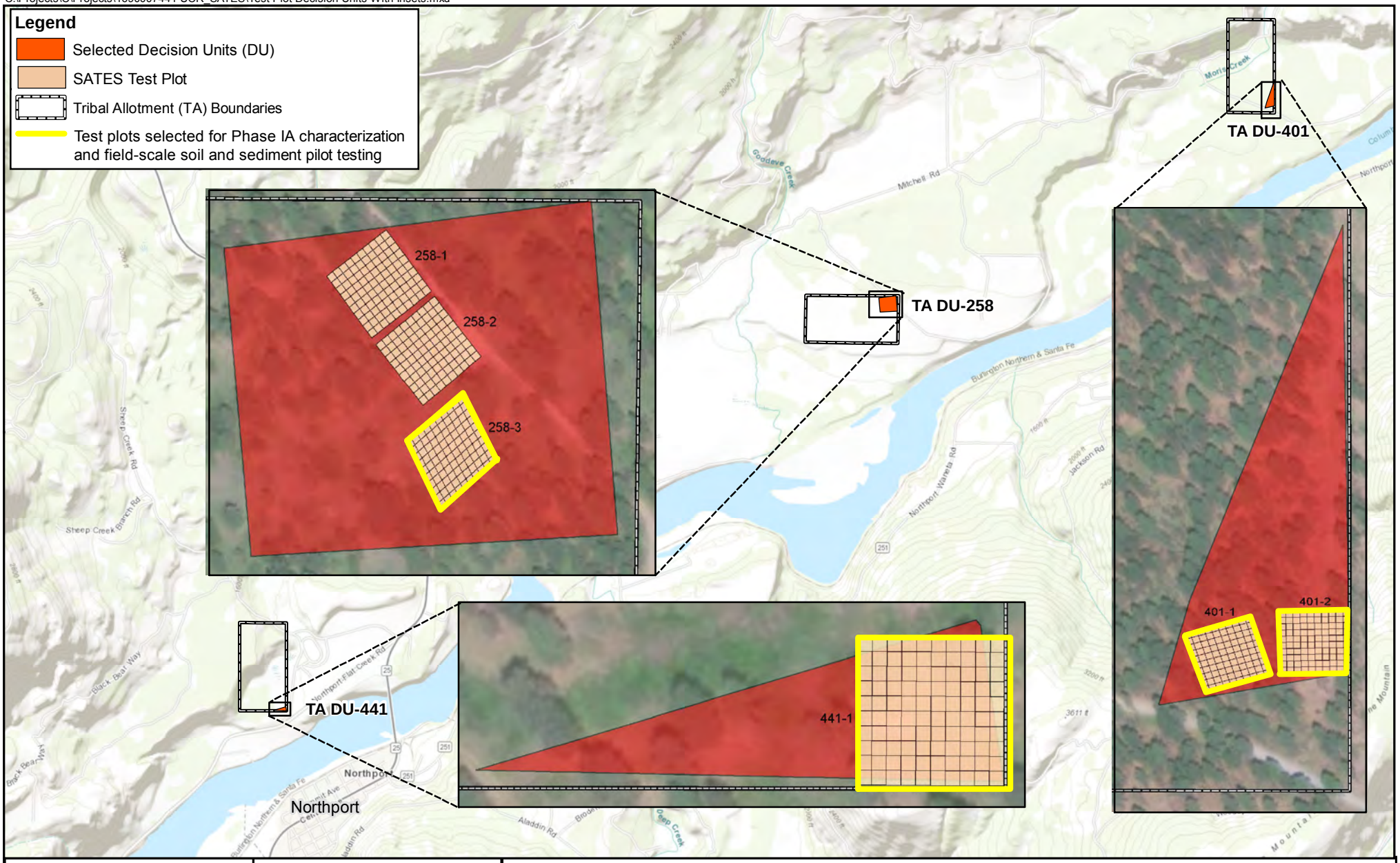
DRAFT



RAMBOLL

Map 1-1
Test Plot Decision Units
Upper Columbia River, WA

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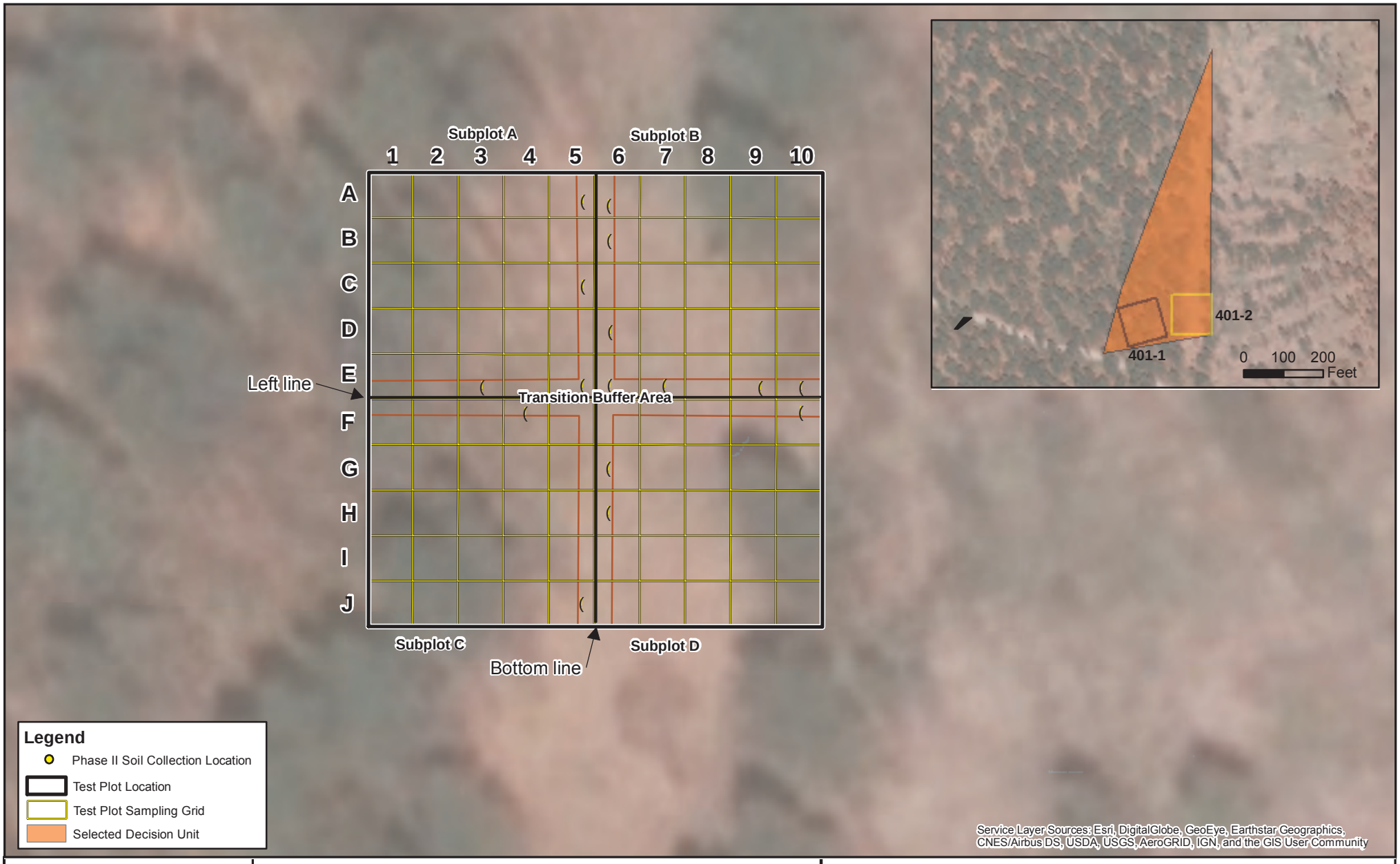


RAMBOLL

0 12.5 25 Meters

0 50 100 Feet

DRAFTED BY: RGM

Date: 3/6/2019

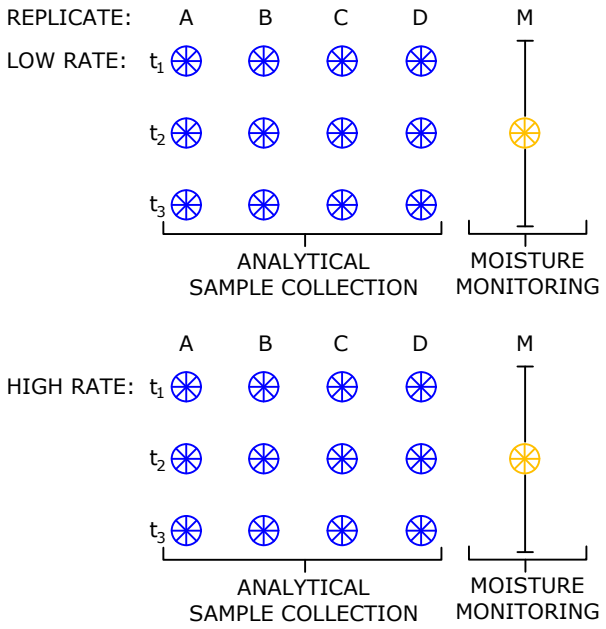
Map 2-1
Test Plot 401-2: Phase II Bench-Scale Treatability Testing
Soil Collection Locations
Upper Columbia River, WA

FIGURES

GMILES 3/6/19 F:\GRAEME\1690010651-001 < BENCH_SCALE_STUDY_SCHEMATIC_NF >

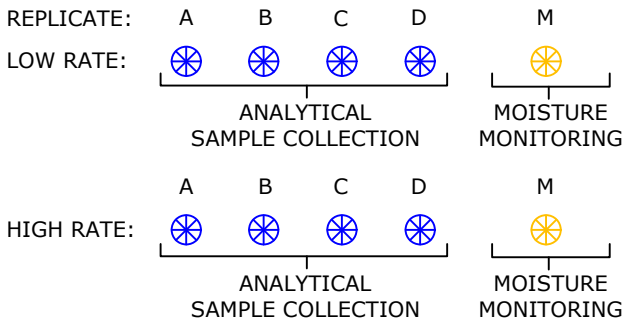
POT SET FOR EACH AMENDMENT

SURFACE APPLICATION OF AMENDMENT



SURFACE APPLICATION OF AMENDMENT POT SUBSET TOTAL = 26 POTS

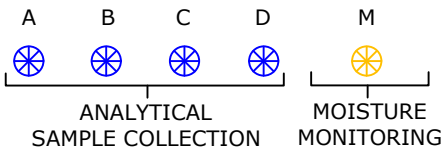
INCORPORATED AMENDMENT



INCORPORATED AMENDMENT POT SUBSET TOTAL = 10 POTS

26 POTS + 10 POTS = TOTAL OF 36 POTS NEEDED PER AMENDMENT

CONTROL POT SET



CONTROL SET POT TOTAL = 5 POTS

TOTAL OF 5 POTS NEEDED FOR CONTROL

POTS FOR:

ANALYTICAL:

MOISTURE:

NOTE: Baseline (t_0) samples are not depicted. Soil samples will be collected for analysis to evaluate the progress of the treatments and control soil at three time points: 1 month after the amendments are applied (t_1), at 4 months (t_2), and at 6 months (t_3).

Figure 5-1: Conceptual Plan View of Bench-Scale Testing Pot Sets

DATE: 1/30/2019
DRAFTED BY: RGM

TABLES

Table 2-1. Soil Prescreening for Total Lead Concentrations by XRF Analysis

Sample ID	OSU Bucket ID	Lead (mg/kg) by XRF Analysis
D-401-2-E9-101818-3	1	1,260
D-401-2-A5-101818-3	2	1,030
D-401-2-G6-101818-3	3	1,921
D-401-2-E3-101818-3	4	1,230
D-401-2-J5-101818-3	5	1,744
D-401-2-A6-101818-3	6	1,649
D-401-2-A6-101818-3	7	2,222
D-401-2-D6-101818-3	8	2,217
D-401-2-E6-101818-3	9	2,571
D-401-2-E7-101818-3	10	2,074
D-401-2-H6-101818-3	11	2,075
D-401-2-E9-101818-3	12	833
D-401-2-E10-101818-3	13	1,816
D-401-2-J5-101818-3	14	1,005
D-401-2-D6-101818-3	15	1,157
D-401-2-G6-101818-3	16	2,622
D-401-2-E9-101818-3	17	669
D-401-2-B6-101818-3	18	1,333
D-401-2-B6-101818-3	19	1,858
D-401-2-E3-101818-3	20	1,530
D-401-2-F4-101818-3	21	2,416
D-401-2-E7-101818-3	22	1,745
D-401-2-C5-101818-3	23	1,091
D-401-2-H6-101818-3	24	1,956
D-401-2-E5-101818-3	25	1,070
D-401-2-E10-101818-3	26	1,534
D-401-2-F10-101818-3	27	937
D-401-2-G6-101818-3	28	1,469
D-401-2-E10-101818-3	29	1,623
D-401-2-J5-101818-3	30	1,041
D-401-2-D6-101818-3	31	1,813
D-401-2-E3-101818-3	32	1,179
D-401-2-C5-101818-3	33	395
D-401-2-A6-101818-3	34	1,489
D-401-2-F10-101818-3	35	2,348
D-401-2-E6-101818-3	36	2,042
D-401-2-B6-101818-3	37	1,378
D-401-2-F4-101818-3	38	952
D-401-2-E7-101818-3	39	1,000
D-401-2-F4-101818-3	40	1,089
D-401-2-C5-101818-3	41	415
D-401-2-F10-101818-3	42	1,454
D-401-2-A5-101818-3	43	1,928
D-401-2-E5-101818-3	44	1,456
D-401-2-A5-101818-3	45	2,290
D-401-2-H6-101818-3	46	1,864
D-401-2-E6-101818-3	47	1,436
D-401-2-E5-101818-3	48	1,350

Notes:
mg/kg = milligrams per kilogram
OSU = The Ohio State University
XRF = x-ray fluorescence

Table 3-1a. Soil Amendment Prescreening Lead Sorption Analysis Results

	Analysis	Lead Sorption[a]		
	Analysis Method	EPA Biochar Protocol[b]		
	Analyte	Soil Lead Pre-Treatment	Soil Lead Post-Treatment	Lead
	Units	SPLP Extract (µg/L)	SPLP Extract (µg/L)	% Reduction[c]
Soil Amendment	Sample Name			
Phosphorus fertilizer	Fert-01	64.4	< 2	> 97
Wood ash	Landfill ash 5-10-18	64.4	< 2	> 97
Compost (potting soil)	PS-01	64.4	3.18	95
Water treatment residuals	Water treatment residuals	64.4	13.4	79
Biosolids	Municipal biosolid	64.4	4.42	93
Biochar[d]	ARS Wood	43.6[e]	< 2.41	> 94
Biochar[d]	Black Owl	43.6[e]	< 2.41	> 94

Notes:

[a] Lead sorption was assessed for each soil amendment, which required use of archived SATES soils. The < 2-mm fraction from an increment composite (IC) sample collected in test plot 401-2 subplot A (IC1-401-2A-101217) was chosen for prescreening analysis because: 1) the soil is generally representative of site soils; 2) Phase IA total and bioavailable lead results were available for lead sorption assessment; and 3) sufficient archived soil mass was available for prescreening.

[b] This method was developed by Dr. Mark Johnson of the EPA National Health and Environmental Effects Research Laboratory, and implemented by OSU. The method evaluates amendment sorption potential and the reversibility of sorption that occurs. The method involves conducting the synthetic precipitation leaching procedure (SPLP) on the soil sample, filtering solution extract, then challenging the amendment with the extract. The lead sorption reversibility of the amendment is evaluated through a second extraction of the amendment with 0.01 molar calcium solution (salt solution.)

[c] Lead sorption was calculated as a percent (%) reduction. % reduction = 100*[(soil SPLP [Pb] – amended soil SPLP [Pb]) / soil SPLP [Pb]]. When treatment resulted in a lead concentration less than the method detection limit, the detection limit (DL) value was used as the concentration after treatment. Because the concentration after treatment is less than the DL, the % reduction is assumed to be greater than the calculated result. Results of the extraction with 0.01 molar calcium solution were below analytical instrument DLs, thus, are not included in the percent lead reduction.

[d] Performed by EPA National Health and Environmental Effects Research Laboratory (USEPA 2019a).

[e] The average SPLP solution concentration of lead was 43.6 ± 2.8 ppb (mean ± standard error of the mean for 8 replicates) (USEPA 2019a).

EPA = U.S. Environmental Protection Agency

Lead Post-Treatment = lead concentration remaining in SPLP extract

Lead Pre-Treatment = SPLP extract from test plot soil with known lead content

µg/L = microgram(s) per liter

mm = millimeter

NA = not analyzed

OSU = The Ohio State University

SPLP = synthetic precipitation leaching procedure

Table 3-1b. Soil Amendment Prescreening Oxalate Extraction and Total Metals Analysis Results

		Analysis	Oxalate Extraction						Total Metals						Total Carbon and Nitrogen	
		Analysis Method	McKeague and Day 1966						EPA 6010						Nelson and Sommers 1996	
		Analyte	Aluminum	Iron	Manganese	Phosphorus	P_{sat}[a]	Available Phosphorus[b]	Arsenic	Cadmium	Copper	Nickel	Lead	Zinc	Carbon	Nitrogen
		Units	g/kg	g/kg	g/kg	g/kg	%	g/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	%
Soil Amendment	Sample Name															
Phosphorus fertilizer	Fert-01		3.1	2.1	0.1	78.7	1,651	77.5	**8.07**	**54.7**	30.9	81.0	1.10	796.9	4.29	12.8
Biosolids	Municipal biosolid		10.1	28.3	0.3	25.1	91	18.2	**5.17**	**2.8**	**597**	23.7	30.9	1,187	36.0	4.71
Wood ash	Landfill ash 5-10-18		9.8	5.0	1.3	4.52	31	0.820	**17.6**	**5**	49.0	14.2	13.3	499	31.0	0.046
Biochar[c]	ARS Wood		0.262	1.32	0.378	0.47	37.8	0.199	<5	<1	11.0	52.5	3.89	13.3	67	0.043
Biochar[c]	Black Owl		0.505	0.324	0.314	0.558	59.7	0.354	<5	<1	21.9	2.25	<1	6.06	60	0.067
Compost (potting soil)	PS-01		0.4	2.6	0.1	1.4	74	0.947	<1	0.2	136	4.14	1.17	91	35.2	0.935
Water treatment residuals	Water treatment residuals		74.4	12.4	0.3	0.1	0.160	0.000	**6.79**	0.6	52.6	4.60	5.79	18.0	36.8	1.99
Ecology MTCA Method A									20	2	NE	NE	250	NE	NE	NE
Ecology MTCA Method B (non-cancer/cancer)									24 / 0.667	80 / NE	3,200 / NE	880 / NE	NE / NE	24,000 / NE	NE	NE
Ecology MTCA Protective of Groundwater Vadose @ 25 degrees Celsius									2.92	0.69	284	NE	3,000	5,970	NE	NE
EPA Part 503 Biosolid Land Application Limits (Pollutant Concentrations)									41	39	1,500	420	300	2,800	NE	NE

Notes:

[a]P_{sat} = 100 x [(oxalate-extractable P mol/kg)/(oxalate-extractable Al mol/kg)+(oxalate-extractable Fe mol/kg)+(oxalate-extractable Mn mol/kg)]

[b]Potentially available phosphorus, calculated from oxalate-extractable phosphorus as mg of phosphorus per kg of total material beyond 25% $P_{sat.}$

[c]Analyses performed by EPA National Health and Environmental Effects Research Laboratory (USEPA 2019a).

Bolded results in shaded cells are greater than one or more MTCA criterion.

Ecology = Washington State Department of Ecology

EPA = U.S. Environmental Protection Agency

g/kg = grams per kilogram

mg/kg = milligrams per kilogram

MTCA = Washington State Model Toxics Control Act Regulation

mol/kg = mole(s) per kilogram

NE = not established

P_{sat} = phosphorus saturation

% = percent

Table 3-2. Proposed Soil Amendments for Phase II Bench-Scale Testing

Number	Amendment	Rationale for Selection: General	Rationale for Selection: Prescreening Results
Individual Amendments			
1	Soluble phosphate	Clear link between lead pyromorphite formation and bioaccessibility reduction demonstrated in several studies of phosphorus amendment of soils	• Reduced bioaccessible lead from soil extract by > 97%
2	Biosolids	Reductions in bioaccessibility are associated with lead sorption to iron oxide surfaces and/or to pyromorphite formation	• Material is high in reactive iron (> 28 g/kg) • Reduced bioaccessible lead from soil extract by > 93%
3	Wood ash	Locally available material with moderate phosphorus content	• Material includes reactive manganese (> 1 g/kg) • Reduced bioaccessible lead from soil extract by >97%
4	Biochar	Highest carbon content of any of the materials	• 100%[a]
5	Compost	Locally available material with high carbon content	• Reduced bioaccessible lead from soil extract by 95%
Amendment Combinations			
6	Soluble phosphate and biosolids	• Combination of binding mechanisms: pyromorphite formation and sorption to iron oxide -Iron oxide in biosolids could mitigate increase in arsenic bioaccessibility due to phosphorus amendment • Evaluation of soil quality parameters contributed from biosolid in the presence of favorable pyromorphite-forming conditions	NA
7	Soluble phosphate and biochar	• Potential combination of binding mechanisms (depending on the content of the biochar) • Evaluation of soil quality parameters contributed from biochar in the presence of favorable pyromorphite-forming conditions	NA
8	Soluble phosphate and compost	• Evaluation of soil quality parameters contributed from compost in the presence of favorable pyromorphite-forming conditions	NA
9	Biosolids and wood ash	• Potential combination of binding mechanisms of pyromorphite formation, sorption to manganese oxide, and sorption to iron oxide • Evaluation of soil quality parameters contributed from biosolid in the presence of wood ash	NA
10	Wood ash and biochar	• Potential combination of binding mechanisms of pyromorphite formation, and sorption to Mn oxide • Evaluation of soil quality parameters contributed from biochar in the presence of wood ash	NA
11	Wood ash and compost	• Evaluation of soil quality parameters contributed from compost in the presence of wood ash	NA
12	Biochar and compost	• Evaluation of lead sorption by biochar in the presence of compost • Evaluation of soil quality parameters contributed from biochar and compost	NA

Notes:

[a] Performed by EPA National Health and Environmental Effects Research Laboratory (USEPA 2019a).

N/A - not applicable

g/kg = grams per kilogram

% = percent

Table 4-1. Proposed Bench-Scale Testing Soil Amendment Application Rates

Treatment Number	Soil Amendment	Treatment Rate	Rate Rationale	Estimated Amount per Pot
Individual Amendments				
1	Soluble phosphate	Based on a 3-inch soil depth. Low: 1.625 ton/A MAP or 1.875 TSP ton/A + 0.375 KCl ton/A High: 4.875 ton/A MAP or 5.625 ton/A TSP + 0.375 KCl ton/A	Low: Approximately 5 times the P/Pb molar ratio + 2 times the Cl/Pb molar ratio for pyromorphite formation High: 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 as to induce long-term increases in salinity.	Low: 1.3 g MAP or 1.5 g TSP + 0.3 g KCl (0-0-60) fertilizer High: 3.9 g MAP or 4.5 g TSP (TSP preferred) + 0.3 g KCl (0-0-60) fertilizer
2	Biosolid	Based on biosolid bulk density half the soil bulk density. Actual values will be determined on homogenized soil and biosolids for bench testing. Low (TBD): 1/4-inch application is estimated to be 22 ton/A High (TBD): 1-inch application is estimated to be 89 ton/A	Low: A 1/4-inch application is a reasonable application of biosolid without major disturbance of existing vegetation High: A 1-inch application is the maximum depth that would be considered	Low: 16.6 g High: 133.5 g
3	Wood ash	Low: 1 percent addition by mass estimated to be 5 ton/A High: 3 percent addition by mass estimated to be 15 ton/A	Low: A 1% application is a reasonable application of biochar without major disturbance of existing vegetation High: A 3% application is the maximum mass that would be considered	Low: 4 g High: 12 g
4	Biochar	Low: 1 percent addition by mass estimated to be 5 ton/A High: 2.5 percent addition by mass estimated to be 12.5 ton/A	Low: A 1% application is a reasonable application of biochar without major disturbance of existing vegetation High: A 2.5% application is the maximum mass that would be considered	Low: 4 g High: 10 g
5	Compost	Based on conpost bulk density half the soil bulk density. Actual values will be determined on homogenized soil and biosolids for bench testing. Low (TBD): 1/4-inch application is estimated to be 22 ton/A High (TBD): 1-inch application is estimated to be 89 ton/A	Low: A 1/4-inch application is a reasonable application of compost without major disturbance of existing vegetation High: A 1-inch application is the maximum depth that would be considered	Low: 16.6 g High: 133.5 g
Amendment Combinations				
6	Soluble phosphate and biosolids	Low: Low phosphate + low biosolid High: High phosphate + high biosolid	NA	Low: 1.3 g MAP, or 1.5 g TSP + 33.25 g biosolid + 0.3 g KCl fertilizer High: 3.9 g MAP or 4.5 g TSP + 267 g biosolid + 0.3 g KCl fertilizer
7	Soluble phosphate and biochar	Low: Low phosphate + low biochar High: High phosphate + high biochar	NA	Low: 1.3 g MAP, or 1.5 g TSP + TBD biochar + 0.3 g KCl fertilizer High: 3.9 g MAP or 4.5 g TSP + TBD biochar + 0.3 g KCl fetilizer
8	Soluble phosphate and compost	Low: Low phosphate + low compost High: High phosphate + high compost	NA	Low: 1.3 g MAP, or 1.5 TSP + 33.25 g compost + 0.3 g KCl fertilizer High: 3.9 g MAP or 4.5 g TSP + 267 g compost + 0.3 g KCl fertilizer
9	Biosolids and wood ash	Low: Low biosolid + low wood ash High: High biosolid + high wood ash	NA	Low: 33.25 g biosolid + 4 g wood ash High: 266 g biosolid + 12 g wood ash
10	Wood ash and biochar	Low: Low wood ash + low biochar High: High wood ash + high biochar	NA	Low: 4 g wood ash + 33.25 g biochar High: 12 g wood ash + 267 g biochar
11	Wood ash and compost	Low: Low wood ash + low compost High: High wood ash + high compost	NA	Low: 4 g wood ash + 33.25 g compost High: 12 g wood ash + 267 g compost
12	Biochar and compost	Low: Low biochar + low compost High: High biochar + high compost	NA	Low: 16.63 g biochar + 16.63 g compost High: 267 g biochar + 267 g compost

Notes:
Cl = chloride
Cl/Pb = chloride-to-lead molar ratio
g = grams
g/kg = grams per kilogram
KCl = potassium (i.e., potash) fertilizer (0-0-60)
kg = kilograms
MAP = monoammonium phosphate (11-52-0)
NA = not applicable
P/Pb = phosphate-to-lead molar ratio
TBD = to be determined
ton/A = dry tons per acre
TSP = triple super phosphate (0-46-0)

Table 5-1. Proposed Bench-Scale Study Design

Treatability Study Component/Parameter	Proposed	Rationale
Goals/objectives	• Determine if soil amendments show potential to reduce lead bioaccessibility • Determine the impact of amendments on key soil chemical and physical properties • Obtain data that can be used to reduce uncertainty about selection of amendment technologies for pilot-scale testing	While the overall goal of the SATES project more broadly addresses human and ecological risk, these goals focus only on the Phase II bench-scale portion of SATES.
Number of soil collection sites	One as identified in the Phase II Soil Collection Work Plan (test plot 401-2)	Sampling for the bench study is to be done only in buffer areas of the test plot to minimize disturbance prior to field-scale trials. Only one test plot (401-2) met the criteria established for soil collection laid out in the work plan. • Lead concentrations >800 mg/kg in soil • Lead minerology representative of potential treatment areas • Lead bioaccessibility >60% in soil
Amendment screening	• Target analyte list (TAL) metals • Semi-volatile organic compounds (SVOCs) • Volatile organic compounds (VOCs)	These analytes will assess potential contamination or drawbacks to amendment materials.
Amendment application rates	Minimum of two rates	Identify target application rates for field trials. Rationale for rate selection is included in Tables 4-1a and 4-1b.
Amendment application method	Surface application and incorporated into the soil	• Surface application mimics the anticipated application method in the field. • While field application will not include incorporation (to prevent vegetation disturbance), incorporated bench-scale analysis of each amendment will provide a potential or maximum benefit that the amendment could provide over time as the amendment infiltrates the soil.
Containers	Plastic pots that are 5 1/2 inches high and have a 4 1/2- inch top diameter and a 3 1/2-inch bottom diameter will be used; the bottom of the pots will be perforated and lined with fine polyethylene mesh	Dimensions allow for approximately 3 inches of soil plus amendments to mimic target treament zone and the depth from which the soil was collected. Perforated bottom allows for drainage, and prevents potential loss of lead and/or treatment.
Soil amount	400 grams	An average 2-millimeter bulk density of 34.2 at a 3-inch depth (as measured in Phase I) in the selected container size will result in an estimate of 330 grams of soil per pot. Using 400 grams will ensure that there is at least a 3-inch depth of soil.
Replicates	Four replicates of treatment pots, four replicates of control pots	• Allows for 12 treatments (based on the bench-scale study design and the quantity of soil collected). • Will provide enough statistical power to detect the expected reductions in bioaccessible lead due to treatment.
Soil moisture	Held just below soil water holding capacity (i.e., amount of water that remains in the soil after it is gravity drained; 90%)	Provides optimum and realistic conditions for reactions to occur.
TAL metals	TAL metals will be conducted once on the control pots (with replicates) and the incorporated treatment pots (with replicates)	Determine values to be used in calculating percent IVBA.
Bioaccessible lead and arsenic determination on treatments	• pH 1.5 performed on control time points and replicates only • pH 2.5 performed on all treatment and control time points and replicates	Based on in vivo data available, in vitro at pH 1.5 is suitable for untreated soils, but pH 2.5 is suitable for treated soils.
Soil quality measures	Measurements taken at the same time as bioaccessible lead and arsenic • Mehlich III or other extraction for availability of nutrients and metals • Readily plant available and mineralizable N • Total carbon and nitrogen • Organic carbon	Analysis of these parameters will assess modifications in soil quality parameters due to treatment. These parameters include those that can increase vegetative growth.
Leachability of metals and nutrients	Synthetic precipitation leaching procedure (SPLP) extraction for TAL metals and phosphorus	• Identify changes in potential leachability due to soil amendments, including arsenic.
Time points	Three, at 1 month, 4 months, and 6 months (at the end)	• Incorporated treatment and control replicates for time points will be re-sampled out of a single pot (i.e., two samples, one for each time point, will be collected from one pot). • Surface application treatment replicates for time points will be done in separate pots because the entire pot will need to be homogenized prior to sampling.
Duration	6 months	This duration allows for enough time to ensure the reactions can occur. The sampling point at 4 months will allow for evaluation of the reaction completeness.

Notes:
SATES = Soil Amendment Technology Evaluation Study

Table 6-1. Data Requirements for Bench-Scale Testing

Analysis	Rationale	Laboratory
Soil moisture holding capacity	Determine water content for incubations	OSU
Total TAL metals (except mercury)	Determine total Pb and As for determination of percent bioaccessible; identify changes in total metal content due to treatment	OSU
pH	Affects bioavailability of metals and plant nutrients	OSU
SPLP TAL metals (except mercury)	Monitor changes in leachability of metals	OSU
Bioaccessible arsenic and lead pH 1.5	Characterize bioaccessibility of arsenic and lead in soil collected for bench testing	OSU
Bioaccessible arsenic and arsenic pH 2.5	Evaluate treatment effect on bioaccessible arsenic and lead	OSU
Mehlich III extractable lead and phosphorous	Evaluate treatment effect on available lead and phosphorus	OSU
Mineralizable nitrogen	Evaluate potentially available nitrogen	OSU
Total carbon and nitrogen	Evaluate treatment effect on nutrient balance	OSU
Total organic carbon	Evaluate treatment effect on soil quality and nutrient balance	OSU
Lead/arsenic and general soil mineralogy, synchrotron x-rays	Evaluate treatment effect on changes in lead and arsenic minerology	EPA

Notes:

EPA = U.S. Environmental Protection Agency

OSU = The Ohio State University

SPLP = synthetic precipitation leaching procedure

TAL = target analyte list

Table 6-2. Monitoring and Analysis Plan for Phase II Bench-scale Soil Treatability Testing

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 Per Sample (grams)	Total Number of Original Samples
Amendment Samples									
Total TAL metals (except mercury)	EPA 3051A	Acid digestion	EPA 6010	ICP-AES	Amendments	Baseline	NA	0.5	5
Mercury	7471B	Acid/Permanganate digestion	7471B	CVAA	Amendments	Baseline	NA	15	5
Volatile organic compounds	EPA 5035	Purge and trap	EPA 8260	GC/MS	Amendments	Baseline	NA	90	5
Semivolatile organic compounds	EPA 3510	Separatory Funnel Liquid - Liquid Extraction	EPA 8270	GC/MS	Amendments	Baseline	NA	120	5
Oxalate extraction	McKeague and Day 1966	0.2 molar acid ammonium oxalate solution (pH 3.0)	EPA 6010	ICP-AES	Amendments	Baseline	NA	0.25	6
Total carbon and nitrogen	NA	NA	Bremner and Mulvaney 1982, Nelson and Sommers 1996	Dry combustion at 900°Celsius	Amendments	Baseline	NA	0.1	7
Baseline and Progress Soil Samples									
Bioaccessible arsenic and lead	EPA Method 1340	Glycine extraction (Extract at pH 1.5)	EPA 6010B	ICP-AES	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<150 micrometer	1	592
Bioaccessible arsenic and lead	EPA Method 1340	Glycine extraction (Extract at pH 2.5)	EPA 6010B	ICP-AES	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<150 micrometer	1	592
Mehlich III extractable lead and phosphorus	Mehlich 1984	Acetic and nitric acid; ammonium fluoride and ammonium nitrate; EDTA	EPA 6010	ICP-AES	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<2 millimeter	1	592
Total TAL metals (except mercury)	EPA 3051A	Acid digestion	EPA 6010	ICP-AES	Baseline	Baseline	<2 millimeter	0.5	4
Mercury	7471B	Acid/Permanganate digestion	7471B	CVAA	Baseline	Baseline	<2 millimeter	15	4
Total arsenic and lead	EPA 3051A	Acid digestion	EPA 6010	ICP-AES	Baseline	Baseline	<150 micrometer	0.5	4
					Treatments and controls	t_1	<150 micrometer	0.5	196
SPLP TAL metals (except mercury) and phosphorus	EPA 1312	SPLP	EPA 6010	ICP-AES	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<2 millimeter	1.5	592
pH	NA	NA	Thomas 1996	Electrode	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<2 millimeter	5	592
Total carbon and nitrogen	NA	NA	Bremner and Mulvaney 1982, Nelson and Sommers 1996	Dry combustion at 900°Celsius	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<2 millimeter	10	592
Mineralizable nitrogen	Bremner 1964	Short-term (7-day) anaerobic incubation for mineralizable N from organic matter	Waring and Bremner 1964	Lachat	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<2 millimeter	5	592
Total organic carbon	NA	NA	Heanes 1984	Dichromate oxidation	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<2 millimeter	0.5	592
Soil moisture holding capacity	0 bar	Water saturation	Cassel and Nielsen 1986	Gravimetric	Baseline, treatments	Baseline	<2 millimeter soil + bulk amendment	400g	25
Soil moisture	NA	NA	Direct measurement	Gravimetric	Baseline, treatments, and controls	Bi-weekly and during Baseline, t_1, t_2, t_3	<2 millimeter	0	592
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	Baseline, treatments, and controls[a]	Baseline, t_1, t_2, t_3[a]	<2 millimeter	20	≥4[a]

Notes:
[a]Based on baseline analytical results and the discretion of the project technical team
ASTM = American Society for Testing and Materials
EDTA = ethylenediaminetetraacetic acid
EPA = United States Environmental Protection Agency
ICP-AES = inductively coupled plasma - atomic emission spectroscopy
GC/MS = gas chromatography/mass spectroscopy
mg = milligrams
NA = not applicable
NRMRL QMP = National Risk Management Research Laboratory Quality Management Plan
PVP = polyvinylpyrrolidone
SPLP = synthetic precipitation leaching procedure
t_1 = One month after pot preparation
t_2 = Four months after pot preparation
t_3 = Six months after pot preparation
TAL = target analyte list
TBD = to be determined

Table 6-3. Analytical Parameters, Methods, and Target Laboratory Reporting Limits

Analyte	Units	CAS Number	Laboratory MDL	Laboratory RL	Preservation	Holding Time (days)
TAL Metals (6010)						
Aluminum	mg/kg	7429-90-5	30	30	Oven dry at 60°C	180
Antimony		7440-36-0	2	4		
Arsenic		7440-38-2	2	4		
Barium		7440-39-3	0.3	0.8		
Beryllium		7440-41-7	0.08	0.2		
Cadmium		7440-43-9	0.09	0.2		
Calcium		7440-70-2	1	100		
Chromium		7440-47-3	0.3	0.8		
Cobalt		7440-48-4	0.2	0.4		
Copper		7440-50-8	0.4	0.8		
Iron		7439-89-6	2	40		
Lead		7439-92-1	0.7	2		
Magnesium		7439-95-4	0.2	100		
Manganese		7439-96-5	0.04	1.0		
Nickel		7440-02-0	0.2	0.8		
Potassium		7440-09-7	10	100		
Selenium		7782-49-2	2	5		
Silver		7440-22-4	0.3	0.8		
Sodium		7440-23-5	5	100		
Thallium		7440-28-0	1	2		
Vanadium		7440-62-2	0.3	2		
Zinc		7440-66-6	0.2	5		
Other Analyses						
SPLP TAL metals (except mercury) and phosphorus	mg/L	NA	0.7	1	Oven dry at 60°C	180
Bioaccessible arsenic and lead (at pH 1.5 and pH 2.5)	%	NA	NA	NA	Oven dry at 60°C	180
pH	mg/kg	NA	NA	NA	Oven dry at 60°C	*in situ*
Mehlich III extractable lead and phosphorus	unitless	NA	NA	NA	Oven dry at 60°C	180
Total carbon and nitrogen	%	NA	Equal to RL	Varies	Oven dry at 60°C	60
Mineralizable nitrogen	mg/kg	NA	Equal to RL	Varies	Oven dry at 60°C	60
Total organic carbon	%	NA	1,000	1,000	Oven dry at 60°C	60
Soil moisture capacity	%	NA	NA	NA	Oven dry at 60°C	60
Lead/arsenic and general soil mineralogy	NA	NA	NA	NA	Oven dry at 60°C	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 would be 0.7% for C and 0.05% for N.

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

mg/L = milligrams per liter

NA = not applicable

RL = reporting limit

SPLP = synthetic precipitation leaching procedure

TAL = target analyte list

USEPA = United States Environmental Protection Agency

APPENDICES

APPENDIX A
STANDARD OPERATING PROCEDURES

CONTENTS

SOP 1
X-Ray Fluorescence Analysis of Soils

Standard Operating Procedure 1
X-Ray Fluorescence Analysis of Soils
Soil & Environmental Chemistry Program, The Ohio State University
Version 1

1.0 Operation Safety Thermo Niton FXL-959 XRF

1.1 Labeling: The XRF will maintain a clearly visible radiation caution label that states

1.1.1 The equipment produces radiation when energized

1.1.2 To be operated only by qualified personnel

1.2 Warning Lights: Warning lights indicating "X-RAY ON" are activated on both sides of the instrument when a scan is initiated.

1.3 Interlock: The interlock is a safety control that immediately and automatically shuts down radiation when access to the bean is attempted while the radiation source is active. The interlock should be tested by OSU radiation safety inspections at regular intervals.

1.4 Key Control: The XRF is protected by keyed access to authorized personnel only. Authorization must be granted by the laboratory manager by contacting Whitacre.39@osu.edu.

1.5 Operating Log

1.5.1 Create a runlist for samples to be analyzed by XRF. The runlist indicates the samples to be run, the instrument operator. The beam voltage is a consistent 50kV.

1.5.2 Conduct analysis according to the procedure and download sections of the operating procedure below

1.5.3 From the raw download, calculate the minutes of beam time and copy to the XRF Operating Log (W drive/SEC lab/XRF/year/XRF Operating log.xls

2.0 Competency

2.1 New users will familiarize themselves with the written protocol.

2.2 New users will observe one imaging session from start to finish and take notes as needed.

2.3 After observing an imaging session from start to finish, the new user will begin participating in the procedure under supervision of the training lab member.

2.4 At the discretion of the training lab member, the new user will be allowed to do imaging sessions independently

3.0 SCOPE XRF Analysis of Soils

3.1 XRF analysis is utilized to determine the total elemental concentration for the following elements within a sample: Ba, Cs, Te, Sb, Sn, Cd, Ag, Pd, Mo, Zr, Sr, U, Rb, Th, Pb, Au, Se, As, Hg, Zn, W, Cu, Ni, Co, Fe, Mn, Cr, V, Ti, Sc, Ca, K, Cl, S, P, Si, Al, and Mg. It is a nondestructive technique insofar as the sample employed for XRF analysis can subsequently be subjected to additional analyses.

4.0 DEFINITIONS

4.1 Laboratory Control Sample: The laboratory control sample is a reference material whose elemental content is indicated on a Certificate of Analysis.

4.2 Preparation Blank: The Preparation Blank is a reference material (Blank 180-647) that consists of 99.995 % (w/w) SiO2.

4.3 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 a given method.

4.4 Reporting Limit: Lowest reportable concentration of an element based on a demonstrated accuracy of ±30% with a certified reference material.

4.5 Detection Limit: The theoretical limit of detection supplied by the manufacturer.

5.0 EQUIPMENT AND SUPPLIES

5.1 Niton FXL FM-XRF Analyzer.

5.2 Samples that have been processed to pass through sieve screen of 2 mm opening size.

5.3 Sample containers: bags of thin plastic (e.g., ziplock bags), or sample cups whose open end is covered by a circle of polypropylene thin film. If samples are contained in bags, approximately 1 teaspoon-full of sample should be utilized per bag. If samples are contained in cups, the sample should fully cover the thin film that is positioned at the cup opening.

5.4 Blank 180-647.

5.5 QC Material 180-661 (RCRA1)

5.6 CRM 180-649 (NIST 2709a)

5.7 NIST 2711a

5.8 RM 180-706 USGS SdAR-M2

5.9 DTSC material EM8

6.0 PROCEDURE

6.1 Press switch on back of instrument to turn it on.

6.2 Press latch upward on front of instrument to access touchscreen. Enter password

6.3 (1,2,3,4).

6.4 Press “Method Setup” to select analysis mode. When analyzing soil samples,

6.5 select “Soils” mode; when analyzing other materials, select “TestAll Geo” mode.

6.6 To begin analysis, press “Test.”

6.7 Open instrument lid. Place sample on center of surface so that it fully covers the

6.8 illuminated square. Close lid.

6.9 Press “Start.” Sample analysis will take approximately 217 s. Record the reading number – which will be indicated on the XRF screen – on the runlist.

6.10 Analyze all QC materials prior to analyzing samples. Repeat above steps until all samples have been analyzed.

6.11 Log off (System > log off).

6.12 Turn off instrument and return touchscreen to closed position.

6.13 Note: Instrument will not analyze samples unless it has been calibrated within the past 7 days. If calibration is required, a message will appear on the XRF screen. To perform calbration, go to System > System Check. To find out the date of the most recent calibration, go to: System > Specs.

7.0 Download Data

7.1 To begin downloading data from the XRF onto the desktop PC, connect the XRF

7.2 to the PC with the designated USB cable. (Note: the XRF must be on in order to download data from it).

7.3 Open Thermo Scientific NDT on the PC by clicking on the icon that is present on the desktop.

7.4 Click the “Download” icon at the top of the page.

7.5 Click the “Test” icon at the left of the pop-up. If the connection is good, an icon will pop up saying “Hardware is successfully communicating”. Click OK.

7.6 Click "Query Readings". This will bring up all readings stored in the XRF. Select desired readings. Alternatively, clicking the boxes under "Reading Types" will select all readings of that type.

7.7 Ensure that "W:\SEC lab\XRF\year (e.g., 2018)" is the destination folder.

7.8 Name the file ("XRF Year-#" e.g. "XRF 18-4").

7.9 Select the option that the data be simultaneously downloaded to MS Excel.

7.10 Click "Download" (located below "Query Readings"). The blue bar at the bottom of the pop-up shows the download's progress.

7.11 When finished, press Done. The data should now be shown in both the NDT program and in an Excel file that will open automatically.

8.0 QUALITY CONTROL

8.1 Laboratory Control Sample (LCS): The laboratory control sample must fall within ± 20% of the known value.

8.2 Reporting limit is set by the lowest value in the QC materials (3.4 – 3.8) that is accurate to ±30%. For analytes that fall below the reporting limit, must be run by USEPA 3051a to obtain values.

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

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

8.4 Preparation Blank: If an analyte is detected in the blank, concentrations for that analyte in samples should not be reported if they do not exceed 10x the blank concentration unless accuracy is demonstrated by the reporting limit.

9.0 REFERENCES

9.1 USEPA. 2007. Method 6200. Field Portable X-Ray Fluorescence Spectrometry For The Determination Of Elemental Concentrations In Soil And Sediment. In SW-846. U.S. Environmental Protection Agency, Washington, DC

SOP 2
Bulk Soil Processing and Homogenization for Laboratory Studies

Standard Operating Procedure 2

Bulk Soil Processing and Homogenization for Laboratory Studies
Soil Environmental Chemistry Program, The Ohio State University
Version 3

1.0 Scope of Method

1.1 This method provides soil processing procedures that ensures and maintains homogeneity of field collected soils (<2mm) within and across storage containers. This is necessary for comparable experimental results across laboratories for the same soil.

2.0 Definitions

2.1 homogeneity: Analyte homogeneity within a soil matrix is achieved when analyte variation between test portions of the sample are not significantly different at $p<0.1$

2.2 < 2mm: The size fraction of soil that passes through a No. 10 mesh screen.

2.3 <250 um: The size fraction of soil that passes through a No. 60 mesh screen.

3.0 Equipment and Supplies

3.1 Electric cement mixer.

3.2 Drying oven

3.3 2mm mesh sieve and catch pan.

3.4 250µm mesh sieve and catch pan.

3.5 Ro-Tap sieve shaker

4.0 Homogenization and < 2mm Sieving Procedure

4.1 Oven Dry soil at 60°C.

4.2 sieve soil to <2mm

4.3 Place soil to be homogenized into mixer.

4.4 Allow mixer to homogenize soil for two hours.

5.0 <250µm Sieving Procedure.

5.1 Place 200g (± 50g) of soil into 2mm sieve attached to catch pan and place lid atop the sieve/catch pan stack.

5.2 Secure sieve/catch pan stack in Ro-Tap sieve shaker.

5.3 Shake sieve/catch pan stack for 20 minutes.

5.4 The soil collected in the catch pan is the <250µm size fraction. Pour into appropriately labeled (sample name and <250µm) tubs.

5.5 Repeat procedure until desired amount of <250µm is obtained.

6.0 Homogeneity Evaluation

Adapted from McClure, 2001.

6.1 Sampling procedure

6.1.1 Divide homogenized sample into 8 containers, c = 8 containers.

6.1.2 Randomly obtain n = 3 test portions (sub-samples) from each container.

6.1.3 Analyze the n x c = 24 samples by USEPA Method 3051a for As.

6.2 Evaluate Within Container Variance

6.2.1 Calculate the Cochrans test statistic C_0 by dividing the largest within container variance (s_H^2) by the sum of all the within container variances ($\sum s_i^2$).

$$C_0 = s_H^2 / \sum s_i^2$$

6.2.2 Compare the calculated C_0 to the test statistic $C_{.05,c,(n-1)} = 0.52$. If $C_0 > 0.52$, the hypothesis that within-container variances are homogenous is rejected.

6.3 Across Container Variance

6.3.1 Use a one-way ANOVA to test across container variation to test the hypothesis:

$$H_0: \sigma^2_c = 0$$

At $p<0.1$

7.0 Corrective Action

7.1 If either within container or across container homogeneity tests fail, perform homogeneity evaluation (5.0) a second time.

7.2 If within container or across container homogeneity tests fail a second time, repeat homogenization procedure (4.0) and homogeneity evaluation (5.0).

8.0 Storage / Use of Processed Soil

8.1 Homogenized soil should be stored in 4 liter plastic or glass containers. Before use, the soil containers should be completely inverted 10 to 20 times to thoroughly remix soil and eliminating non-homogeneity due to settling during storage

9.0 References

9.1 McClure, R.D. 2001. A statistical model to evaluate analyte homogeneity for a material. Journal of AOAC International. 84:947-954

9.2 United States Environmental Protection Agency. Method 3051A. Microwave assisted acid digestion of sediments, sludges, soils, and oils. In SW-846; U.S. EPA: Washington, DC, 1998.

SOP 3
Lead Sorption Test of Potential Remedial Treatments, Johnson 2018

Standard Operating Procedure 3
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.

SOP 4
Soil Carbon and Nitrogen determination by Dry Combustion

Standard Operating Procedure 4

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.

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.

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		

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		

SOP 5
Oxalate Extraction for Reactive Metal Oxides, McKeague and Day, 1966

Standard Operating Procedure 5

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.

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		

SOP 6
Soil Moisture Holding Capacity, 0 bar

Standard Operating Procedure 6
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.

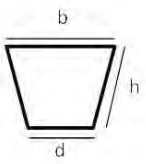
4.2 Weigh the empty pots with cheese cloth and record the mass (determining an average pot/cheesecloth mass may be appropriate when working with a large number of pots).

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.

SOP 7
Bioaccessible Arsenic and Lead, EPA Method 1340

Standard Operating Procedure 7

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.

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

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

SOP 8
pH, Tomas 1996

Standard Operating Procedure 8

pH, Tomas 1996
Soil Environmental Chemistry Program, The Ohio State University
Version 8

1.0 SCOPE

1.1 This method utilizes one sample preparation procedure for determination of pH (Thomas, 1996) and electrical conductivity in soil and soil like media. pH is an operationally defined measure of the H^+ ions that are active in soil solution, and EC provides an operationally defined measurement of a soils salinity (Rhoades, 1996).

2.0 DEFINITIONS

2.1 pH = -Log(H^+) - unit less

2.2 Electrical Conductivity is a measurement of a solutions ability to conduct electricity with units reported in decisiemens (dS m^{-1})

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

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

2.5 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.

3.0 EQUIPMENT AND SUPPLIES

3.1 pH meter and probe.

3.2 Conductivity meter and probe.

3.3 pH 4 and 7 buffer solutions.

3.4 1.399 dS m^{-1} (1.399 millimho (m℧ cm^{-1})) conductivity standard.

3.5 Deionized water (DI).

3.6 Reciprocating shaker.

4.0 PROCEDURE

4.1 Weigh 10g soil and add 10mL DI to 50mL centrifuge tube to make a 1:1 soil:deionized water solution.

4.1.1 Record pipette calibration in Appendix (10ml ± 0.2mL).

4.2 Place on reciprocating shaker for 30 minutes, remove and let stand for 10 minutes.

4.3 Calibrate pH meter using pH 4 and 7 buffer solutions according to manufacturer recommendations and record in appendix.

4.4 Insert the electrode directly into the soil suspension but not touching the bottom of the tube, allow meter to stabilize and read pH.

4.5 Rinse electrode with deioized water in between each samp

4.6 Calibrate the EC meter by adjusting the temperature correction on the conductance meter to match the standard solution EC value (appropriate when standard solution and soil extract are the same temperature).

4.7 Insert the electrode directly into the soil suspension making sure that the probes of the electrode are in contact with the solution and report conductance in millimho ($m\mho\ cm^{-1}$) off of the meter.

4.8 Rinse electrode with deionized water in between each sample.

5.0 QUALITY CONTROL

5.1 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.

5.2 Sample Duplicates: The % relative standard deviation (%RSD) must be no more than 20%. One duplicate analysis from each group of samples of a similar matrix type and concentration (i.e., low, medium) must be run at an interval of every twenty samples processed.

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

6.0 REPORTING

6.1 Fill in appendix for pipettes used during the course of this SOP.

6.2 Unit conversions:

6.2.1 1000 micromho ($\mu\mho\ cm^{-1}$) = 1 millimho ($m\mho\ cm^{-1}$)

6.2.2 1 millimho ($m\mho\ cm^{-1}$) = 1 deciSiemens ($dS\ m^{-1}$)

7.0 CORRECTIVE ACTION

8.0 REFERENCES

8.1 Brady, N.C. and R.R. Weil. 1996. The Nature and Property of Soils. Prentice-Hall Inc. Upper Saddle River, NJ.

8.2 Kabata-Pendias, A. 1992. Trace Elements in Soils and Plants. 2nd ed. CRC Press, Boston, MA, USA.

8.3 Rhoades, J.D. 1996. Salinity, electrical conductivity, and total dissolved solids. p. 417-435. *In* D.L. Sparks (ed.) Methods of Soil Analysis. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.

8.4 Thomas, G.W. 1996. Soil pH and soil acidity. p. 475-490. *In* D.L. Sparks (ed.) Methods of Soil Analysis. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.

9.0 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

pH Calibration		
pH 4 Buffer	Expiration Date	Start date of use

pH 7 Buffer	Expiration Date	Start date of use

% Slope		

10.0 INTERPRETATION

10.1 Soil pH is important when considering human and plant health. The solubility of metals in soil is influenced by soil pH. Growing plants in contaminated soil can result in seemingly healthy plants that have levels of metals toxic to humans (Kabata-Pendias, 1992). Soil pH affects plant growth primarily through nutrient availability. Plant essential nutrients tend to be most available to the plant at a neutral pH. A soil pH range of 5.5 to 8 is ideal for most plants (Brady and Weil, 1996).

SOP 9
Mehlich III Extractable Lead and Phosphorus, Mehlich 1984

Standard Operating Procedure 9

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

SOP 10
Total TAL Metals (Except Mercury), EPA 3051A

Standard Operating Procedure 10

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

SOP 11
SPLP TAL Metals (Except Mercury), EPA 1312

Standard Operating Procedure 11

SPLP TAL Metals (Except Mercury), EPA 1312

Soil Environmental Chemistry Program, The Ohio State University

Version3

1.0 Scope of Method

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

2.0 Definitions

2.1 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.

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

3.0 Equipment and Supplies

3.1 Agitation apparatus

3.2 high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride(PVC) extraction vessels

3.3 pH Meter accurate to 0.05 units

3.4 Laboratory Balance: Any laboratory balance accurate to within + 0.01 grams may be used (all weight measurements are to be within + 0.1 grams).

3.5 60/40 weight percent mixture of 10% H_2SO_4/ 10% HNO_3.

3.6 ≥18 MΩ deionized water (DI).

3.7 Laboratory Balance: Any laboratory balance accurate to within +/- 0.01 grams may be used (all weight measurements are to be within +/- 0.1 grams)

4.0 Procedure

4.1 Oven dry sample at 60°C.

4.2 Grind solid sample until it is capable of passing through a 9.5 mm sieve.

4.3 Prepare extraction solution.

4.3.1 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 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.

4.3.2 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.

4.4 Weigh 1.5g of sample into extraction vessel.

4.5 Add 30g/mL of extraction fluid. Calibrate fluid dispenser and record in Pipette Calibration table.

4.6 Close the extractor bottle tightly, secure in agitation device, and agitate for 18 ± 2 hours.

4.7 Remove from rotary agitation device, centrifuge at 10,000g for 15 minutes, and remove 25 mL into falcon tubes for ICP analysis. Samples should be preserved by addition of 1 drop of concentrated HNO_3. Calibrate pipette used to remove solution and record in Pipette Calibration table.

4.8 To continue the extraction; add 25 g/mL of extraction fluid and replace tubes to agitation device. Calibrate fluid dispenser and record in Pipette Calibration table. Agitate for 18 ± 2 hours and repeat process until 20 time points have been removed or the analyte concentration has become asymptotic.

5.0 Quality Control

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

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

5.2 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.

6.0 References

6.1 United States Environmental Protection Agency. Method 1312. Synthetic Precipitation Leaching Procedure. In SW-846; U.S. EPA: Washington, DC, 2007.

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

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

SOP 12
EPA 6010, ICP-AES

Standard Operating Procedure 12
EPA 6010, ICP-AES
Soil Environmental Chemistry Program, The Ohio State University
Version 8

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

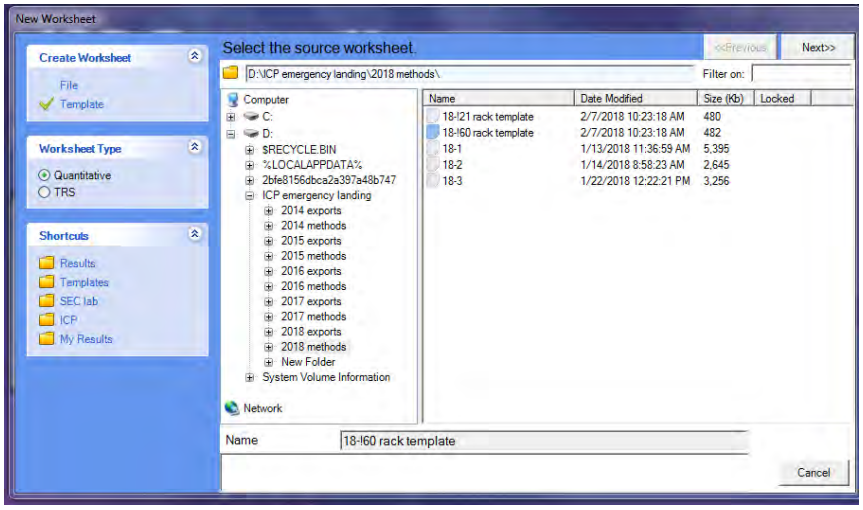
7.5.1 Load method from appropriate template

7.5.2 Agilent: Select File-New…. Under Create Worksheet, select Template.

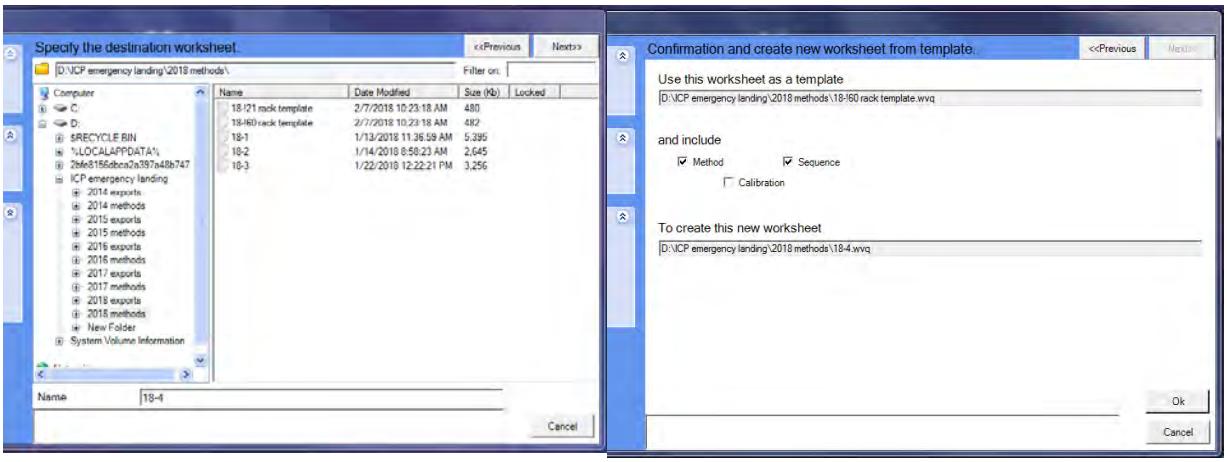
7.5.3 Go to D:\IDP emergency landing\YYYY methods\

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.

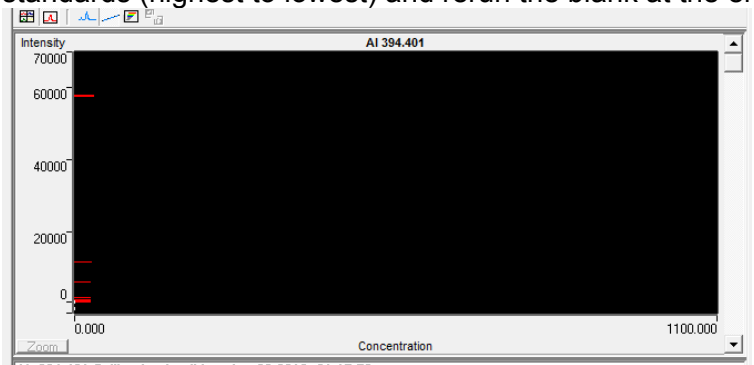
7.8.2 If more than ten standards are required, go to the "Autosampler Setup…" tab to change the standard rack from the 11 rack to the third 60 rack. Under "Rack Properties", change the Type and Use.

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

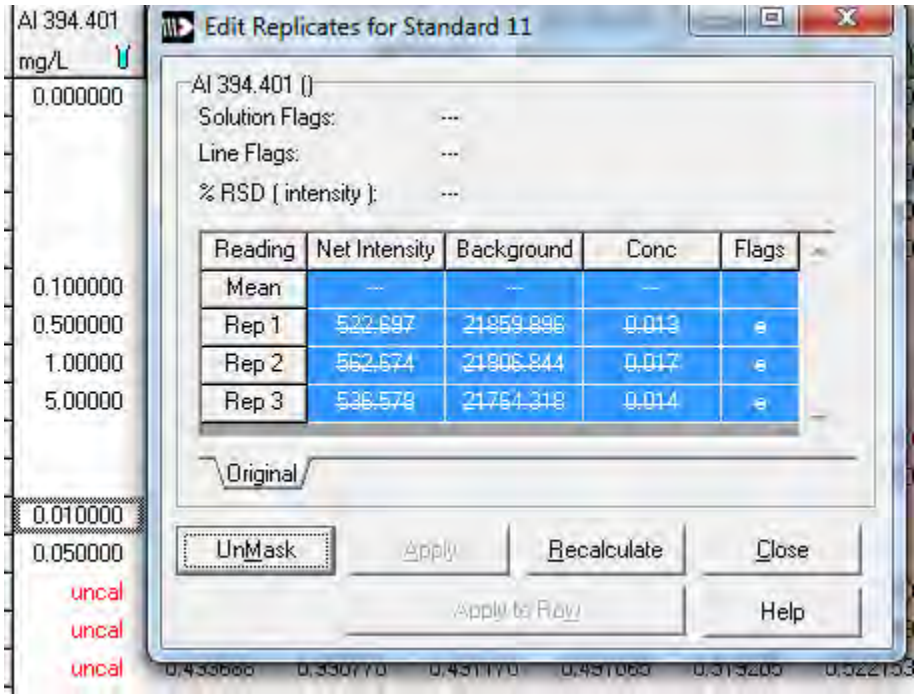
Standard	Flags	Int (c/s)	Std Conc	Calc Conc	Error	%Error
Blank	---	418.2	0.000000	0.003851	0.004	
Standard 5	---	1503.8	0.100000	0.099676	0.000	-0.324
Standard 6	---	5847.6	0.500000	0.483090	-0.017	-3.382
Standard 7	---	11453.1	1.00000	0.977869	-0.022	-2.213
Standard 8	---	57681.6	5.00000	5.05830	0.058	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.



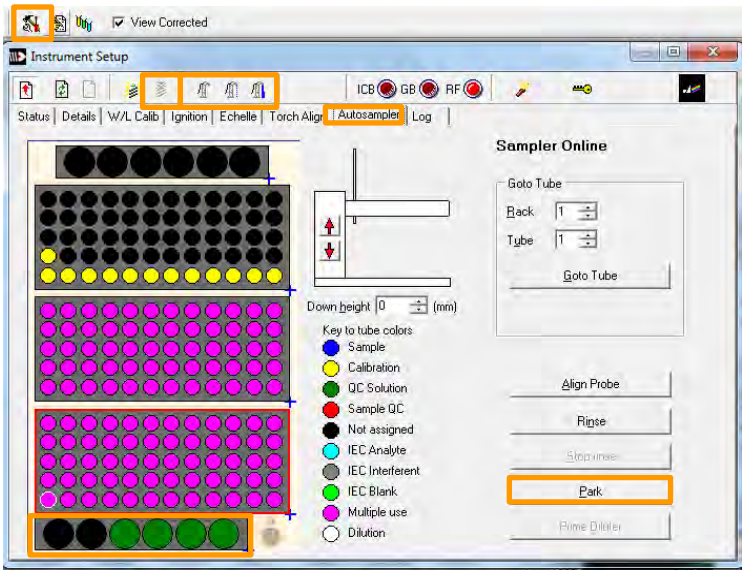
8.0 Running

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).

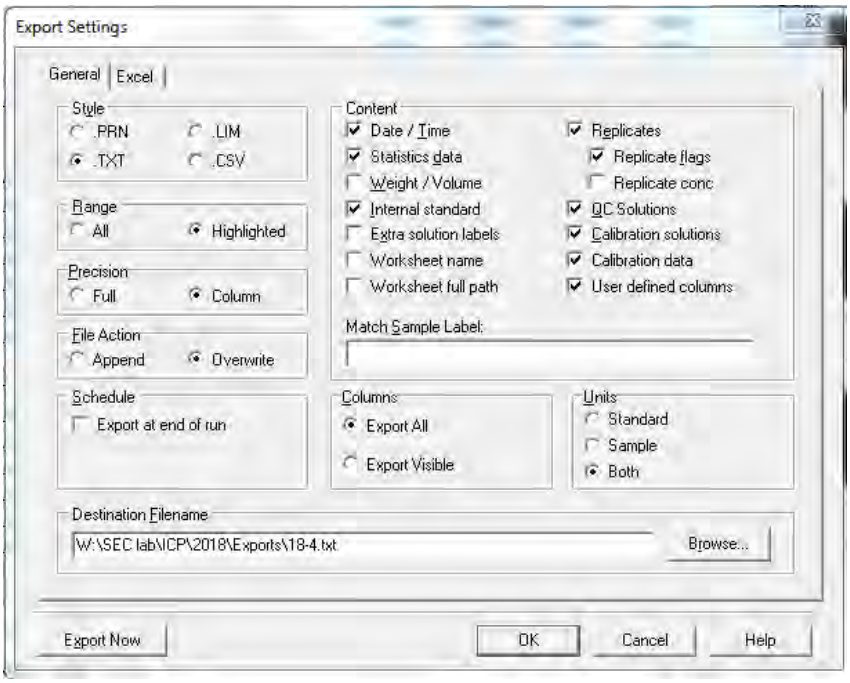
10.2.2 Bring up the Export Settings by pressing ctrl+E or File>Export Settings. The default settings are shown below.

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.

SOP 13
EPA 6010, ICP-AES Data Export and Summary

Standard Operating Procedure 13
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.

APPENDIX B
SOIL HOMOGENEITY TESTING RESULTS

Table B-1. Homogeneity Testing Results for Bulk Soil Samples Within and Across Containers

SUMMARY statistics

Groups	n	Average (n=3) Pb (mg/kg)[a]	Pb Within-Container Variance (mg/kg)
Bucket 1	3	1,427	50,893
Bucket 2	3	1,183	3,266
Bucket 3	3	1,283	63,290
Bucket 4	3	1,114	10,227
Bucket 5	3	1,245	10,846
Bucket 6	3	1,200	37,614
Bucket 7	3	1,322	8,396
Bucket 8	3	1,335	13,144
Cochran's results for within-container homogeneity			
Source of Variation	*C*	*C statistic*	
Between groups	0.32	0.52	
C < C statistic, accept the hypothesis that within-container variances are homogenous			
ANOVA results for across-container homogeneity			
Source of Variation	*F*	*P-value*	*F statistic*
Between groups	1.19	0.36	2.13
F < F statistic and P > 0.1, accept hypothesis that there is no statistical difference in Pb concentration between buckets			

Notes:

[a]Lead screening concentrations measured using a portable benchtop x-ray fluorescence (XRF) meter.

If *C* is < *C statistic*, soil within the containers is homogeneous

If *F* is < *F statistic*, this indicates across-container homogeneity

ANOVA = analysis of variance

C = calculated Cochran's statistic based on observed data

C statistic = P < 0.05 Cochran's test statistic

F = calculated F value based on observed data

F statistic = statistic used to evaluate ANOVA results

n = number of sub-samples

P-value = probability out of 1 of statistically different concentrations across containers

Table B-2. Within Container Results for Homogeneity Testing of Bulk Soil Samples

Groups	Lab Identifier	Lead Concentration (mg/kg)[a]	2-sigma error	Standard Deviation	Mean Lead by Bucket (mg/kg)
Bucket 1	1_A	1298.91	9.12		
	1_B	1687.22	10.26		
	1_C	1294.09	13.41	184.20	1426.74
Bucket 2	2_A	1184.74	12.69		
	2_B	1238.59	12.79		
	2_C	1124.35	12.42	46.66	1182.56
Bucket 3	3_A	1221.3	13.23		
	3_B	1559.58	14.73		
	3_C	1067.88	12.3	205.41	1282.92
Bucket 4	4_A	1138.64	12.75		
	4_B	1200.86	13.05		
	4_C	1003.08	11.86	82.57	1114.19
Bucket 5	5_A	1140.79	12.54		
	5_B	1349.08	13.68		
	5_C	1245.48	13.15	85.03	1245.12
Bucket 6	6_A	1288.42	13.19		
	6_B	1333.74	13.73		
	6_C	977.46	11.73	158.35	1199.87
Bucket 7	7_A	1401.99	13.94		
	7_B	1221.95	13.06		
	7_C	1341.58	13.72	74.81	1321.84
Bucket 8	8_A	1465.67	14.39		
	8_B	1289.55	13.4		
	8_C	1250.45	13.08	93.61	1335.22

Notes:

[a]Lead screening concentrations measured using a portable benchtop x-ray fluorescence (XRF) meter.

2-sigma error = variability estimate provided by the XRF unit

XRF = x-ray fluorescence

Table B-3. Homogenization and Bucket Laboratory Quality Control Results

Homogenization (Run 19-2)				
	SiO_2 blank	**NIST 2709a**		
		Measured	**Standard**	**Percent Recovery**
Units	mg/kg	mg/kg	mg/kg	%
Lead Result	<MDL	17.28	17.30	99.88
Bucket (Run 18-25)				
	SiO_2 blank	**NIST 2709a**		
		Measured	**Standard**	**Percent Recovery**
Units	mg/kg	mg/kg	mg/kg	%
Lead Result	<MDL	16.88	17.30	97.57

Notes:

Note that although blanks and standards were screened, the laboratory team did not complete duplicate sample screenings as indicated in Standard Operating Procedure (SOP). The triplicate XRF measurements completed for each sample obviated the value of further duplicate evalution.

% = percent

<MDL= below method detection limit

NIST 2709a = NIST (National Institute of Standards and Techonology) standard reference material for soil with certified total lead content of 17 mg/kg.

SiO_2 = quartz sand blank

Table B-4. Results for Soil Standard Reference Materials with Repeated Measures

Run	XRF ID	Lead (mg/kg)	Certified Lead Value (mg/kg)	Percent Recovery
NIST 2709a				
18-1	405	18.06	17	104.39
18-2	487	15.42	17	89.13
18-3	500	17.13	17	99.02
18-4	518	15.96	17	92.25
18-5	804	16.56	17	95.72
18-6	1013	17.75	17	102.60
18-7	1043	17.83	17	103.06
18-8	1104	16.84	17	97.34
18-9	1148	16.77	17	96.94
18-10	1174	16.13	17	93.24
18-11	1203	15.97	17	92.31
18-11a	1209	16.83	17	97.28
18-12	1209	16.83	17	97.28
18-13	46	17.02	17	98.38
18-14	64	16.72	17	96.65
18-15	75	14.73	17	85.14
18-16	92	17.26	17	99.77
18-16a	108	15.71	17	90.81
18-17	207	17.28	17	99.88
18-18	235	17.58	17	101.62
18-19	337	15.55	17	89.88
18-20	388	16.13	17	93.24
18-21	364	16.92	17	97.80
RCRApp 180-661				
18-11	1208	472.29	500	94.46
18-12	1208	472.29	500	94.46
18-13	45	465.57	500	93.11
18-14	63	588.95	500	117.79
18-16	91	585.57	500	117.11
18-16a	107	586.83	500	117.37
18-17	206	577.21	500	115.44
18-18	234	582.95	500	116.59
18-21	363	590.19	500	118.04
SiO_2 blank				
18-11	1207	<MDL	NA	NA
18-12	1207	<MDL	NA	NA
18-13	44	<MDL	NA	NA
18-14	62	<MDL	NA	NA
18-15	74	<MDL	NA	NA
18-16	90	<MDL	NA	NA
18-16a	106	<MDL	NA	NA
18-17	205	<MDL	NA	NA
18-18	233	<MDL	NA	NA
18-19	336	<MDL	NA	NA
18-20	387	<MDL	NA	NA
18-21	362	<MDL	NA	NA

Notes:

<MDL= below method detection limit

NA = not applicable

NIST 2709a = NIST (National Institute of Standards and Techonology) standard reference material for soil with certified total lead content of 17 mg/kg.

RCRApp 180-661 = NIST standard reference material for soil with certified total lead content of 500 mg/kg.

SiO_2 blank = quartz sand blank

XRF ID = x-ray fluorescence identification

APPENDIX C
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

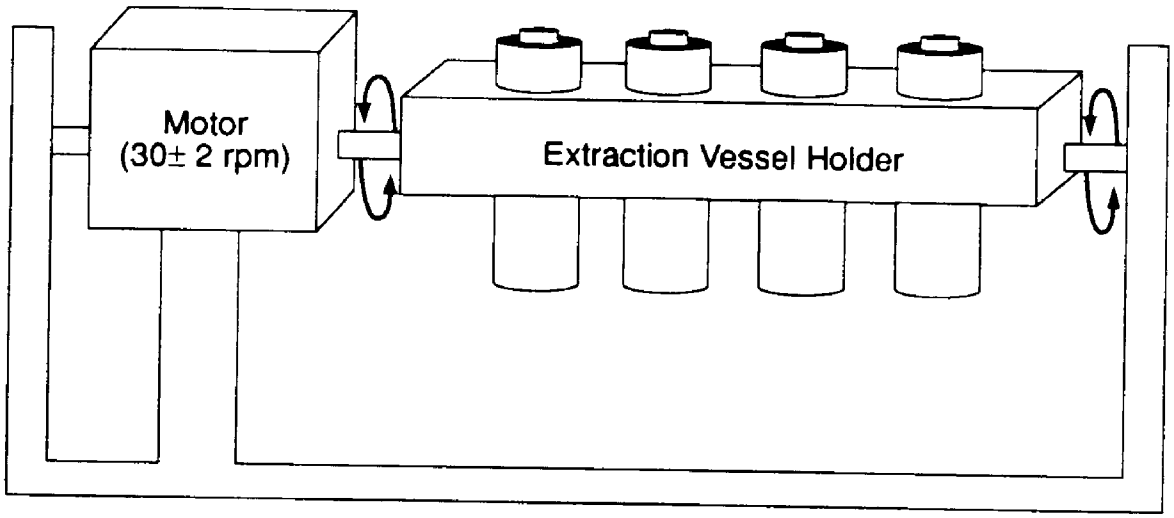


Figure 1. Rotary Agitation Apparatus

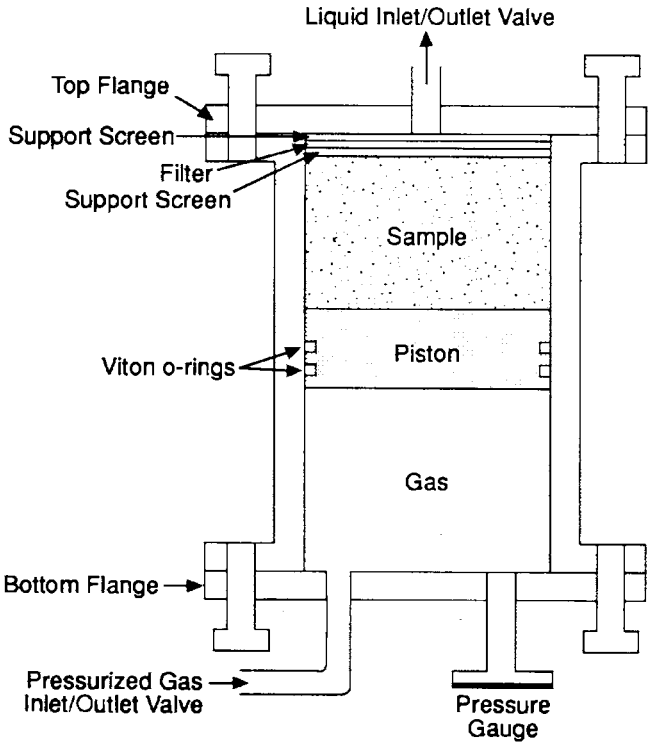
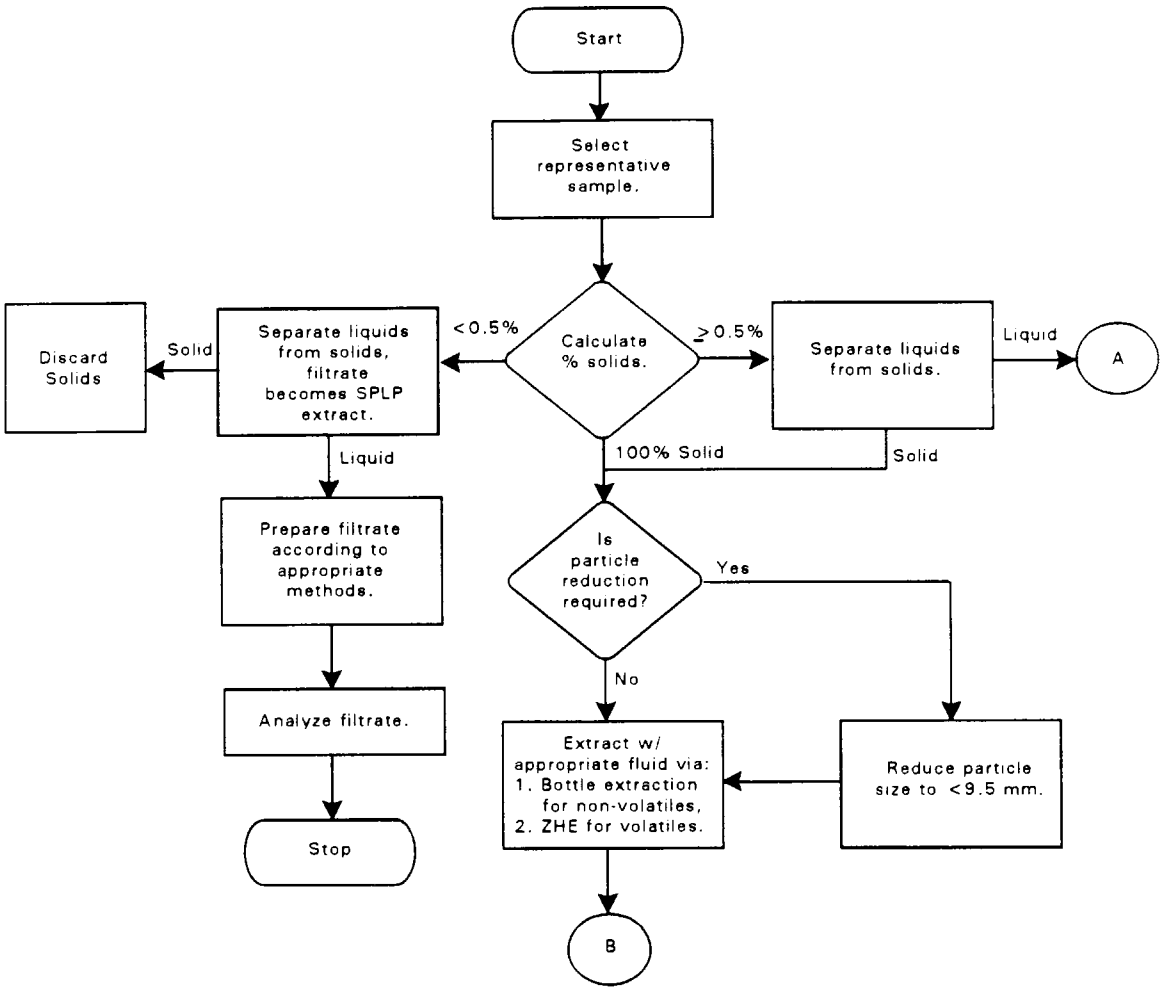
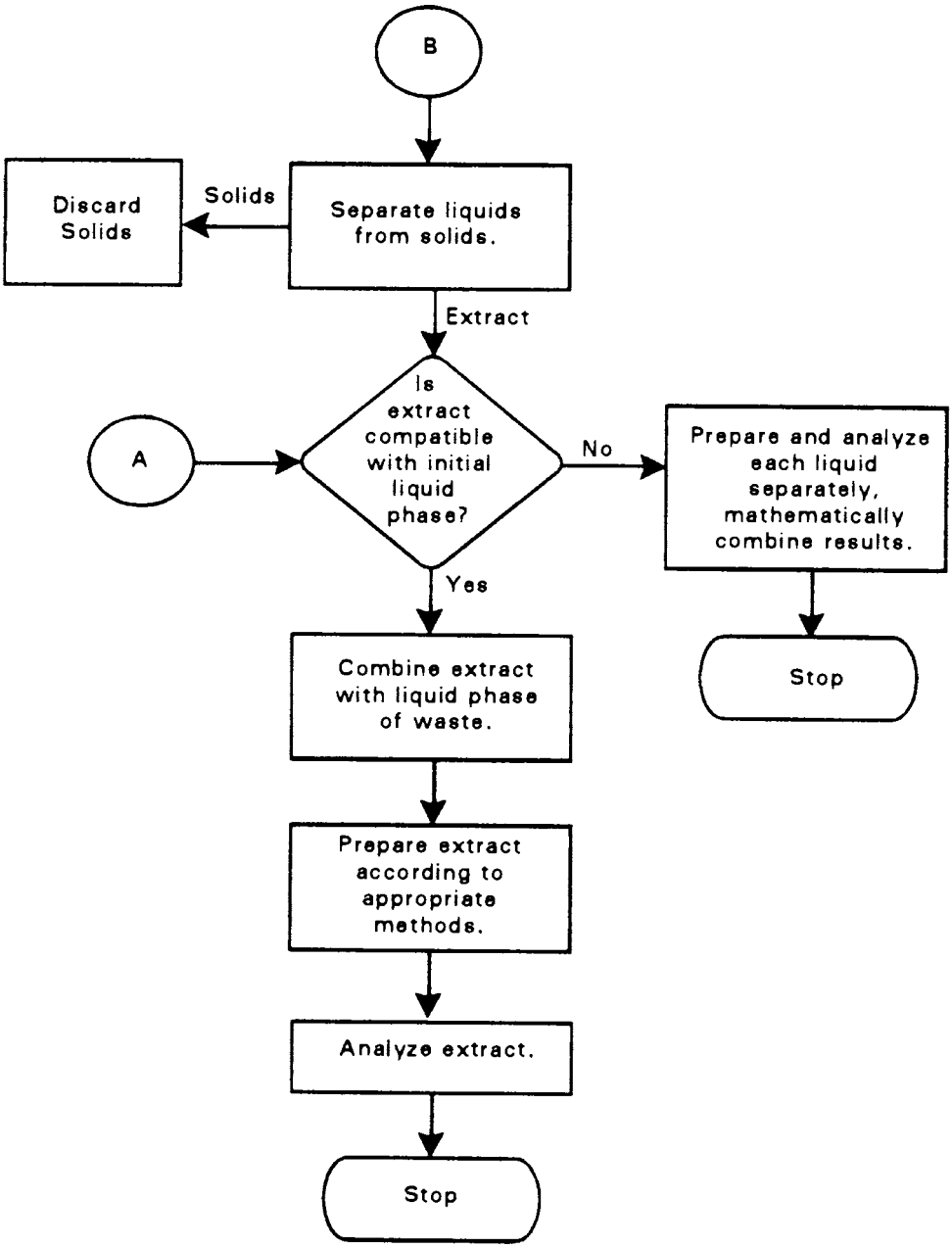


Figure 2. Zero-Headspace Extractor (ZHE)

SYNTHETIC PRECIPITATION LEACHING PROCEDURE



SYNTHETIC PRECIPITATION LEACHING PROCEDURE (continued)



APPENDIX D
POT ASSIGNMENT SUMMARY

Table D-1. Pot Assignment Summary

Pot Type	Amendment[a]	Application Method	Aplication Rate	Time Point	Replicate	Number of Pots
Control	**Water Holding Capacity Pots = 1 pot**					
	NA	Incorporated	NA	t_1	NA	1
	Bench Study Pots = 4 pots					
	NA	NA	NA	t_1, t_2, t_3	A B C D	4
Treatment	**Water Holding Capacity Pots = 4 pots**					
	For each amendment: Biochar, Biochar + Compost, Biosolid, Biosolid + Wood Ash, Soluble Phosphate, Soluble Phosphate + Biochar, Soluble Phosphate + Biosolid, Soluble Phosphate + Compost, Wood Ash, Wood Ash + Biochar, Compost, Wood Ash + Compost	Surface	Low	t_1	NA	1
			High	t_1	NA	1
		Incorporated	Low	t_1	NA	1
			High	t_1	NA	1
	Bench Study Pots = 32 pots per amendment					
	For each amendment: Biochar, Biochar + Compost, Biosolid, Biosolid + Wood Ash, Soluble Phosphate, Soluble Phosphate + Biochar, Soluble Phosphate + Biosolid, Soluble Phosphate + Compost, Wood Ash, Wood Ash + Biochar, Compost, Wood Ash + Compost,	Surface	Low	t_1	A B C D	24
			High	t_1	A B C D	
			Low	t_2	A B C D	
			High	t_2	A B C D	
			Low	t_3	A B C D	
			High	t_3	A B C D	
		Incorporated	Low	t_1, t_2, t_3	A B C D	8
			High	t_1, t_2, t_3	A B C D	

Notes:

NA = not applicable

t = time point. Soil samples will be collected for analysis to evaluate the progress of the treatments at three time points: at the beginning (t_1) of the program 1 month immediately after the amendments are applied, at 4 months (t_2), and at 6 months (t_3).

[a] See SATES Phase II Work Plan Tables 4-2a and 4-2b for treatment descriptions.

APPENDIX E
CORRECTIVE ACTION FORM

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: _____