UPPER COLUMBIA RIVER

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

Prepared for

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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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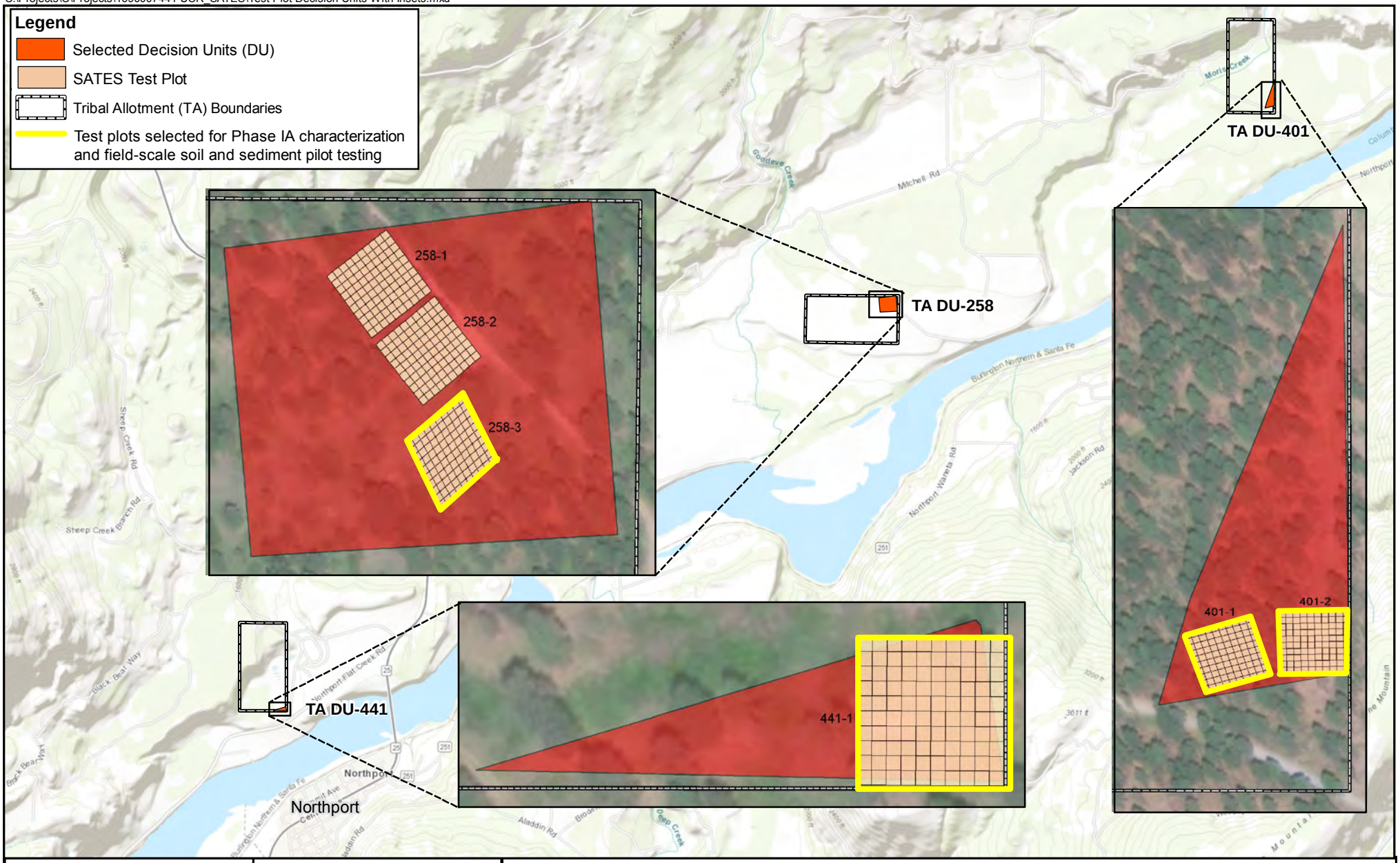
DRAFT



RAMBOLL

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

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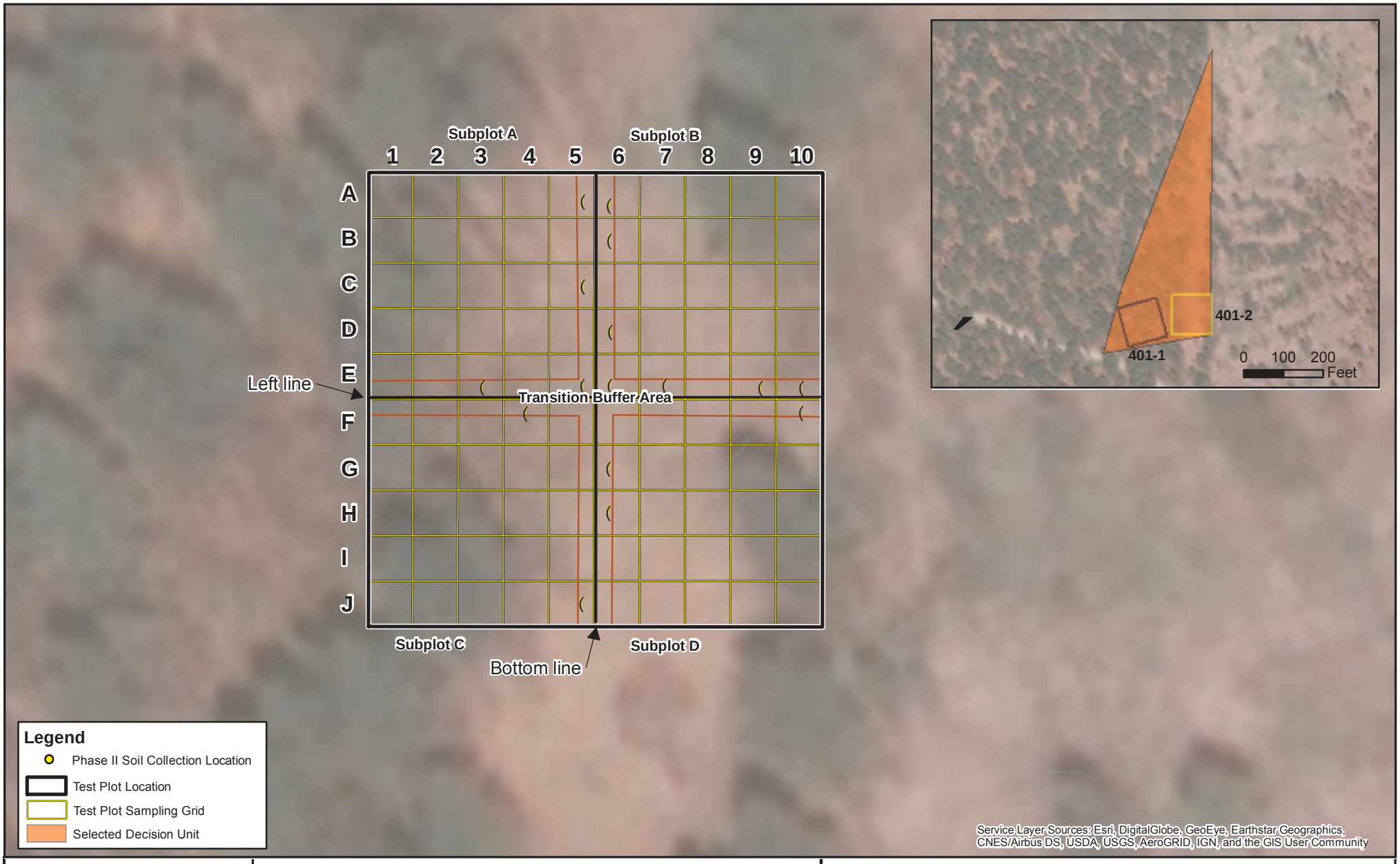


RAMBOLL

0 12.5 25 Meters

0 50 100 Feet

DRAFTED BY: RGM

Date: 3/6/2019

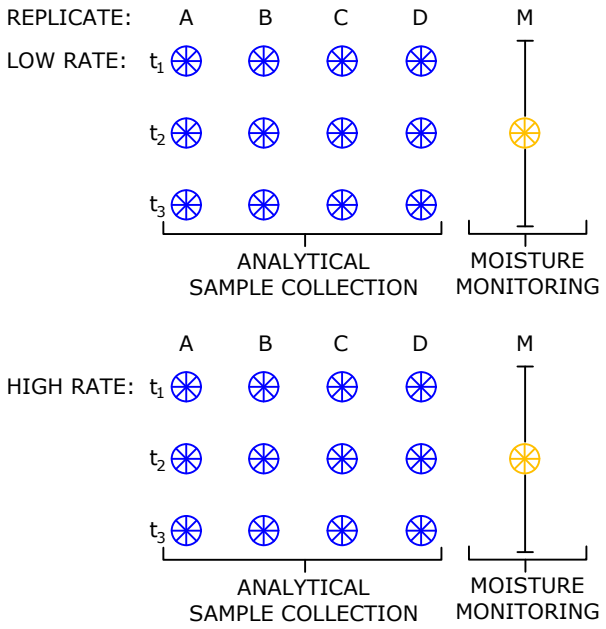
Map 2-1
Test Plot 401-2: Phase II Bench-Scale Treatability Testing
Soil Collection Locations
Upper Columbia River, WA

FIGURES

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

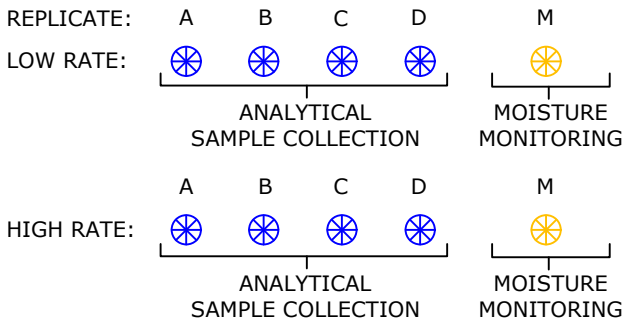
POT SET FOR EACH AMENDMENT

SURFACE APPLICATION OF AMENDMENT



SURFACE APPLICATION OF AMENDMENT POT SUBSET TOTAL = 26 POTS

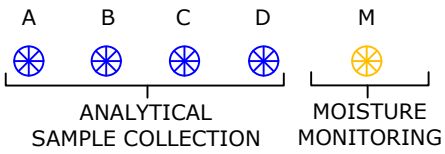
INCORPORATED AMENDMENT



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) • Polychlorinated biphenyls (PCBs)	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.

Note:
SATES = Soil Amendment Technology Evaluation Study

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

Analysis	Rationale	Laboratory
Volatile organic compounds	Additional pre-screening of amendments	ALS
Semi-volatile organic compounds	Additional pre-screening of amendments	ALS
Polychlorinated Biphenyls	Additional pre-screening of amendments	ALS
Soil moisture holding capacity	Determine water content for incubations	OSU
pH	Affects bioavailability of metals and plant nutrients	OSU
Electric Conductivitiy (Salinity)	Evaluate treatment effect on soil quality	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
SPLP TAL metals (except mercury)	Monitor changes in leachability of metals	OSU
Mercury	Additional pre-screening of amendments and assess potential changes due to treatment	ALS
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:

ALS = ALS Environmental Laboratory

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 Soil 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 May be collected in the same jar as mercury	5
Polychlorinated biphenyls	EPA 3540/3541/3550/3546	Soxhlet/auto-Soxhlet/sonication/microwave	8082A - Low Level	GC/ECD	Amendments	Baseline	NA	120 May be collected in the same jar as SVOCs and mercury	1
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									
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
Soil moisture holding capacity	0 bar	Water saturation	Cassel and Nielsen 1986	Gravimetric	Baseline, treatments	Baseline	<2 millimeter soil + bulk amendment	400	25
pH	NA	NA	Thomas 1996	Electrode	Baseline, treatments, and controls	Baseline, t_1, t_2, t_3	<2 millimeter	5	592
Electrical Conductivity (Salinity)	NA	NA	SM2510B	Conductivity meter	Treatments and controls	Baseline, t_1, t_3	<2 millimeter	5	209
Total TAL metals (except mercury)	EPA 3051A	Acid digestion	EPA 6010	ICP-AES	Baseline	Baseline	<2 millimeter	0.5	4
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
Mercury	7471B	Acid/Permanganate digestion	7471B	CVAA	Baseline	Baseline	<2 millimeter	15	4
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 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
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 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
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
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]

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 Soil Mass Per Sample (grams)	Total Number of Original Samples

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 = U.S. 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
SVOCs = semi-volatile organic compounds
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 6-3a. Analytical Parameters, Methods, and Target Laboratory Reporting Limits - The Ohio State University Laboratory

Analyte	Units	CAS Number	Laboratory MDL[1]	Laboratory RL[1]	Preservation	Holding Time (days) *From the time OSU containerizes the sample
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						
Soil moisture capacity	%	NA	NA	NA	Oven dry at 60°C	60
pH	unitless	NA	NA	NA	Oven dry at 60°C	24 hours
Electrical Conductivity (Salinity)	mS/m	NA	NA	NA	Oven dry at 60°C	28
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
Mehlich III extractable lead and phosphorus	mg/kg	NA	NA	NA	Oven dry at 60°C	180
Mineralizable nitrogen	mg/kg	NA	Equal to RL	Varies[2]	Oven dry at 60°C	60
Total carbon and nitrogen	%	NA	Equal to RL	Varies[2]	Oven dry at 60°C	60
Total organic carbon	%	NA	1,000	1,000	Oven dry at 60°C	60
Lead/arsenic and general soil mineralogy	NA	NA	NA	NA	Oven dry at 60°C	180

Notes:

1. MDL and RL concentrations are reported in mg/kg dry weight, unless otherwise noted.

2. 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.

% = percent
CAS = Chemical Abstracts Service
MDL = method detection limit
mg/kg = milligram(s) per kilogram
mg/L = milligram(s) per liter
mS/m = millisemen(s) per meter
NA = not applicable
RL = reporting limit
SPLP = synthetic precipitation leaching procedure
TAL = target analyte list
USEPA = U.S. Environmental Protection Agency

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

Analyte	Units	CAS Number	Laboratory MDL[1]	Laboratory RL[1]	Preservation	Holding Time (days measured from the time OSU containerizes the sample)
VOCs[2] (8260C)						
1,1,1,2-Tetrachloroethane	µg/kg	630-20-6	0.11	5.0	One methanol and two sodium bisulfate preserved vials (at a ratio of 1 mL of preservative to 1 g of material)	14
1,1,1-Trichloroethane (TCA)		71-55-6	0.11	5.0		
1,1,2,2-Tetrachloroethane		79-34-5	0.13	5.0		
1,1,2-Trichloroethane		79-00-5	0.15	5.0		
1,1-Dichloroethane		75-34-3	0.12	5.0		
1,1-Dichloroethene		75-35-4	0.25	5.0		
1,1-Dichloropropene		563-58-6	0.13	5.0		
1,2,3-Trichlorobenzene		87-61-6	0.19	20		
1,2,3-Trichloropropane		96-18-4	0.45	5.0		
1,2,4-Trichlorobenzene		120-82-1	0.13	20		
1,2,4-Trimethylbenzene		95-63-6	0.054	20		
1,2-Dibromo-3-chloropropane		96-12-8	0.4	20		
1,2-Dibromoethane (EDB)		106-93-4	0.094	20		
1,2-Dichlorobenzene		95-50-1	0.077	5.0		
1,2-Dichloroethane (EDC)		107-06-2	0.07	5.0		
1,2-Dichloropropane		78-87-5	0.13	5.0		
1,3,5-Trimethylbenzene		108-67-8	0.092	20		
1,3-Dichlorobenzene		541-73-1	0.094	5.0		
1,3-Dichloropropane		142-28-9	0.12	5.0		
1,4-Dichlorobenzene		106-46-7	0.086	5.0		
1,4-Dioxane*		123-91-1	14	250		
2,2-Dichloropropane		594-20-7	0.098	5.0		
2-Butanone (MEK)		78-93-3	0.9	20		
2-Chlorotoluene		95-49-8	0.12	20		
2-Hexanone		591-78-6	0.93	20		
4-Chlorotoluene		106-43-4	0.088	20		
4-Isopropyltoluene		99-87-6	0.064	20		
4-Methyl-2-pentanone (MIBK)		108-10-1	1.8	20		
Acetone		67-64-1	2.9	20		
Acrolein*		107-02-8	1.7	100		
Benzene		71-43-2	0.054	5.0		
Bromobenzene		108-86-1	0.088	5.0		
Bromochloromethane		74-97-5	0.24	5.0		
Bromodichloromethane		75-27-4	0.16	5.0		
Bromoform		75-25-2	0.14	5.0		
Bromomethane		74-83-9	0.2	5.0		
Carbon Disulfide		75-15-0	0.092	5.0		
Carbon Tetrachloride		56-23-5	0.094	5.0		
Chlorobenzene		108-90-7	0.065	5.0		
Chloroethane		75-00-3	0.74	5.0		
Chloroform		67-66-3	0.11	5.0		
Chloromethane		74-87-3	0.18	5.0		
cis-1,2-Dichloroethene		156-59-2	0.12	5.0		
cis-1,3-Dichloropropene		10061-01-5	0.13	5.0		
Dibromochloromethane		124-48-1	0.18	5.0		
Dibromomethane		74-95-3	0.28	5.0		
Dichlorodifluoromethane		75-71-8	0.12	5.0		
Ethylbenzene		100-41-4	0.094	5.0		
Hexachlorobutadiene		87-68-3	0.4	20		
Isopropylbenzene		98-82-8	0.081	20		
m,p-Xylenes		179601-23-1	0.1	5.0		
Methyl tert-Butyl Ether*		1634-04-4	0.12	5.0		
Methylene Chloride		75-09-2	0.16	10		
Naphthalene		91-20-3	0.13	20		

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

Analyte	Units	CAS Number	Laboratory MDL[1]	Laboratory RL[1]	Preservation	Holding Time (days measured from the time OSU containerizes the sample)
VOCs[2] (8260C) (continued)						
n-Butylbenzene	µg/kg	104-51-8	0.069	20	One methanol and two sodium bisulfate preserved vials (at a ratio of 1 mL of preservative to 1 g of material)	14
n-Propylbenzene		103-65-1	0.13	20		
o-Xylene		95-47-6	0.081	5.0		
sec-Butylbenzene		135-98-8	0.074	20		
Styrene		100-42-5	0.14	5.0		
tert-Amyl Methyl Ether		994-05-8	0.2	10		
Tetrachloroethene (PCE)		127-18-4	0.16	5.0		
Toluene		108-88-3	0.15	5.0		
trans-1,2-Dichloroethene		156-60-5	0.12	5.0		
trans-1,3-Dichloropropene		10061-02-6	0.11	5.0		
Trichloroethene (TCE)		79-01-6	0.15	5.0		
Trichlorofluoromethane		75-69-4	0.085	5.0		
Vinyl Acetate*		108-05-4	0.31	20		
Vinyl Chloride		75-01-4	0.18	5.0		
4-Bromofluorobenzene (surr)	%	460-00-4	0.17	N/A		
Dibromofluoromethane (surr)		1868-53-7	0.19			
Toluene-d8 (surr)		2037-26-5	0.073			
SVOCs[3] (8270)						
1,2,4-Trichlorobenzene	mg/kg	120-82-1	0.011	0.33	N/A	14 days to extraction, subsequently 40 days to analysis
1,2-Dichlorobenzene		95-50-1	0.018	0.33		
1,2-Diphenylhydrazine		122-66-7	0.014	0.33		
1,3-Dichlorobenzene		541-73-1	0.018	0.33		
1,4-Dichlorobenzene		106-46-7	0.018	0.33		
2,4,5-Trichlorophenol		95-95-4	0.018	0.33		
2,4,6-Trichlorophenol		88-06-2	0.014	0.33		
2,4-Dichlorophenol		120-83-2	0.016	0.33		
2,4-Dimethylphenol		105-67-9	0.015	0.33		
2,4-Dinitrophenol		51-28-5	0.11	2		
2,4-Dinitrotoluene		121-14-2	0.015	0.33		
2,6-Dinitrotoluene		606-20-2	0.016	0.33		
2-Chloronaphthalene		91-58-7	0.01	0.33		
2-Chlorophenol		95-57-8	0.0099	0.33		
2-Methyl-4,6-dinitrophenol		534-52-1	0.14	2		
2-Methylnaphthalene		91-57-6	0.011	0.33		
2-Methylphenol		95-48-7	0.017	0.33		
2-Nitroaniline		88-74-4	0.017	0.33		
2-Nitrophenol		88-75-5	0.014	0.33		
3,3'-Dichlorobenzidine		91-94-1	0.027	0.33		
3-Nitroaniline		99-09-2	0.018	0.33		
4-Chloro-3-methylphenol		59-50-7	0.017	0.33		
4-Chloroaniline		106-47-8	0.014	0.33		
4-Chlorophenyl Phenyl Ether		7005-72-3	0.016	0.33		
4-Methylphenol		106-44-5	0.017	0.33		
4-Nitroaniline		100-01-6	0.18	2		
4-Nitrophenol		100-02-7	0.15	2		
Acenaphthene		83-32-9	0.013	0.33		
Acenaphthylene		208-96-8	0.016	0.33		
Aniline		62-53-3	0.022	1		
Anthracene		120-12-7	0.014	0.33		

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

Analyte	Units	CAS Number	Laboratory MDL[1]	Laboratory RL[1]	Preservation	Holding Time (days measured from the time OSU containerizes the sample)
SVOCs (8270)[3] (continued)						
Atrazine*	mg/kg	1912-24-9	0.017	0.33	N/A	14 days to extraction, subsequently 40 days to analysis
Azobenzene		103-33-3	0.014	0.33		
Benz(a)anthracene		56-55-3	0.012	0.33		
Benzo(a)pyrene		50-32-8	0.02	0.33		
Benzo(b)fluoranthene		205-99-2	0.017	0.33		
Benzo(g,h,i)perylene		191-24-2	0.02	0.33		
Benzo(k)fluoranthene		207-08-9	0.019	0.33		
Benzoic Acid		65-85-0	0.14	2		
Benzyl Alcohol		100-51-6	0.017	0.33		
Biphenyl*		92-52-4	0.009	0.33		
Bis(2-chloroethoxy)methane		111-91-1	0.011	0.33		
Bis(2-chloroethyl) Ether		111-44-4	0.012	0.33		
2,2'-Oxybis(1-chloropropane)		108-60-1	0.014	0.33		
Bis(2-ethylhexyl) Phthalate		117-81-7	0.019	0.33		
Butyl Benzyl Phthalate		85-68-7	0.016	0.33		
Caprolactam*		105-60-2	0.15	0.33		
Chrysene		218-01-9	0.012	0.33		
Dibenz(a,h)anthracene		53-70-3	0.027	0.33		
Dibenzofuran		132-64-9	0.012	0.33		
Diethyl Phthalate		84-66-2	0.014	0.33		
Dimethyl Phthalate		131-11-3	0.016	0.33		
Di-n-butyl Phthalate		84-74-2	0.012	0.33		
Di-n-octyl Phthalate		117-84-0	0.024	0.33		
Fluoranthene		206-44-0	0.011	0.33		
Fluorene		86-73-7	0.013	0.33		
Hexachlorobenzene		118-74-1	0.015	0.33		
Hexachlorobutadiene		87-68-3	0.014	0.33		
Hexachlorocyclopentadiene		77-47-4	0.012	0.33		
Hexachloroethane		67-72-1	0.022	0.33		
Indeno(1,2,3-cd)pyrene		193-39-5	0.039	0.33		
Isophorone		78-59-1	0.014	0.33		
Naphthalene		91-20-3	0.014	0.33		
Nitrobenzene		98-95-3	0.026	0.33		
N-Nitrosodimethylamine		62-75-9	0.025	2		
N-Nitrosodiphenylamine		86-30-6	0.018	0.33		
N-Nitrosodi-n-propylamine		621-64-7	0.019	0.33		
Pentachlorophenol		87-86-5	0.13	2		
Phenanthrene		85-01-8	0.01	0.33		
Phenol		108-95-2	0.019	0.33		
Pyrene		129-00-0	0.014	0.33		
Pyridine*		110-86-1	0.02	0.33		
2,4,6-Tribromophenol (surr)	%	118-79-6	N/A	N/A		
2-Fluorobiphenyl (surr)		321-60-8				
2-Fluorophenol (surr)		367-12-4				
Nitrobenzene-d5 (surr)		4165-60-0				
Phenol-d6 (surr)		13127-88-3				
Terphenyl-d14 (surr)		1718-51-0				

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

Analyte	Units	CAS Number	Laboratory MDL[1]	Laboratory RL[1]	Preservation	Holding Time (days measured from the time OSU containerizes the sample)
PCBs (8082A-LL)						
Aroclor 1016	µg/kg	12674-11-2	2.1	10	N/A	14 days to extraction, subsequently 40 days to analysis
Aroclor 1221		11104-28-2	2.1	20		
Aroclor 1232		11141-16-5	2.1	10		
Aroclor 1242		53469-21-9	2.1	10		
Aroclor 1248		12672-29-6	2.1	10		
Aroclor 1254		11097-69-1	2.1	10		
Aroclor 1260		11096-82-5	2.1	10		
Aroclor 1262		37324-23-5	2.1	10		
Aroclor 1268		11100-14-4	2.1	10		
Mercury (7471B)						
Mercury	mg/kg	7439-97-6	0.002	0.02	NA	28

Notes:

1. MDL and RL concentrations are reported in mg/kg dry weight, unless otherwise noted.
2. The laboratory notes that, during the analysis of VOCs, high levels of phosphorus in fertilizer may have some surfactant effects that will hinder the analytes from purging out of the samples, such that spike recoveries may be low for the fertilizer analysis.
3. The laboratory notes that, during the analysis of SVOCs, high levels of phosphorus in fertilizer may cause low surrogate and matrix spike recoveries. Dilutions may be performed or RLs may be elevated.

* Compound is outside of the standard VOC or SVOC list of analytes and must be requested specifically on the chain-of-custody form submitted with the samples to ALS Environmental.

% = percent
CAS = Chemical Abstracts Service
MDL = method detection limit
mg/kg = milligram(s) per kilogram
mg/L = milligram(s) per liter
N/A = not applicable
RL = reporting limit
USEPA = U.S. Environmental Protection Agency

APPENDICES

APPENDIX A
STANDARD OPERATING PROCEDURES

(Revised July 2019 for inclusion in Work Plan Addendum No. 1)

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.

Standard Operating Procedure 4
Soil Carbon and Nitrogen determination by Dry Combustion
Soil Environmental Chemistry Program, The Ohio State University
Appendix A

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

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

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.

Standard Operating Procedure 5

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

Extraction Solution pH at time of extraction _____

Initials/Date _____

Pipette Calibration

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

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

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

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

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

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

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.

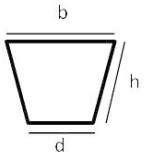
4.2 Weigh the empty pots with cheese cloth and record the mass (determining an average pot/cheesecloth mass may be appropriate when working with a large number of pots).

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.

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

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

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

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

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

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

6.0 Reporting

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

7.0 References

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

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

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

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

Appendix

Pipette Calibration
Verification

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

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

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

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

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

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

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

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

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

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 Method 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
	Iv	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 Method 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
ICP-AES, EPA Method 6010

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

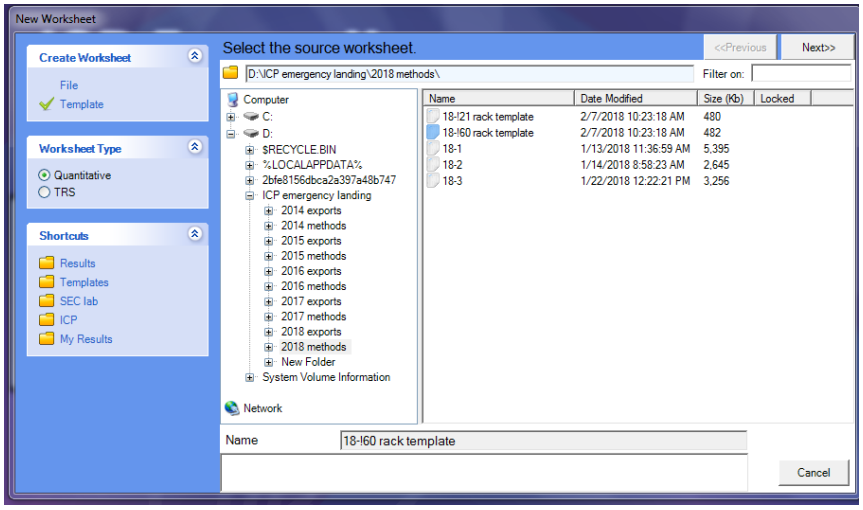
7.5.1 Load method from appropriate template

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

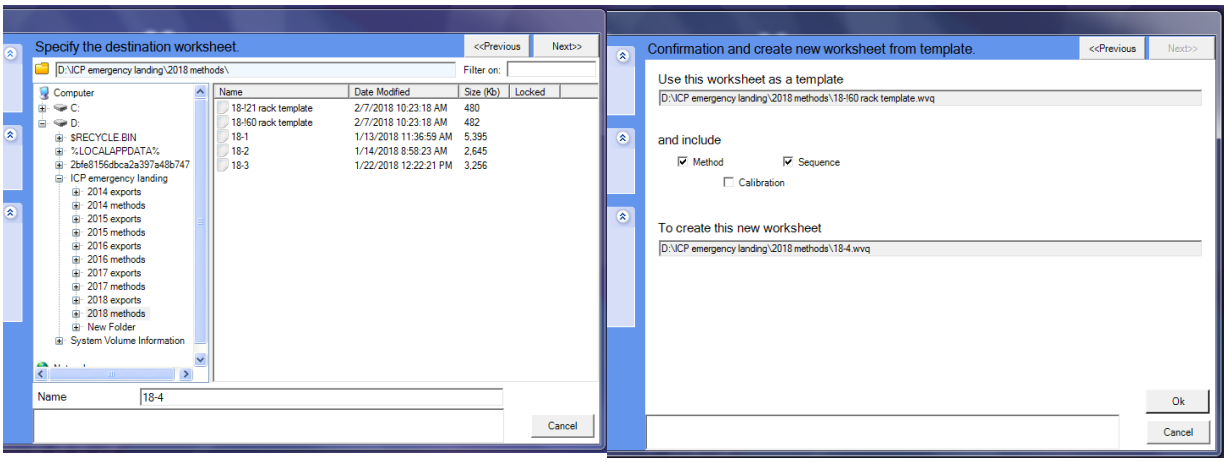
7.5.3 Go to D:\IDP emergency landing\YYYY methods\

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.

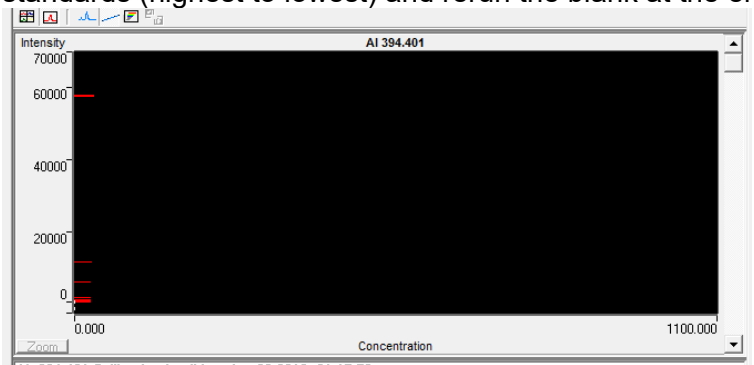
7.8.2 If more than ten standards are required, go to the "Autosampler Setup…" tab to change the standard rack from the 11 rack to the third 60 rack. Under "Rack Properties", change the Type and Use.

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

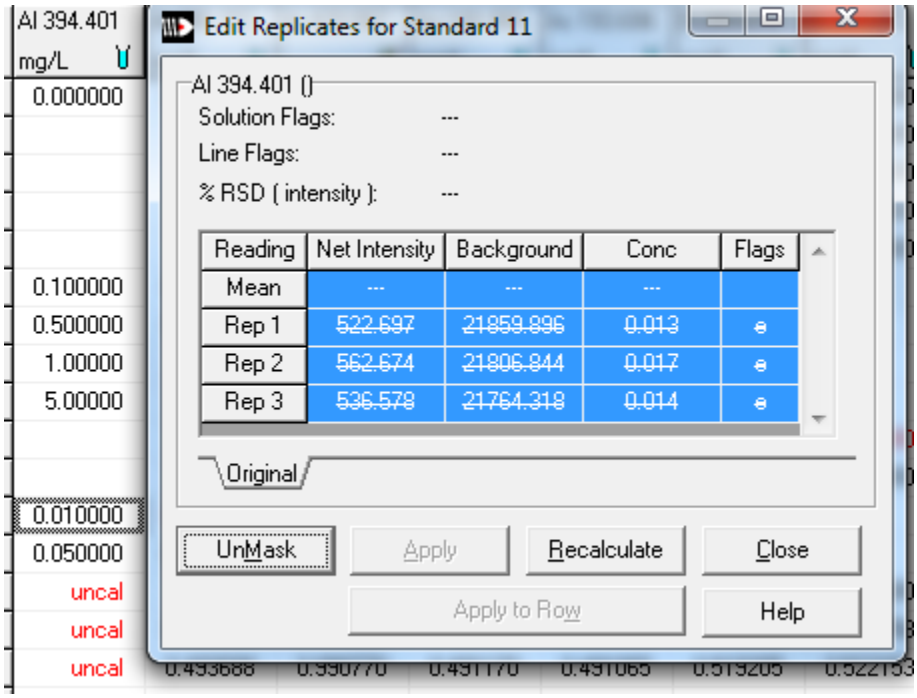
Standard	Flags	Int (c/s)	Std Conc	Calc Conc	Error	%Error
Blank	---	418.2	0.000000	0.003851	0.004	
Standard 5	---	1503.8	0.100000	0.099676	0.000	-0.324
Standard 6	---	5847.6	0.500000	0.483090	-0.017	-3.382
Standard 7	---	11453.1	1.00000	0.977869	-0.022	-2.213
Standard 8	---	57681.6	5.00000	5.05830	0.058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

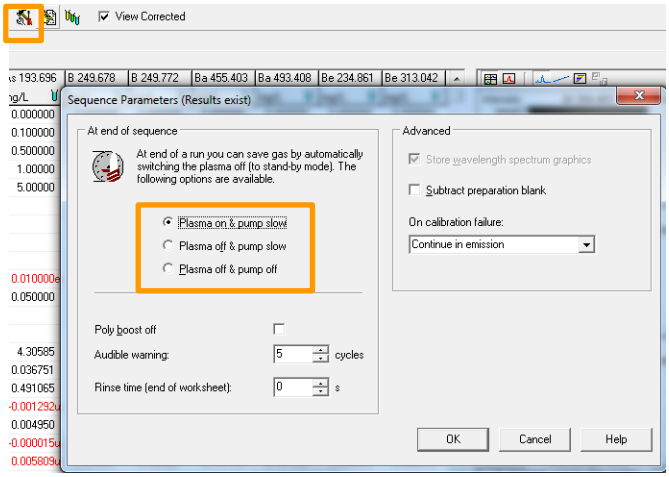
calculated concentrations from the regression within 15% for each standard in the calibration. If these conditions are not met, the line will not calibrate. In this case, examine the % error for each element on the "Single Graph Calibration Graph  screen.

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

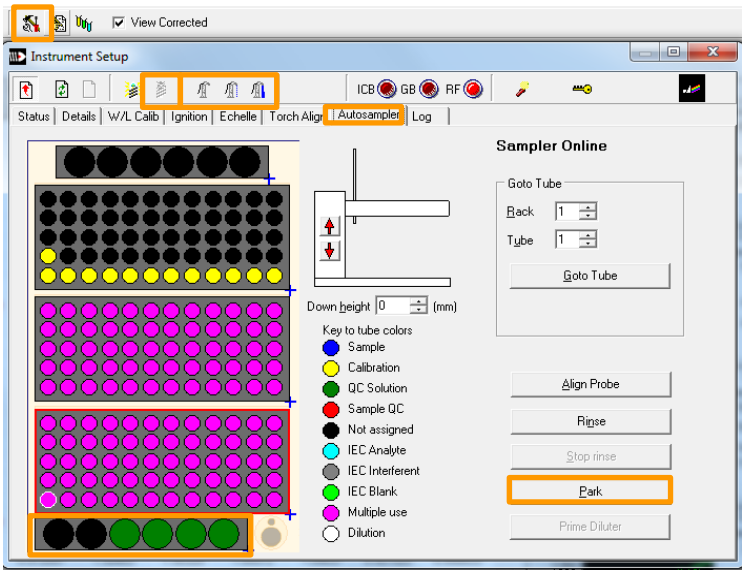
8.1 After calibration, the run can be started. QC sets are run after the initial calibration and after every 10 samples. QC actions can pause a run if the operator will be nearby (under Sequence Parameters, select "Plasma on & pump slow", or end a run if absent ("Plasma off & pump off").



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).

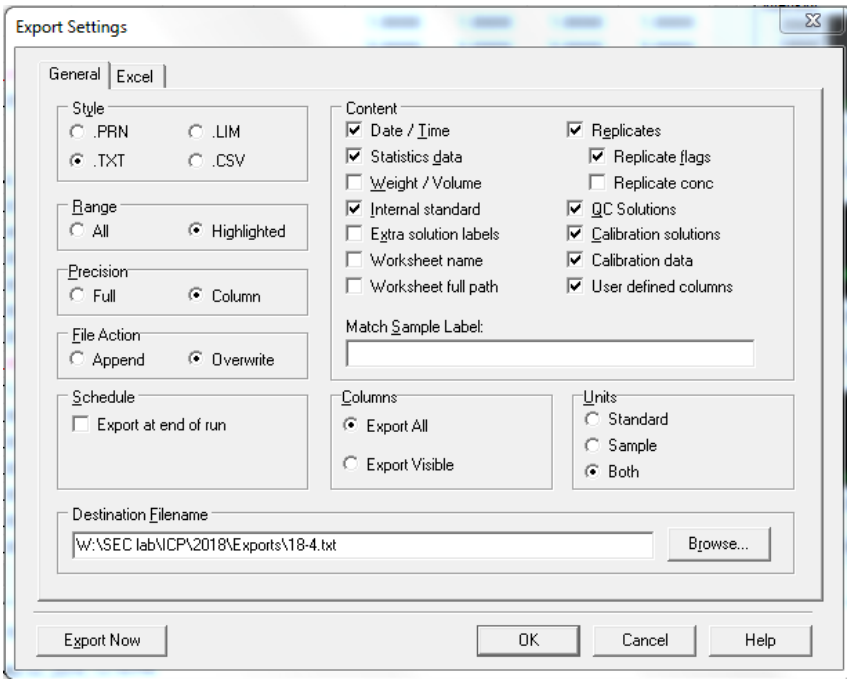
10.2.2 Bring up the Export Settings by pressing ctrl+E or File>Export Settings. The default settings are shown below.

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
ICP-AES Data Export and Summary, EPA Method 6010

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.

SOP 14
Mercury in Solid or Semisolid Waste, EPA Method 7471A/B

MERCURY IN SOLID OR SEMISOLID WASTE

EPA 7471 A/B

DOCUMENT I.D. MET-7471

Approved By: _____ Date: 4/13/18
Supervisor/Technical Director, Jeff Coronado

Prepared By: _____ Date: 4/13/18
Quality Assurance Manager, Carl Degner

Prepared By: _____ Date: 4/13/18
Laboratory Director, Jeff Grindstaff

Annual Review:

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Doc Control ID:	_____	Archived Date:	_____

TABLE OF CONTENTS

1) Scope & Applicability

1.1 This Standard Operating Procedure (SOP) describes the procedure used to determine the concentrations of Mercury in soils, sediments, freeze dried tissues, bottom deposits, and sludge-type materials using Method EPA 7471A or 7471B. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix. Method 7471 is a cold-vapor atomic absorption procedure.

1.2 The Method Reporting Limit (MRL) is 0.02 mg/kg. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. A Method Detection Limit (MDL) of 0.002 mg/kg has been achieved using this procedure. Refer to the ALS Kelso DQO Table for current data quality objectives.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DOD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD/ADM-DOD5)* may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 A representative aliquot of sample is prepared as described in this procedure. The mercury is reduced to its elemental state and aerated from solution and measured with an atomic absorption spectrometer. The mercury vapor passes through a cell positioned in the light path of the AA where absorbance is measured as a function of mercury concentration.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not listed. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8 Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.9 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.10 Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.11 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. The department supervisor/manager or designee performs final review and sign-off of the data.

4.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency is also the responsibility of the department supervisor/manager or designee.

5) Interferences

5.1 Potassium permanganate is added to eliminate possible interference from sulfide. Samples high in chlorides require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which absorbs radiation at 253 nm.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

6.3 Hydrochloric and/or Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Glass, plastic, and polytetraflouroethylene (PTFE) containers are suitable in most cases.

7.2 Non-aqueous samples are stored at 4 ± 2 ºC from receipt until analysis, unless otherwise dictated by project specifications.

7.3 Samples must be analyzed within 28 days of sampling.

8) Apparatus and Equipment

8.1 CETAC M-6100A Mercury Analyzer. See Attachments for instrument parameters.

8.2 Environmental Express Block Digestion Unit.

8.3 Pipettors, Eppendorf and Finn pipette fixed and adjustable volume.

8.4 Polypropylene graduated cylinders, 50 mL.

8.5 125 mL Digestion Vessel tubes.

8.6 Laboratory balance, top-loader capable of readings .001g (3-place). Mettler, Ohaus, or equivalent Standards,

9) Reagents, and Consumable Materials

9.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Standards, reagents and consumable material documentation shall indicate traceability to purchased neats or compounds. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

9.2 All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

9.3 Mercury stock solution (1,000 mg/L). Commercially prepared certified solution stored at room temperature. The expiration date determined by manufacturer.

9.4 Mercury working standard (100µg/L). Prepared from the intermediate stock solution listed above. Store at room temperature and prepare a new standard daily.

9.5 Laboratory Control Sample – ERA Priority Pollutant/CLP Inorganic Soil reference material. Store at room temperature in the original container and use the vendor expiration date.

9.6 Matrix spike solution (1 mg/L) – Prepare by making a 1:1000 dilution of the mercury stock solution. Store at room temperature and prepare a new standard monthly.

Note: See the Procedure section for details on preparation of calibration and ICV standards. See the Quality Assurance section for QC sample preparation.

9.7 Reagent water - ASTM Type II water (laboratory deionized water).

9.8 Acids - Purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the Method Reporting Limit.

9.8.1 Nitric Acid (HNO_3) 69-70% – JT Baker-Baker Instra-Analyzed® or equivalent.

9.8.2 Sulfuric Acid concentrated (H_2SO_4) – EMD-OmniTrace® or equivalent.

9.8.3 Hydrochloric Acid concentrated (HCL) – VWR – BHD-Aristar® or equivalent.

9.9 Potassium permanganate solution, 5% w/v. To prepare, add 50 g of solid reagent to 1000 mL of D.I. water and place on magnetic stir plate for approximately 30 minutes until dissolved.

9.10 Sodium chloride/hydroxylamine hydrochloride solution, 12% w/v each. To prepare, add 120g sodium chloride and 120 g of hydroxylamine hydrochloride to 1000 mL of D.I. water and place on magnetic stir plate for approximately 15 minutes until dissolved.

9.11 Stannous chloride, 10% w/v in HCl (7% v/v). To prepare, add 100g stannous chloride crystals and 70 mL of concentrated hydrochloric acid in 1000 mL of D.I. water. Seal lid on mixing bottle and shake until the stannous chloride is dissolved.

9.12 Aqua Regia – Prepare immediately before use by carefully adding 3 parts of concentrated HCL to one part of HNO_3.

10) Preventive Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in

the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

10.2 ALS staff performs all routine maintenance and troubleshooting. Preventative maintenance activities listed below should be performed when needed as determined by instrument performance (i.e. stability, sensitivity, etc.) or by visual inspection. Repairs of an extraordinary nature may or may not require factory service, depending on the nature of the task.

10.3 Keep the instrument free of dust, deposits, and chemical spills.

10.4 Replace the peristaltic and autosampler rinse tubing.

10.5 Remove and clean the Gas-Liquid separator.

10.6 Remove, dismantle, and clean the optical cells (sample cell and reference cell) including the sapphire windows.

10.7 Replace the Hg lamp bulb when the Lamp Over-Range is triggered. (The new instrument does not display a value).

11) Procedure

11.1 Sample Preparation

11.1.1 Mix the sample thoroughly to achieve homogeneity. For soil, sediment, solids, weigh approximately 0.5 g of well-homogenized sample and place in the bottom of a 125 mL digestion tube and record the weight to the nearest 0.01g. Add 5.0 mL of reagent water and 5.0 mL of aqua regia, then heat in the Block Digestion Unit for 2 minutes at 95ºC.

11.1.2 Cool then add 10 mL of reagent water and 15 mL of potassium permanganate solution. If the purple color does not persist for 15 minutes, add additional potassium permanganate until it does so. Any additional potassium permanganate solution must also be added to the blanks and standards in equal proportion.

Note: Spiking solution is added prior to acidification.

11.1.3 Mix thoroughly and place in the heating block for 30 minutes at 95ºC. The temperature of the block is monitored with a thermometer that is calibrated annually.

11.1.4 Cool and add 6 mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate. Perform this addition under a hood as Cl_2 could be evolved.

11.1.5 Add 27 mL of reagent water and the sample is ready for analysis. (The vapor generator does the step of adding the stannous chloride solution automatically.)

11.2 Calibration

11.2.1 To prepare calibration standards a 10 ppm intermediate stock solution is first prepared by aliquoting 1.0 mL of commercially prepared 1000 ppm stock standard into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This solution must be prepared monthly. Next, a 100 ppb working solution is prepared by aliquoting 1.0 mL of the 10 ppm intermediate stock solution into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This solution must be prepared daily.

Note: All standard aliquots are measured using calibrated fixed or adjustable volume autopipettors or calibrated disposable 5.0 or 10.0 mL pipettes.

11.2.2 Transfer 0, 0.1, 0.25, 0.5, 2.5 and 5.0 mL aliquots of the working solution to a series of labeled 125 mL digestion tubes. Add the appropriate amount of reagent water to bring each bottle to a volume of 5mL. Add 5.0 mL of aqua regia and heat in the heating block for 2 minutes at 95ºC. The final concentrations of the prepared standards are 0, 0.2, 0.5, 1.0, 5.0, 10.0 ppb.

11.2.3 The Initial Calibration Verification (ICV) is prepared by first making a 1000 ppb intermediate solution. 0.10 mL of commercially prepared 1000 ppm stock standard, from a different manufacturer and lot than the calibration standard, is aliquoted into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO_3. This solution must be prepared monthly. Prepare the ICV standard by aliquoting 0.25 mL to a labeled 125 mL digestion tube. Add the 4.75 mL of reagent water and 5.0 mL of Aqua Regia.

11.2.4 Cool and then add 10 mL of reagent water and 15 mL of potassium permanganate solution and return the tubes to the Block Digestion Unit for 30 minutes.

11.2.5 Cool and add 6.0 mL of sodium chloride-hydroxylamine hydrochloride solution. Add 27 mL of reagent water and the standards are ready for analysis.

11.2.6 CETAC Calibration and Sample Analysis

11.2.6.1 Turn on the CETAC instrument, including the Hg lamp, and autosampler. After this is done turn open the operating software (Mercury Analyzer 1.6.5).

11.2.6.2 The rinse station for the autosampler turns on automatically, but the peristaltic pump must be started manually. Make sure all sample uptake and drain tubes are placed correctly on the pump and are secured with the appropriate tension. Place the reagent uptake tube in the stannous chloride and start the pump.

11.2.6.3 From the software's main screen select "File", then: "New From". Under "Template Worksheet", click "Browse" and then select "Kelso Hg Template II". Enter the name of the worksheet and click: OK.

11.2.6.4 Go to the "Sequence Editor" tab to generate a sequence, then enter the QC and field samples to be analyzed in the appropriate order.

11.2.6.5 Transfer the solutions to be analyzed to labeled 12mL polyethylene test tubes and place them in the appropriate spaces on the autosampler trays.

11.2.6.6 Transfer the calibration blank and standards (0.2, 0.5, 1.0, 5.0, and 10 ppb) from their digestion tubes to the standard tubes located behind the autosampler trays. The calibration blank is placed in the left most tube and the other standards are placed in ascending order to the right.

11.2.6.7 Click start and the analysis will begin.

11.2.6.8 After the calibration standards have run the software will use linear regression to create a calibration curve based on the concentration and measured absorbance of each standard. The form of regression line is $y = mx + b$. If the correlation coefficient of the curve is greater than 0.995 the analysis will continue, if not the analysis will be terminated and corrective action will be needed by the analyst.

11.3 As the analysis sequence proceeds, next analyze the following QC standards.

- ICV (5.0 ppb standard prepared from a second source)
- ICB
- CRA (0.2 ppb calibration standard)
- CCV (5.0 ppb calibration standard)
- CCB

11.3.1 If either the ICV or CCV are different from their true values by more than 10% the software will terminate the analysis. If either the ICB or CCB is greater than the MRL the software will terminate the analysis. Method 7471A does not contain criteria for the CRA, however, the result must be a positive measured concentration. For 7471B analyses the criteria are ±30% of the true value. Also, specific project requirements may apply.

Note: For projects falling under DoD QSM requirements, the QSM criteria for CRA standards is ±20% and for ICB and CCB standards no analytes detected > LOD. (The ICV limit is as listed above.)

11.4 Sample Analysis

11.4.1 The samples are analyzed with the CETAC analyzer in the same manner as the calibration standards. The analyzer does the step of adding the stannous chloride solution automatically. Check the baseline between samples to verify that the spectrometer reading has stabilized at the normal baseline level.

11.4.2 The analytical sequence should be set up to include all samples, QC samples, blanks, and calibration verification standards at necessary intervals. Refer to the SOP for Sample Batches.

11.5 Sample digestion batches are analyzed with a set of CCV and CCB standards which are run at the beginning and end of the analytical run and at a minimum every 10 samples during the run. The same criteria listed above are applied to the CCVs and CCBs and if one is found to be outside these limits the analysis is terminated.

12) Quality Assurance/Quality Control Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 This method shall operate under the formal Quality Assurance Program established at ALS and must maintain records that define the quality of data that is generated. Data shall be compared to established criteria in order to determine if the results of the analyses meet the performance characteristics of the method. It is required that an initial demonstration of capability and periodic analysis of laboratory reagent blanks, laboratory fortified blanks, and other QC solutions as a continuing check on performance. The accuracy and precision of the procedure must be validated *before* analyses of samples begin, or whenever significant changes to the procedures have been made.

12.1.2 Initial demonstration of capability must be performed by each analyst performing sample analysis and documented in the laboratory records.

12.2 Method Detection Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates with a MDL spiking solution near the MRL and analyze. Refer to *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011).

12.2.2 Calculate the average concentration found (x) in µg/L, and the standard deviation of the concentrations (s) in µg/L for each analyte. Calculate the MDL for each analyte. Refer to *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011).

Note: Method Detection Limits are subject to change as new MDL studies are completed.

12.3 Limits of Quantification (LOQ

12.3.1 The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within 70-130% of the true values to verify the data reporting limit. Refer to *Performing Method Detection Limit Studies and Establishing Limits of*

Detection and Quantification (CE-QA011).

12.4 For method 7471B, an LLQC sample (a CRA that is carried through the digestion) must be analyzed to verify accuracy at the MRL. The recovery must be ±30%.

12.5 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual, in ADM-BATCH, *Sample Batches*. For this analysis, these include:

12.5.1 Prepare one method blank (MB) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures. The Method Blank should be < MRL. Re-digest the associated samples if sample levels are <20X MB level.

Note: For projects falling under DoD QSM requirements, the QSM criteria for method blanks is no analytes detected > ½ MRL.

12.5.2 Prepare one Laboratory Control Sample (LCS) per digestion batch, or per 20 samples. Weigh 0.25 g of the current lot of "Environmental Resource Associates Priority Pollutant/CLP Inorganic Soil" prepared reference material in to a 125 mL Digestion vessel tube and prepare as per the procedure.

12.5.3 Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

Apply LCS recovery criteria from the DQO Table, unless project-specific or in-house limits are established. For method 7471B, the LCS recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range.

Note: For DoD QSM projects, the QSM LCS criterion is 80-120%. If the LCS fails the acceptance criteria, re-digest the batch of samples.

12.5.4 Prepare one sample duplicate and one matrix spike sample per each digestion batch, or per twenty samples, whichever is more frequent. For the matrix spike, add 0.25mL of the matrix spike solution to the designated spike sample, resulting in a spike concentration of 0.5 mg/kg. At times, specific samples will be assigned as duplicates or spikes depending on client requirements.

Note: Duplicate samples are routinely analyzed; however some projects may require a MSD. All DOD projects require a MSD. The MSD sample is prepare as described above.

12.5.5 The RPD criterion for duplicates is 20%. If not, flag the data or re-digest samples. Apply matrix spike recovery criterion listed in the DQO Table, unless project-specific limits are required. For method 7471B, the recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range. For DoD QSM work, MS recoveries are assessed using the QSM LCS control limits. If the MS (and/or MSD where applicable) recovery is

outside acceptance limits proceed with the additional interference tests. Based on results of these tests, the physical nature of the sample (e.g. homogeneity), and any specific project requirements, a determination can then be made as to appropriate corrective action (e.g. re-digestion, reporting with a qualifier, alternative methodologies, etc.). If the analyte concentration is >4x the spike level the spike control limit is no longer applicable and no action is required.

Note: For DoD QSM projects, the duplicate RPD limit is 20% and MS recoveries are assessed using the QSM LCS control limits 80-120%.

12.5.5.1 Calculate percent recovery (%R) as:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

12.5.5.2 Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1= Higher Result
R2= Lower Result

12.5.6 Interference Tests: Prepare one post spike for every batch of samples and if samples are sufficiently high (10x the MRL/LOQ) a serial dilution. The serial dilution must agree within 10% of the original sample result. Post spike recovery acceptance limits for method 7471A and 7471B are 80-120% for project falling under SW-846 Update IV. When both the post spike and dilution tests fail all of the samples in the associated preparation batch must be quantified via Method of Standard Additions (MSA).

13) Data Reduction and Reporting (or Documentation and Records)

13.1 It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12.

13.2 Record all sample weight, volumes and dilutions on an A.A. benchsheet (see Attachments).

13.3 Solution concentrations are calculated by the Mercury Analyzer software based on the linear regression calibration curve created when the calibration standards are analyzed. The absorbance measured for each sample is applied to the linear regression curve and the final solution concentration is determined and displayed as the instrument result.

13.4 Calculate sample results using the data system printouts and digestion information. The digestion and dilution information is entered into the data system. The data system then uses the calculations below to generate a sample result. Solid samples are reported in mg/Kg:

$$mg/Kg\ (Sample) = C^{*}\ x\ Post\ Digestion\ Dilution\ Factor\ x\ \frac{Digestion\ Vol.(ml)}{Sample\ wt.(g)}\ x\ \frac{1mg}{1000ug}\ x\ \frac{1L}{1000ml}\ x\ \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in ug/L (in digestate).

NOTE: If results are to be reported on a dry weight basis as required by certain projects, the Sample Wt. (g) component of the equation should be the dry-weight derived from a determination of %moisture of a separate aliquot of the sample using the SOP for Total Solids.

13.5 Record all concentrations determined at the instrument and calculate the final results in mg/Kg. Record the final results on the A.A. Benchsheet.

13.6 The data packet for the sequence is submitted for review by supervisor or designee. The results are transferred to the appropriate report form located in the ALS network directory R:\ICP\WIP. Once the results are transferred, the report is reviewed.

13.7 A daily run log of all samples analyzed is maintained. All data should be printed and stored after operator has checked for evenness of burns. A copy of this document will go with each package of Tier III or higher data run that day.

13.8 Refer to the *SOP for Laboratory Data Review Process* (ADM-DREV) for general instructions for data review.

14) Method Performance

14.1 Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as in the determinative procedure. The method detection limit(s) and method reporting limit(s) are established for the determinative procedure. See *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* (CE-QA011.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented

on the treatment by generator record. See the ALS Lab Waste Management Plan for details.

16) Corrective Actions for Out-of-Control Data or Unacceptable Data

16.1 Refer to the SOP for *Non Conformance and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Review literature Review this SOP. Also review the applicable SDS for all reagents and standards used. Following these reviews, observe the procedure performed by an experienced analyst.

17.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.4 Training is documented following the *ALS-Kelso Training Procedure* (ADM-TRAIN). When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor acknowledges that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 There are no known differences from the reference method.

19) Summary of Changes

19.1 Updated to latest ALS SOP format.
19.2 Minor typographical, grammatical, and formatting revisions.
19.3 Section 12; Deleted obsolete IDL performance check requirement.
19.4 Updated safety terminology referenced throughout the document.
19.5 Updated reference section to include TNI and DOD.

20) References and Related Documents

20.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Final Update II, Method 7471A, September 1994.

20.2 USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update IV, Method 7471B, Revision 2, February 2007.

20.3 DoD Quality Systems Manual for Environmental Laboratories Version4.2/5.0/5.1.

20.4 TNI Standard, Volume 1- 2009.

21) Attachments/Appendices

21.1 Attachment 1 Instrument Parameters.

21.2 Table 1: Summary of Corrective Actions

Analysis Parameters

Instrument M-6100 Mercury Analyzer

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	30.00	60.00	50.00	4	2.00		253.65

Instrumental Zero

Zero before first sample: No

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)
5.00	10.00		

Standby Mode

Enabled: Yes

Standby Options: gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	Yes	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of
Lower (%)	Upper (%)	Lower (%)	Upper (%)	Determination
75	125	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

TABLE 1

Summary of Corrective Actions				
Method Reference	**Control**	**Specification and Frequency**	**Acceptance Criteria**	**Corrective Action**
EPA 7471A/B	ICAL	Prior to sample analysis	R2 ≥ 0.995	Correct problem then repeat ICAL
EPA 7471A/B	ICV	After ICAL	± 10%	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 7471A/B	CCV	Prior to sample analysis	± 10%	Correct problem then repeat CCV or repeat ICAL
EPA 7471A/B	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 7471A/B	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO	If exceeds limits, re-extract and re-analyze
EPA 7471A/B	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 7471A/B	Sample Duplicates	Include with each analysis batch (up to 20 samples)	≤ 20 % RPD	Re-homogenize and re-analyze if result is > 5 X the MRL

SOP 15
Volatile Organic Compounds by GC/MS,
EPA Method 8260

VOLATILE ORGANIC COMPOUNDS BY GC/MS

DOCUMENT I.D. VOC-8260

Approved By: _____ Date: 2/23/18
Organics Manager, Todd Poyfair

Prepared By: _____ Date: 2/23/18
Quality Assurance Manager, Carl Degner

Prepared By: _____ Date: 2/23/18
Laboratory Director, Jeff Grindstaff

Annual Review:

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Doc Control ID:	_____	Archived Date:	_____

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1) Scope & Applicability

1.1 This procedure is used to determine the concentration of volatile organic compounds in water and soil using USEPA Method 8260C. This method is also applicable to TCLP ZHE leachates and may also be applicable to various types of aqueous and non-aqueous waste samples.

1.2 The analyte reporting list and current Method Reporting Limits (MRL), Method Detection Limits (MDL)/Lower Limits of Quantitation (LLOQ), Limits of Quantitation (LOQ), and Limits of Detection (LOD) can be found in the ALS-Kelso Data Quality Objective (DQO) Tables.

1.3 The nominal quantitation range for water samples is 0.5 – 80 µg/L. The nominal quantitation range for low concentration soils is 5-200 µg/kg. The nominal quantitation range for high concentration soils is 50-8000 µg/kg.

2) Summary of Procedure

2.1 This procedure gives gas chromatographic/mass spectrometric (GC/MS) conditions for the detection of parts per billion (ppb) levels of volatile organic compounds. A sample aliquot is injected into the gas chromatograph (GC) by either the purge and trap method or by direct injection. The compounds are separated on a fused silica capillary GC column. The compounds are detected by a mass selective detector (MSD), which gives both qualitative as well as quantitative information.

2.2 In the purge and trap process an inert gas, helium, is bubbled through the sample aliquot, at room temperature. This gas stream sweeps the volatile organic compounds out of the aqueous phase and into the gas stream - it purges the compounds out of the sample. The gas stream then passes through a sorbent column which selectively adsorbs, (traps) these compounds out of the helium. The preparation and analysis of soil samples uses procedures described in USEPA Method 5030B or 5035/5035A. After the purging sequence is done, the sorbent column (the trap) is heated and desorbed onto the GC column. The GC column separates the compounds and passes then onto the MSD for identification and quantification.

2.3 The sensitivity of this method depends on the level of background contamination (i.e. interferences) rather than on instrumental limitations. Highly contaminated waste samples will require a methanol extraction prior to analysis. This will elevate the reporting levels and may mask low levels of compounds of interest.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The window begins with the injection of the tune verification standard. After this standard has passed the method specific criteria a 12 hour analysis window is started. Next, a calibration curve or a continuing calibration standard (CCV see below) is run. If the CCV meets the specified criteria, sample and QC analyses are run until the 12 hour time limit closes. A new window must then be opened and the sequence repeated.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Internal Standards - Internal standards are organic compounds which are similar to the analytes of interest but which are not found in the samples. The chosen internal standards are used to help calibrate the instrument's response and to compensate for slight instrument variations from injection to injection.

3.5 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked,

and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at 5-10X the MRL or at levels specified by a project analysis plan.

3.6 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.7 Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

3.8 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.9 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.10 Independent Verification Standard (ICV) - A standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.11 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.12 Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.13 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes:

- To help develop accurate methods of analysis
- To calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a

property at the state-of-the-art limit

- To ensure the long-term adequacy and integrity of measurement quality assurance programs.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

4.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the *ALS-Kelso Training Procedure* (ADM-TRAIN) is also the responsibility of the department supervisor/manager.

5) Interferences

5.1 Interferences by common laboratory extraction solvents, such as Methylene Chloride, Acetone, and Freon 113 can cause problems. The area where volatile organic analyses are performed is kept free of these solvents through the design of the air handling systems and its isolation from other areas of the lab that use these solvent. Laboratory experience has shown that when Methylene Chloride is a problem it is due to maintenance activities or air handling equipment failures. In the rare event this happens, ultra-pure water can be used for all samples and calibration standards for that analytical batch.

5.2 Other interferences include but are not limited to impurities in the inert purge gas, dirty plumbing/purge vessels, cross contamination by highly contaminated samples to clean ones in transport and storage, and carry over from one analysis to subsequent ones.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Environmental, Chemical Hygiene Plan and the appropriate SDS prior to beginning this method.

6.3 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Care must be taken when handling stock standard solutions of these compounds and should be handled in a hood.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Refer to procedures for methods 5030 and 5035 for sample container and collection procedures. Pre-cleaned sample containers are purchased from a lab equipment

supplier. All containers should be of glass or amber glass and equipped with a screw top cap and PFTE (Teflon) lined septa.

7.2 Samples collected using EPA Method 5035 should be shipped in Encore sample tubes or collected in VOA vials containing sodium bisulfate (low concentration) and/or methanol (high concentration).

7.3 Collect all samples in duplicate, triplicate when possible. Prepare the proper number of sample bottles/containers prior to the sampling event with preservatives to adjust the samples pH to <2 with 1:1 HCl (water samples).

7.4 Slowly fill sample bottles to just overflowing taking care not to flush out the preservative or to entrain air bubbles in the samples. Seal the bottles with PFTE lined septa toward the sample and invert to check for entrained air bubbles.

7.5 Experimental evidence has shown refrigeration at 4°C alone will not stop biological degradation of some aromatic volatile organics. Adjusting the pH of the replicate samples to less than two (pH <2) with 1:1 HCl (@ 2-3 drops per 40 mL) preserves samples for 14 days after collection. Residual chlorine can also degrade some organic compounds, generating trihalomethanes (THMs).

7.6 All samples must be stored at 4 ± 2°C and must be analyzed within 14 days of collection. See SOP VOC-5035 for additional holding time information. Any free product samples to be tested do not have any set holding times but should be analyzed as soon as possible.

7.7 The analysis of 2-CVE in water by method 8260 requires the collection of an unpreserved sample. 2-Chloroetheyl Vinyl Ether is highly reactive and preservation may accelerate loss by polymerization or other rapid chemical reaction. Therefore, the accuracy of results from a preserved sample cannot be guaranteed. If a client requests 2-CVE they must collect three preserved and three unpreserved vials and the sample must be logged in for a separate 2-CVE analysis.

8) Apparatus and Equipment

8.1 Gas Chromatograph/Mass Spectrometer System

8.1.1 Each GC/MS system is set up with a GC capable of cooling the GC oven/column, injection onto a capillary column, and a transfer line interfaced with the MSD. Each MSD is a 5973, 5975, or 5977 that is controlled by the HP-MSDOS ChemStation software.

Instrument ID	Configuration	Column
MS13, MS18, MS19, MS23, MS24, MS27, MS46, MS30	Split/splitless – capillary direct	RTX-624, 20m, 0.18mm, 1um

8.1.2 Instrument systems and associated test methods are listed below.

Instrument ID	Description	Tests Performed
MS13	6890/5973	8260W, 8260S
MS18	6890/5973	8260W, 8260S, 8260 SIM
MS19	6890/5973	Screening
MS23	6890/5973	624

MS24/MS27	7890/5975	8260W, 8260S
MS46	7890/5977	8260W, 8260S
MS30	7890/5977	8260SIM

8.2 Purge and Trap with Autosampler – Each volatile GC/MS analytical system uses a purge and trap to introduce the sample onto the GC column. Each purge and trap has an autosampler (A/S) attached to run multiple samples, one at a time, and run unattended for extended periods of time. Teledyne Tekmar or EST Analytical autosamplers and Purge and Traps are preferred for extended unattended automated analyses.

8.3 GC Columns

8.3.1 Restek RTX-624 (or equivalent) 20 M x 0.18 mm id fused silica column 1.0 µm film thickness

8.4 Each volatile GC/MS data processing station uses the most recent version of the EPA/NIST Mass Spectral Library. The current version is the NIST98k library.

8.5 Analytical balance - Capable of accurately weighing to 0.001 g, Mettler PE160 or equivalent.

8.6 Syringes, Hamilton Gas-Tight in 10 µL, 25 µL, 100 µL, 500 µL, and 1000 µL sizes.

8.7 Standard storage vials, screw thread with Mini-inert caps.

9) Standards, Reagents, and Consumable Materials

9.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

9.2 Methanol, purge and trap grade or equivalent.

9.3 Reagent water, prepared from deionized water, by charcoal filtration and then purging with high purity helium or nitrogen that is set at 4-5 psi for approximately 2 hours prior to use.

9.4 Blank soil matrix – Ottawa sand, AccuStandard specialty sands.

9.5 Helium, compressed high purity grade.

9.6 BFB Tuning Verification Stock Standard – A 25,000 ppm stock standard is purchased (AccuStandard). This stock solution is diluted in methanol to give a working standard of 50 ppm.

9.7 Stock Standard Solutions

9.7.1 Commercially prepared and certified stock standards are used routinely for all the method specified analytes. All such mixtures are also routinely checked against an independent source for both analyte identification and analyte concentration. All such stock standard mixtures have expiration dates given by the manufacturer and must be replaced if the comparison with the independent check standards indicates a problem. Alternatively, stock standards may be prepared from neat chemicals. Store according to

manufacturer's instructions. If no storage instructions are provided, store with minimal headspace, at -10° to -20°C and protect from light.

9.7.2 When preparing stock standards from neat chemicals accurately weigh approximately 0.1 g of material and dilute with methanol to 10 mL in a volumetric flask. If the purity of the neat chemical is <96%, adjust the calculated concentration accordingly.

9.8 Working Standards - Prepare these standards from stock solutions. Prepare at concentrations which facilitate ease of preparation of instrument-level standards (calibration standards, etc.). Refer to Table 1 for Standard Expiration Date Guidelines. Store standards with minimal headspace in appropriately sized standard storage vials with mini-inert caps. Solutions should be checked for degradation or evaporation prior to use.

9.9 Calibration Standards

9.9.1 A minimum of five different concentration levels for all the analytes are prepared by diluting working standards into reagent water. The lowest concentration level must be at the method reporting level, or a level corresponding to a sample concentration meeting project-specific data quality objectives, with the remaining four levels defining the working linear range of the analytical system. The permanent gas stock standards used to prepare calibration standards must not be more than one week old.

9.9.2 The suggested levels are 0.5, 2, 10, 20 and 40 ppb for waters; and 5, 20, 50, 100, and 200 ppb for soils. All calibration solutions are made up daily.

9.9.3 The continuing calibration verification (CCV) solution is prepared by adding 10 µL of a 50 ppm working standard to 50 mL of prepared reagent water, resulting in a 10 ppb (nominal concentration) standard. The CCV solution is prepared daily.

9.10 ICV Standard

9.10.1 The independent calibration verification (ICV) solution is prepared by adding 10 µL of a 50 ppm intermediate to 50 mL of prepared reagent water, resulting in a 10 ppb (nominal concentration) standard. Acrolein is added at 50 µL directly from a 100 ppm stock into the 50 mL of prepared reagent water yield a final concentration of 100 ppb in. The ICV solution is prepared with each initial calibration.

9.11 Internal Standards and Surrogates

9.11.1 The surrogates recommended are Dibromofluoromethane, Toluene-d_8 and 4-Bromofluorobenzene. The internal standards recommended are: Fluorobenzene, 1,4-Dichlorobenzene-d_4 and Chlorobenzene-d_5. Other internal standards and surrogates may be used, depending on the analysis requirements. All internal standards are added to every calibration standard. The spike level for samples, blanks, and matrix spikes is 10 µg/L for waters and 50 µg/L for soils.

9.12 Spiking Solutions

9.12.1 Waters are typically spiked at 10 ppb and soils are typically spiked at 50 ppb.

9.12.2 Matrix spike and laboratory control spike solutions should contain the full list of analytes of interest. However, a subset may be reported.

Note: Refer to Table 1 for Standard Expiration Date Guidelines.

10) Preventive Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

10.2 Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

10.3 Purge and Trap /Autosamplers

10.3.1 The purge/trap system should be baked out and back-flushed daily as needed, generally prior to use on a daily basis.

10.3.2 Replace the trap monthly or sooner if performance deteriorates.

10.3.3 The heating cup temperature is checked each time the instrument is calibrated and documented on the calibration run log.

10.4 Gas Chromatograph

10.4.1 Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column cutting tool.

10.4.2 Over time, the column will exhibit poorer overall performance, as indicated by poor peak shape and reduced responses. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in performance is evident, more thorough maintenance is necessary. Some steps are to solvent rinse the split vent and septum lines with a mix of 20% methanol in DCM. When these and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

10.5 Mass Spectrometer

10.5.1 Tune the MS as needed to result in consistent and acceptable performance while meeting the required ion abundance criteria given in section 11.

10.5.2 For units under service contract, certain maintenance is performed by instrument service staff, including pump oil changed, vacuuming boards, etc.,

as recommended by the manufacturer.

10.5.3 MS source cleaning should be performed as needed, depending on the performance of the unit. This may be done by the analyst or by instrument service staff.

11) Procedure

11.1 Sample Preparation

11.1.1 Water Samples

11.1.1.1 No preparation is generally required, other than dilution with reagent water to bring analytes into the upper half of the calibration range. Thus, a 10 mL sample volume is run straight from the sample vial. See the SOP for *Purge and Trap for Aqueous Samples* (VOC-5030) for details.

11.1.1.2 All water samples must be checked to have a pH $\leq$ 2 after sample analysis has taken place. Narrow range pH paper is used and the results are recorded on the injection log.

11.1.1.3 TCLP ZHE leachates are diluted 1:400 in reagent water prior to analysis. The TCLP samples and method blanks are diluted from the acidified ZHE extract; and the TCLP MS and LCS are diluted from a non-acidified extract, spiked, and poured into an HCL preserved VOA vial.

11.1.2 Soil samples are analyzed as either low concentration (direct purge) or high concentration (methanol preservation/extraction). Refer to the SOP for *Purge and Trap/Extraction for Volatile Organics in Soil and Waste Samples, Close System* (VOC-5035) for details.

11.1.2.1 For low concentration analyses, one of the sampling options given in method 5035 is to be used. Depending on the option used, follow the instructions given in the method. Typically, 1-5 g is weighed out into the sample vial and 5 mL of reagent water is added. QC spikes and internal standards are then added, and the sample is purged at a temperature of 40ºC ± 1º. Calibration standards, LCS, and method blanks require 5 g Ottawa sand as the matrix.

11.1.2.2 In the event that low concentration analyses are specified but samples were not taken using a EPA Method 5035 procedure, a portion of the sample is analyzed via direct heated purge of soil and EPA Method 5030A is cited. The analytical report should also be narrated with a statement indicating that 5030A has been deleted from SW-846. The low concentration analyses require a calibration specific to direct soil analysis.

11.1.2.3 The mid-level type is a methanol extraction method. In general, a 5 g wet weight of soil is extracted with 5 mL of purge-and-trap methanol in a scintillation vial. Place 5 mL of purge-and-trap

methanol into vial, tare, and add 5 g of sample, and record the weight. Quickly cap and vortex until the sample is thoroughly mixed. A 1:100 dilution (500 µL to 50 mL) of this extract is then prepared in reagent water and analyzed using the water calibration. The extract weight, volume used, and methanol lot number are recorded on the injection log (or a bench sheet).

NOTE: For soil/solid samples requiring VOA and non-VOA analyses and only one container was submitted to the lab, sample receiving will label the sample container as "VOA Analysis First" and/or attach a "VOA FIRST" tag. The VOA department will remove a sample aliquot first for their analyses. The sample should be handled as if it were a Rush analysis, so that the other non-VOA analyses will not be unduly delayed. The VOA analyst who opens the container will either break the custody seal and will initial and date it when the container was opened or sign and date the "VOA FIRST" tag. A VOA Analysis First note will also be included on the SR.

11.2 The recommended typical operating conditions are listed below. Minor modification may be necessary based off the various instrument combinations which may be used.

Purge & Trap	Purge flow rate: 40 mL/min, "K" (Vocarb 3000) or "9" Trap; Purge 11 min, desorb 2 min at 240ºC, bake 20 min at 260ºC (Tekmar 3000)
Injection Port Temperature	200ºC
Initial Temperature	35ºC for 1.0 min
Temperature Program	15ºC/min to 140ºC; hold 0 min
Final Temperature	20ºC/min to 200ºC; hold 2.5 min
Detector Temperature	200ºC
MS Scanning	~3.0 scans/second
Scan Range	35 - 270
Carrier Gas	He, 22.7 psig head pressure

11.3 Initial Calibration

NOTE: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in the SOP for *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL) are described as follows:

11.3.1 BFB Tuning

11.3.1.1 Prior to calibration and sample analyses, analyze a 25 ng or 50 ng injection of Bromofluorobenzene (BFB). Each volatile GC/MS analytical system set up to run 8260C must meet the criteria listed in Table 2 for the injection of BFB. The analysis time for BFB is used to define the start of the 12-hour window in which all analyses must be performed. Once the instrument is tuned, all subsequent analyses of standards, samples, and QA/QC samples within the same 12-hour

window must be analyzed using the identical mass spectrometer operating conditions.

11.3.1.2 Obtain the spectrum for evaluation using one of the following options:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

- Use one scan at the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

- Use the average across the entire peak up to a total of 5 scans. Peak integration must be consistent with standard operating procedure. If the peak is wider than 5 scans, the tune will consist of the peak apex scan and the two scans immediately preceding and following the apex. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

- Use the average across the entire peak. Peak integration must be consistent with standard operating procedure. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

11.3.1.3 Evaluate the spectrum against the criteria specified in Table 2. The criteria used must be the same for all ion abundance criteria checks associated with a given analysis. For example, initial calibration, continuing calibration(s), QC, and sample analyses for a given sample must all use the same criteria.

11.3.2 GC/MS Analytical System Initial Calibrations

11.3.2.1 Prior to conducting any sample analyses, a multi-point (5 point minimum) calibration must be run. Recommended calibration levels are 0.5 - 70 ppb for waters, and 5 - 300 ppb for soils. Analyze each calibration standard and tabulate the area response of the

characteristic quantitation ions (Table 3) versus concentration for each compound, internal standard and surrogate. Calculate the response factors (RF) for each compound relative to the specified internal standard by:

$$RF_x = \frac{(A_x)(C_{ISTD})}{(A_{ISTD})(C_x)}$$

Where:

A_x = Area of the characteristic ion for compound being measured.
A_{ISTD} = Area of the characteristic ion for specific internal standard.
C_{ISTD} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

Note: For DoD projects, a multi-point calibration is performed for the surrogates.

11.3.2.2 Calculate the mean response factor $(\overline{RF_x})$ for each analyte from the five calibration levels. Calculate standard deviation (SD) and the percent relative standard deviations (%RSD) for each analyte from the mean with:

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

Where:
RSD = relative standard deviation.
$\overline{RF}$ = mean of 5 initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - RF)^2}{N - 1}}$$

Where:
RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

11.3.2.3 The %RSD should be less than 20% for each compound.

11.3.2.4 If the % RSD for any compound is ≤ 20%, linearity can be assumed over the calibration range, and the relative response factor for each analyte and surrogate is used.

11.3.2.5 If the %RSD for a compound is >20%, then alternative calibration models should be used. See the SOP *Calibration of Instruments for Organics Chromatographic* (SOC-CAL) *Analysis* for further guidance.

11.3.2.6 The mean response factor for each target analyte should meet the minimum response factors listed in Table 5. Meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet this criterion. For these occasions, the analyte is qualified as not meeting the method recommended response factor criterion.

11.3.2.7 When instrument response does not follow a linear model, a non-linear calibration model may be used. Refer to the SOP for *Calibration of Instruments for Organics Chromatographic Analysis* (SOC-CAL) for alternative curve fit guidance.

11.3.2.8 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too imprecise for analysis to begin and corrective action is necessary. Further preventative maintenance may be required or the system may not be adequately *primed* for initial calibration.

11.3.3 Review of calibration curve

11.3.3.1 The calibration curve must be reviewed to ensure it represents the calibration data. This is done by re-fitting each calibration level against the true concentration of each calibration standard. The % difference between the calculated concentration verses the true concentration should be ≤ 30% for each calibration level and may not exceed 50% for any level.

11.3.3.2 Due to the large number of compounds that may be analyzed, one or more analytes may exceed 20% RSD or 0.99 COD. The initial calibration may still be acceptable if the following conditions are met:

- The % difference between the calculated concentrations verses the true concentration for each level of the initial

calibration curve meets the criteria specified in section 11.2.3.1.

- In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit. This is done by re-evaluating the concentrations of the calibrations standards against the calculated concentrations.

NOTE: Certain project plans that fall under the (DoD QSM) contain additional initial calibration acceptance criteria. In these cases, the analyst must refer to the project plan to know if the criteria listed in the DoD QSM or QAPP-specified criteria or EPA method calibration criteria are to be used.

NOTE: The "80/20" criteria allowed under section 11.3.3.2 only applies when the full target compound list is being reported. Individual compounds that are a subset of the entire target analyte list and have ≤20%D may still be reported, e.g. dilutions, reruns, abbreviated reporting lists.

11.3.4 Independent Calibration Verification

11.3.4.1 Following initial calibration, analyze an ICV standard. The ICV solution must be obtained for all analytes that are analyzed and reported. Calculate the percent difference (%D) or % Drift from the ICV true value. The acceptance limits for the ICV are ± 30% of true value.

11.3.4.2 If a second source standard is not available from a second vendor, a second lot number from the same vendor may be used. It is recommended that the lab obtain a written warranty that the lot numbers are prepared from different source materials.

11.3.4.3 After the multi-point calibration has passed all of the above criteria, and the Independent Calibration Verification has been performed, samples can be analyzed. The calibration curve mid-point standard may serve as the CCV for the opening set of samples within the same 12-hour window as the initial calibration.

11.4 Continuing Calibration

11.4.1 The start of a 12-hour analysis window requires a check of the instrument tune via an injection of 25ng or 50 ng of BFB. Refer to section 11.2.1.2 for the procedure. If the criteria found in Table 2 are met, then a check of the initial calibration curve is done. If the first analysis of the BFB fails, inspect the instrument for malfunction and perform maintenance as necessary. A second BFB tune verification may then be performed. If the second run fails, it may be necessary to retune the system.

11.4.2 After the tuning criteria have been verified, the initial calibration must be checked and verified by analyzing a midrange calibration standard. The 10 ppb level for waters and 50 ppb level for soils is recommended. For water, CCVs are prepared by adding 10µl of the 50 ppm 8260 working standard and 5µl of

the 2000 ppm ketone mix into 50 mL reagent water and a 10 mL aliquot is purged. For soil, CCVs are prepared by adding 25µl of the 100ppm (nominal) working standard into 50 mL reagent water, and a 5 mL aliquot is purged.

11.4.3 The CCV result is evaluated for each target compound using the following criteria:

11.4.3.1 If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid.

11.4.3.2 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the ≤ 20% criteria. If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.

Note: The "80/20" criteria allowed under section 11.3.3.2 only applies when the full target compound list is being reported. Individual compounds that are a subset of the entire target analyte list and have ≤ 20% may still be reported (e.g. dilutions, reruns, abbreviated reporting list).

11.4.4 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit.

11.4.5 Non-detected analytes can be reported from analyses when a CCV exhibit a positive bias (i.e., outside the upper control limit), no further documentation is required.

11.4.6 For situations when the CCV fails to meet the criterion in section 11.3.3, and a confirmed detection exceed the MRL, the sample must be reanalyzed to ensure accurate quantification. If it is not possible to reanalyze the sample, the result must be reported as an estimated value.

11.4.7 If the tune criteria and the continuing calibration criteria are met, then the retention times of all compounds, surrogates, and internal standards are checked against the initial calibration. If the retention time for any internal standard changes by more than 10 seconds from the retention time from the mid-point standard of the most recent initial calibration, the system must be inspected for malfunctions and corrections must be made, as required.

11.4.8 If the area for any of the internal standards changes by a factor of 2 (-50% to +100%) from the area from the mid-point standard of the most recent initial calibration, corrections must be made to the system.

11.4.9 Quantitation of all compounds will be based on the initial calibration.

11.5 GC/MS Analysis

11.5.1 Perform GC/MS screening analysis.

11.5.1.1 Samples are typically diluted 50X for liquid matrices and 500X for solid matrices.

11.5.1.2 Quantify chromatographs from the screening analysis and evaluate based on peaks of interest and the high point of the associated analytical instrument calibration.

11.5.1.3 If required, dilutions are typically performed with the intent to bring the high range analytes of interest into the mid-range of the instrument calibration as well as a base run that dilutes the highest peak to approximately three times the highest point of the instrument calibration.

11.5.1.4 Note the requirement of a dilution in the comment section of the analytical instrument injection log.

11.5.2 Prepare samples as described in section 11. Use the same operating conditions as were used for initial calibration.

11.5.3 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place.

11.6 Identification of Analytes

11.6.1 The MSD data system software identifies a sample component by first finding and identifying the surrogate and internal standards. After they have been integrated, the extracted ion chromatogram is searched for all calibrated analytes.

11.6.2 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum is generated from analysis of a calibration standard and is updated with each initial calibration.

11.6.3 The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

11.6.3.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak

containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

11.6.3.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

11.6.3.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

11.6.4 Table 3 lists characteristic ions as given in Method 8260C. If there is no peak found for an analyte in the expected retention time window and the mass spectrum does not match according to the method criteria, then the analyte is "not found". Print out spectra for all confirmed hits.

11.7 The analyst reviews all analyses to confirm (or correct) all data system qualitative interpretations.

11.8 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the SOP for Total Solids.

12) Quality Assurance/Quality Control Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made or when an analyst is new to the procedure. To do this, analyze four water sample spikes, calculate the average recovery and standard deviation, and evaluate as described in EPA SW-846. The concentration of the analytes to be spiked should be in the working calibration range. Initial Demonstration of Capability studies must be performed as part of analyst training. Copies of the studies are maintained in the lab and in the analyst's training file.

12.2 Method Detection Limits/Lower Limit of Quantitation/LOD/LOQ

12.2.1 For projects that require reporting to the method detection limit (MDL), a method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the procedure specified in the corporate QA SOP *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). The MDL studies should be done for each matrix and include data from all instruments on which the test is analyzed.

12.2.2 Calculate the average concentration found (x) in the sample concentration, and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. The MDL study must be verified as specified in CE-QA011.

12.2.3 The Limits of Detection (LOD) and Limits of Quantitation (LOQ) must be established and verified following the procedure in the SOP *Performing Method Detection Limit Studies and Establishing Limits of Detection and* Quantification (CE-QA011).

12.2.4 The Method Reporting Limits (MRLs) used at ALS are the routinely reported Lower Limits of Quantitation (LLOQ) which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). In general, these include:

12.3.1 Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps minimized. No target analytes should be detected above the MRL in the method blank. For some project specific needs, additional requirements or exceptions may be given.

Note: For DoD projects – The Method Blank will be considered contaminated if:

- The concentration of any target analyte in the blank exceeds ½ the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).
- The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).
- The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

12.3.2 A lab control sample (LCS) must be prepared and analyzed with every batch, not to exceed 20 samples. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire preparation and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where:
X = Concentration of the analyte recovered
TV = True value of amount spiked

Compare the %R to LCS acceptance criteria, located in the current ALS-Kelso DQO tables. The accuracy of the analysis is controlled on a subset of target analytes. If the project analyte list is fewer than 20 analytes, all are considered control analytes. For DoD projects all project target analytes are considered control analytes. Analytes which are used for control analytes are listed in Table 4. Project-specific acceptance limits may supersede those listed in this SOP. If the lab control sample (LCS) fails acceptance limits for any of the control compounds, any associated sample data is rejected and corrective action must be taken. This may include evaluation of the sample preparation, analytical system, and calibration; and may require re-extraction, re-analysis, and/or

recalibration and re-analysis.

12.3.3 A matrix spike/duplicate matrix spike (MS/DMS) must be prepared and analyzed with every batch of 20 or fewer samples if adequate sample volume is received (4 or more vials are needed). If insufficient sample is received, an LCS/DLCS pair will be analyzed to establish batch precision. In the event a dilution analysis is necessary on a sample chosen for MS/DMS, the sample will be spiked at the base level.

The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire preparation and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where:
X = Measured concentration of the spiked sample aliquot
X1 = Measured concentration of the unspiked sample aliquot
TV = True value (theoretical concentration) of the amount spiked

Calculate Relative Percent Difference (RPD) as:

$$RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where:
R1 = Measured concentration of the first sample aliquot
R2 = Measured concentration of the second sample aliquot

Compare the %R and RPD to MS/DMS acceptance criteria located in the ALS-Kelso DQO tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken.

Note: For DoD projects, recovery limits for the MS are the same as the LCS limits specified in the QSM.

12.3.4 The acceptance limits for the surrogates are given in the ALS-Kelso DQO tables. If any surrogate recovery is outside acceptance criteria, the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be taken. The sample should be re-analyzed if instrument factors (calibration, poor purge, etc.) are suspected.

12.4 Acceptance criteria and corrective action requirements have been outlined above in the Procedure section and in Table 6.

12.5 Additional QA/QC measures include trend analysis by means of control charts or other means.

13) Data Reduction and Reporting (or Documentation and Records)

13.1 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the midpoint concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

13.2 Calculations

13.2.1 The GC/MS data stations, in current use, all use the H-P RTE Integrator to generate the raw data used to calculate the standards $\overline{RF}_x$ values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions. The results for a sample are calculated as follows when $\overline{RF}_x$ is used:

$$A_x = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF}_x)}$$

Where: A_x = the amount, in ppb, of the analytes in the sample;

$Resp_X$ = the peak area of the analytes of interest;

$Resp_{ISTD}$ = the peak area of the associated internal standard;

Amt_{ISTD} = the amount, in ppb, of internal standard added

$\overline{RF}_x$ = the average response from the five-point for the analytes of interest.

13.2.2 The results for low concentration soil work are calculated by taking the normal print out, in ppb, (see the water results outlined above) and correcting for the total, dry soil sample actually purged:

$$(A_x) = \frac{(5\ grams)}{(ASW_t\ gr)(\%\ Solids)} = A_x\ Low\text{-}Level\ Soil$$

Where: A_X = Amount, in ppb, from the data system

5 g = Nominal amount of soil that is headed and purged.

ASW_t = Actual soil wet weight, in grams, that is purged

% Solids = Correction factor for dry weight.

13.2.3 Results for a high concentration soil samples (methanol extracts) are calculated as follows:

$$(A_x) = \frac{(Dilution)(V_{EXTR})}{(ASW_t)(\%\ Solids)} = A_x\ High\text{-}Level\ Soil\ Amt.$$

Where: A_X = Amount reported from the data station, in ppb
Dilution = Dilution factor of the extract
% Solids = Correction factor for dry weight
V_{EXTR} = Methanol extract volume (mL)*

* The water contained in the native sample is accounted for when determining the final extract volume. The final volume of the methanol extract is the total volume of the methanol/water mixture. Calculate the final volume as follows:

$$FinalVolume\ Methanol/Water = mL\ of\ solvent + \left(\frac{\%Moisture\ \ x\ Sample\ Wt.(g)}{100} \right)$$

13.3 Data Review

13.3.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the *SOP for Laboratory Data Review Process* (ADM-DREV) for details.

13.4 Reporting

13.4.1 Reports are generated in STEALTH or the ALS LIMS which compiles the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file which the Stealth reporting system uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

14) Method Performance

14.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

14.2 The method detection limit (MDL) is established using the procedure described in *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements. Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the

environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Kelso Environmental Lab Waste Management Plan.

15.3 This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected. Table 5 list specific corrective actions that must be made based off method criteria.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

16.2.2 Some examples when documentation of nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision,
- Method blanks or continuing calibration blanks (CCBs) with target analytes above the acceptance limits,
- Sample holding time missed due to laboratory error or operations,
- Deviations from SOPs or project requirements,
- Laboratory analysis errors impacting sample or QC results,
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.),
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Training Outline

17.1.1 Review literature by reading references. Review the EPA methodology and any applicable state-specific methods. Review the SOP. Also review the SDS for methanol.

17.1.2 Observe the procedure performed by an experienced analyst at least three times.

17.1.3 Assist in the procedure under the guidance of an experienced analyst for a period of three months. During this training process, the analyst is expected

to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.4 Following the three-month training period the analyst is expected to complete an initial demonstration of capability study (IDC) for solid samples by direct, solid samples by extraction, and water samples. Summaries of the IDC are reviewed and signed by the technical director and forwarded to the employee's training file.

17.1.4.1 Perform IDC studies by preparing and analyzing four replicate laboratory control samples spiked at a level of 10-20 times the MRL. Calculate average percent recovery and relative standard deviation for the four replicate analyses. Refer to Method 8000C and 8260C for analysis and evaluation guidelines.

17.1.4.2 For applicable tests, IDC studies are be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2 Training is documented following the procedures defined in *ALS-Kelso Training Procedure* (ADM-TRAIN).

17.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 For water samples, a purge volume of 10mL is used, whereas the method (section 7.5.5) states 5mL or 25mL. The use of a 10mL volume ensures sensitivity for "5mL" type analyses *and,* on the analytical systems in use, meets the sensitivity goals of a 25mL purge volume analysis. Also, the use of 10mL rather than 25mL decreases the negative effects of water being introduced into the P/T-GC-MS system.

18.2 11.2.3.1 Reference method recommends recalculation of low point only and that should be ± 30%. This SOP states each point is refit and each point should be with ± 30% but may not exceed ± 50%.

18.3 11.3.3 No limit defined in reference method, so lab assigned a limit of 40% based on CLP protocols.

19) References and Related Documents

19.1 VOC-5030, Purge and Trap for Aqueous Samples.

19.2 VOC-5035, Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Closed System.

19.3 Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, *U.S. EPA, SW-846, Method 8260C, Revision 3, August 2006.*

19.4 Purge and Trap, U.S. EPA, SW-846, Final Updates I and III, Methods 5030A Rev. 1, July 1992, 5030B Rev. 2, December 1996, and 5030C Rev. 3, May 2003.

19.5 Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste, U.S. EPA, SW-846, Final Update III, Method 5035, Rev. 0, December 1996; and Method 5035A Rev. 1, July 2002.

20) Summary of Changes since Last Revision

20.1 Signature page updated.
20.2 Typographical, grammatical and formatting revisions.
20.3 Section 8: Various changes to reflect current practice as requested, dated 2/1/17.
20.4 Section 9.11 – Corrected internal standard name.
20.5 Section 11.2 - Added typical instrument operating conditions.
20.6 Section 11.3.2.2 – Added formulas and parameters for clarification.
20.7 Section 11.3.3.2 - Revised NOTE, Change Request dated 12/6/16.
20.8 Section 11.5.1 – New section addressing screens.
20.9 Section 12 - Sentence deletion.
20.10 Section 13.4.1 – Included ALS LIMS reporting.
20.11 Section 13.4.2 – Removed section on Excel reporting.
20.12 Section 19 – Updated references.
20.13 Updated Safety documentation changes to reflect current practice.

21) Attachments/Appendices

21.1 Table 1 – Standard Expiration Date Guidelines

21.2 Table 2 – 4-Bromofluorobenzene Characteristic Ion Abundance Criteria

21.3 Table 3 – Characteristic Masses (m/z) for Purgeable Organic Compounds

21.4 Table 4 – Control Analytes for Non-DoD Projects

21.5 Table 5 – Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification

21.6 Table 6 – Summary of Corrective Actions.

TABLE 1

Standard Expiration Date Guidelines

Standard	Expiration time
Neat Chemicals supplier's	Expiration date 5 years from date opened, or assigned date.
Stock Standards (unopened ampules, commercially prepared or lab prepared) 1 preparation if no expiration date provided.	Supplier's assigned date, or year from
Opened ampules and working standards	
• concentration ≥ 5000 ppm	6 month expiration date.
• concentration 1000 - <5000 ppm	2 month expiration date.
• concentration 200 - <1000 ppm	1 month expiration date.
• concentration < 200 ppm	7 day expiration date.
Internal Standard Solutions	One month expiration date.

Note: The analyst performing specific analytical procedures should use judgment and take into consideration the solution reactivity, volatility, and concentration when using standards to prepare calibration curves. Certain standards, depending on use and storage, may have shorter usable life than described in these guidelines.

TABLE 2

4-Bromofluorobenzene Characteristic Ion Abundance Criteria

Mass	Ion Abundance Criteria *
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5-9% of mass 174
176	95 -101% of mass 174
177	5-9% of mass 176
Reference:	EPA 8260C

* Manufacturer specified ion abundance criteria may be used

TABLE 3

Characteristic Masses (m/z) for Purgeable Organic Compounds

Analyte	1º Ion	2º, 3º, etc. Ion
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148

TABLE 3 (cont.)

Characteristic Masses (m/z) for Purgeable Organic Compounds

Analyte	1º Ion	2º, 3º, etc. Ion
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-

TABLE 3 (cont.)

Characteristic Masses (m/z) for Purgeable Organic Compounds

Analyte	1º Ion	2º, 3º, etc. Ion
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
b-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Surrogates:		
1,2-Dichloroethane-d4	65	67, 51
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	113	111, 192
Toluene-d8	98	99, 70
Internal Standards:		
1,4-Difluorobenzene	114	63, 88
Fluorobenzene	96	77, 70, 50
1,4-Dichlorobenzene-d4	152	115, 150
Chlorobenzene-d5	117	119, 82

TABLE 4

Control Analytes for Non-DoD Projects

1,1-Dichloroethene
Benzene
Trichloroethene
Toluene
Chlorobenzene
1,2-Dichlorobenzene
Naphthalene
1,1,2-Trichloroethane
2-Chlorotoluene
2-Hexanone
Carbon Tetrachloride
Vinyl Chloride
Ethylbenzene
Chloroform
Bromodichloromethane
1,2,3-Trichloropropane

TABLE 5

Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification

Analyte	Response Factor (RF)
Dichlorodifluoromethane	0.100
Chloromethane	0.100
Vinyl chloride	0.100
Bromomethane	0.100
Chloroethane	0.100
Trichlorofluoromethane	0.100
1,1-Dichloroethene	0.100
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100
Acetone	0.010*
Carbon disulfide	0.100
Methyl Acetate	0.100
Methylene chloride	0.100
trans-1,2-Dichloroethene	0.100
cis-1,2-Dichloroethene	0.100
Methyl tert-Butyl Ether	0.100
1,1-Dichloroethane	0.200
2-Butanone	0.010*
Chloroform	0.200
1,1,1-Trichloroethane	0.100
Cyclohexane	0.100
Carbon tetrachloride	0.100
Benzene	0.500
1,2-Dichloroethane	0.100
Trichloroethene	0.200
Methylcyclohexane	0.100
1,2-Dichloropropane	0.100
Bromodichloromethane	0.200
cis-1,3-Dichloropropene	0.200
trans-1,3-Dichloropropene	0.100
4-Methyl-2-pentanone	0.010*
Toluene	0.400
1,1,2-Trichloroethane	0.100
Tetrachloroethene	0.200
2-Hexanone	0.015*

TABLE 5 (cont.)

Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification

Analyte	Response Factor (RF)
Dibromochloromethane	0.100
1,2-Dibromoethane	0.100
Chlorobenzene	0.500
Ethylbenzene	0.100
m-/p-Xylene	0.100
o-Xylene	0.300
Styrene	0.300
Bromoform	0.100
Isopropylbenzene	0.100
1,1,2,2-Tetrachloroethane	0.300
1,3-Dichlorobenzene	0.600
1,4-Dichlorobenzene	0.500
1,2-Dichlorobenzene	0.400
1,2-Dibromo-3-chloropropane	0.025*
1,2,4-Trichlorobenzene	0.200
Any other analyte not included in this table	0.010

* These analytes have poor purging efficiencies. Response factors based upon USEPA CLP guidance and laboratory performance after system maintenance.

TABLE 6

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C EPA 8260C	ICAL	Prior to sample analysis	% RSD ≤ 20 R2 ≥ 0.995 COD ≥ 0.990	Correct problem then repeat ICAL
EPA 8260C	ICV	After ICAL	± 30% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8260C	CCV	Prior to sample analysis	See Sec. 11.3.3	Correct problem then repeat CCV or repeat ICAL
EPA 8260C	Method Blank	Include with each analysis batch (up to 20 samples)	< MRL DOD <1/2 MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminant, unless samples contain > 20x amount in blank.
EPA 8260C	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO Tables	If exceeds limits on control compounds, perform corrective actions, re-extract and re-analyze
EPA 8260C	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO Tables	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8260C	Matrix Spike Duplicates	Include with each analysis batch (up to 20 samples)	Water: RPD ≤ 30 Soil, L: RPD ≤ 40 Soil, M: RPD ≤ 40	Re-analyze if result is > 5 X the MRL

SOP 16
Semivolatile Organic Compounds by GC/MS,
EPA Method 8270D

SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS - METHOD 8270D

ALS-KELSO

SOP ID:	SVM-8270D	Rev. Number:	5	Effective Date:	05/29/2016

Approved By: _____ Date: 5/16/16
Department Manager/Technical Director - Jon James

Approved By: _____ Date: 5/16/16
QA Manager - Carl Degner

Approved By: _____ Date: 5/16/16
Laboratory Director - Jeff Grindstaff

Issue Date: _____	Doc Control ID#: _____	Issued To: _____

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

ALS-Kelso SOP Annual Review Statement

SOP Code: SVM-8270D
Revision: 5

An annual review of the SOP listed was completed on (date): **3/8/19**

☒ The SOP reflects current practices and requires no procedural changes.

Supervisor: cjw Date: 3/8/19

☐ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision

ALS-Kelso SOP Annual Review Statement

SOP Code: SVM-8270D

Revision: 5

Attach additional pages or information if necessary

ALS-Kelso SOP Annual Review Statement

SOP Code: SVM-8270D
Revision: 5

An annual review of the SOP listed was completed on (date): **6/15/17**

☒ The SOP reflects current practices and requires no procedural changes.

Supervisor: Jon James Date: 6/15/17

☐ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision

TABLE OF CONTENTS

SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS – METHOD 8270D

1. SCOPE AND APPLICATION

1.1. This procedure is used to determine the concentrations of Semi-Volatile Organic Compounds in water and soil using EPA Method 8270D. This procedure may also be applicable to various miscellaneous waste samples. Tables 1A and 1B indicate compounds that may be determined by this method and lists their method reporting limits (MRLs) in water and soil. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. The Method Detection Limits (MDLs) will vary depending on the instrument used and preparation method.

1.2. This procedure can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone phase. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. Other compounds than those listed in Tables 1 may be analyzed. Refer to Section 1 of method 8270D.

1.3. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (*ADM-DOD) may supersede the requirements defined in this SOP.

2. METHOD SUMMARY

2.1. This method provides Gas Chromatography/Mass Spectrometry (GC/MS) conditions for the detection of Semi-volatile Organic Compounds. Prior to the use of this method, an appropriate sample preparation method must be used to recover the analytes of interest. An aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a fused silica capillary column. Compounds of interest are detected by a mass selective detector. Identification of the analytes of interest is performed by comparing the retention times of the analytes with the respective retention times of an authentic standard, and by comparing mass spectra of analytes with mass spectra of reference materials. Quantitative analysis is performed by using the authentic standard to produce a response factor and calibration curve, and using the calibration data to determine the concentration of an analyte in the extract. The concentration in the sample is calculated using the sample weight or volume and the extract volume.

2.2. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration and the chromatography for this compound is poor. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, to a chemical reaction in acetone, and can undergo photochemical decomposition. N-Nitrosodimethylamine is

difficult to separate from the solvent under the chromatographic conditions described. N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-Dinitrophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Chloroaniline, and Benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3. DEFINITIONS

3.1. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2. Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. **Sample**

3.2.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3. **Quality System Matrix** - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1. Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2. Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3. Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4. Nonaqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5. Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7. Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8. Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6. Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

3.7. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.8. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.9. Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.10. Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.11. Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis.

The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.12. Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.13. Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4. INTERFERENCES

4.1. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation of the samples. Corrective action should be taken to eliminate the interferences.

4.2. Accurate determination of phthalate esters can pose difficulties when using this methodology. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware may occur when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

4.3. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in MSDSs where available. Refer to the ALS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. This method uses Methylene Chloride, a known human carcinogen. Viton brand gloves should be used while rinsing, pouring or transferring the solvent.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Containers used to collect samples should be purchased pre-cleaned containers. Alternatively, containers used to collect samples for the determination of semivolatile organic compounds may be soap and water washed followed by methanol (or isopropanol) rinsing. The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may not be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

6.2. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g., if an automatic sampler is used), run reagent water through the sampler and use the rinseate as a field blank.

6.3. Water and soil samples must be iced or refrigerated at 4 ± 2°C from time of collection until extraction.

6.4. Water samples must be extracted within 7 days and the extracts analyzed within 40 days following extraction. Soil samples must be extracted within 14 days and the extract analyzed within 40 days following extraction. Extracts are stored at <-10°C.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

7.2. Solvents: Acetone, methylene chloride, methanol, and other appropriate solvents. Solvents must be of sufficient purity to permit usage without lessening the accuracy of the determination or introducing interferences.

7.3. Stock Standard Solutions (See Table 3)

7.3.1. Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. Commercially prepared stock standards are typically used when available at a concentration of 1000 µg/ml or more. Standard concentrations can be verified by comparison versus an independently prepared standard. Alternatively, prepare stock standard solutions at a concentration of 1000 µg/ml by dissolving 0.0100 g of reference material in methylene chloride or other suitable solvent and diluting to volume in a 10mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Store according to the vendors recommendations.

7.3.2. Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 ± 2°C or per manufacturer's recommendation and protect from light. Stock

standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.3.3. Stock standard solutions must be replaced after one year, or sooner, if comparison with check standards or samples indicates a problem.

7.4. Internal Standard Solutions (See Table 3) - The internal standards are 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12} (See Table 4 for corresponding compounds). The nominal concentration of the standard is 4000 ng/µL. Each 1 ml of sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store at room temperature when not being used. When using premixed certified solutions, store according to the manufacturer's recommendations.

7.5. GC/MS Tuning Standard (See Table 3) - A methylene chloride solution containing 50 ng/µL of Decafluorotriphenylphosphine (DFTPP). The standard should also contain 50 ng/µL each of Benzidine, DDT, and Pentachlorophenol, to verify injection port inertness and GC column performance. Store at 4˚C ±2˚C when not being used, or store according to the manufacturer's recommendations.

7.6. Calibration Standards (See Table 3)

7.6.1. A minimum of five initial calibration standards should be prepared from stock solutions. One of the calibration standards should be at a concentration at or below the method reporting limit; the others should correspond to the range of concentrations found in real samples, but should not exceed the working range of the GC/MS system. At least one calibration standard must be at a concentration corresponding to a sample concentration meeting project-specific data quality objectives. Each standard should contain each analyte for detection by this method. Each 1 ml aliquot of calibration standards should be spiked with 10 µL of the internal standard solution prior to analysis. All calibration standards should be stored at <-10˚C or less and should be freshly prepared once a year, or sooner if check standards indicate a problem.

7.6.2. The daily calibration standard (CCV) is prepared at a nominal 80 ng/µL concentration from stock solutions. The CCV is prepared weekly and can be stored at 4˚C ± 2˚C. The DFTPP standard may be combined with this standard (maintaining 50 ng/µL) providing tuning verification and calibration verification can be done without interferences.

7.7. QC Standards (See Table 4)

7.7.1. Surrogates: Prepare a working solution in methanol containing 2-Fluorophenol, Phenol-d_6, and 2,4,6-Tribromophenol at 150 ng/µL and Nitrobenzene-d_5, 2-Fluorobiphenyl, and Terphenyl-d_{14} at 100 ng/µL. Aliquots of the solution are spiked into all extracted samples, blanks, and QC samples according to the extraction SOP used.

7.7.2. Matrix Spike Standards: Prepare a working solution in methanol containing all analytes of interest ("full list spike") from the standard analyte list (Table1) at 100

ng/µL. Aliquots of the solution are spiked into the selected QC aliquots according to the extraction SOP used.

Note: The spiking level of surrogate and spike may need to be adjusted according to project requirements, if dilutions are expected due to high levels of extracted components, or if a lower calibration range is used.

8. APPARATUS AND EQUIPMENT

8.1. Gas Chromatograph/Mass Spectrometer System

8.1.1. Gas Chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source. Agilent 5890, 6890 or equivalent.

8.1.2. Column: ZB-5MS Guardian- 30 m x 0.25 mm ID x 0.25 µm film thickness silicone-coated fused-silica capillary column. Recommended: Phenomenex with guard.

8.1.3. Mass Spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 2 when 1.0 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

8.1.4. GC/MS Interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

8.1.5. Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. NIST98 Mass Spectral Library is used for spectral comparisons.

8.2. Appropriate analytical balance (0.0001 g), volumetric flasks, syringes, vials, and bottles for standards preparation.

9. PREVENTIVE MAINTENANCE

9.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

9.2. Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

9.3. Gas Chromatograph

9.3.1. Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, seal, washer, o-ring, septum, column ferrule, and autosampler syringe as needed. Liners and seals should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners and seals may be cleaned and re-used.

9.3.2. Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and "clean" (uniform, without fragmentation) by using the proper column cutting tool.

9.3.3. Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

9.4. Mass Spectrometer

9.4.1. Tune the MS as needed to result in consistent and acceptable performance while meeting the required ion abundance criteria given in section 11.

9.4.2. For units under service contract, certain maintenance is performed by instrument service staff, including pump oil changed, vacuuming boards, etc., as recommended by the manufacturer.

9.4.3. MS source cleaning should be performed as needed, depending on the performance of the unit. This may be done by the analyst or by instrument service staff.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the ADM-TRAIN, ALS-Kelso Training Procedure is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. Sample Preparation

11.1.1. Water samples

11.1.1.1. Water samples are prepared using continuous liquid-liquid extraction, EPA method 3520C. Refer to the ALS SOP EXT-3520. In some circumstances, such as rush samples or for TCLP leachates, samples may be prepared using separatory funnel procedures (EPA 3510C). Refer to the ALS SOP EXT-3510.

11.1.1.2. Perform the extraction on a 1000mL aliquot of sample. For TCLP leachates, use 100mL of sample.

11.1.2. Soil, sediment, and solid samples are prepared using automated soxhlet extraction (SOP EXT-3541). The nominal sample size is 30g. Sample amounts may be decreased in the case of high-concentration waste samples.

11.1.3. Product samples are prepared using EPA method 3580A.

11.1.4. Extracts may be screened by GC/FID (SOP SOC-SCR). Cleanup by GPC is performed on solid and waste samples and is optional on water samples.

11.1.5. Following sample preparation, sample extracts are then transferred to the extract storage freezer in the instrument lab. Extracts must be analyzed within 40 days of extraction.

11.2. The recommended GC/MS operating conditions are listed below. The GC conditions may be modified to accommodate specific instrument models and configurations.

Mass range:	35-500 amu
Scan Time:	1 sec/scan
Initial temperature:	40˚C, hold for 3.5 minutes
Temperature program:	40-50˚C at 6˚C/min, 50-270˚C at 15˚C/min, hold for 1.0 min.
Final temperature:	270-320˚C at 6.0 6˚C/min, hold for 3 minutes after Benzo[g,h,i]perylene has eluted
Injector temperature:	150˚C ramp to 300˚C
Detector interface temp:	320˚C
Injector:	split, electronic pressure control with pulse
Sample volume:	1.0 µL
Carrier gas:	Helium at 35 cm/sec

11.3. Initial Calibration

NOTE: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in the ALS SOP for *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL) are described as follows:

11.3.1. Prior to calibration, analyze the GC/MS tuning standard using instrument conditions used for calibration. Obtain the spectrum for evaluation using one of the following options:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

- Use one scan at the apex of the peak. Background subtraction is required and must be performed using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be used only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

- Use one scan either directly preceding or following the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed of instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

- Use the average across the entire peak up to a total of 5 scans. Peak integration must be consistent with standard operating procedure. If the peak is wider than 5 scans, the tune will consist of the peak apex scan and the two scans immediately preceding and following the apex. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

11.3.2. Evaluate the spectrum obtained for DFTPP against the tuning criteria in Table 2 (see 8270D, Section 11.3.1 for guidance). The GC/MS must meet the DFTPP ion abundance criteria prior to further analyses.

11.3.3. The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2. See 8270D, Figure 1 for tailing factor calculation. If excessive tailing, poor chromatography, or degradation of >20% is noted, the injection port may require cleaning. It may also be necessary to remove the first 15-30 cm of the GC column. If hardware tuning criteria cannot be met, the source may need cleaning, filaments replaced or other maintenance.

11.3.4. The internal standards should permit most of the components of interest in the chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Refer to Table 5 for internal standards and corresponding analytes assigned for quantitation (other analytes may be added as needed). Use the base peak ion from the specific internal standard as the primary ion for quantitation (See Table 1 of EPA 8270D). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-Dichlorobenzene-d_4, use 152 m/z for quantitation).

11.3.5. Analyze 1.0 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1 of EPA 8270D). Calculate response factors (RFs) for each compound relative to one of the internal standards as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for compound being measured.

A_{is} = Area of the characteristic ion for specific internal standard.

C_{is} = Concentration of the specific internal standard (ng/µL).

C_x = Concentration of the compound being measured (ng/µL).

11.3.6. The percent relative standard deviation (%RSD) should be less than or equal to 20% for each compound. It is also recommended that a minimum response factor for the most common target analytes, as noted in Table 6, be demonstrated as a means to ensure that these compounds are performing as expected.

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RSD = relative standard deviation.

$\overline{RF}$ = mean of initial RFs for a compound.

SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - RF)^2}{N - 1}}$$

where:

RF_i = RF for each of the calibration levels

N = Number of RF values (e.g., 6)

11.3.7. The relative retention times (RRT) of each compound in each calibration run should agree within 0.06 relative retention time units.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.8. Linearity - If the % RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

11.3.9. If the %RSD for a compound is >20%, then alternative calibration models should be used. Refer to the SOP for *Calibration of Instruments for Organics Chromatographic Analysis* (SOC-CAL) for alternative fit guidance.

11.3.10. If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

11.3.11. When calculating the calibration curves using the alternative curve fits, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000C for additional details). It is not necessary to re-analyze a low concentration standard; rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration.

NOTE: Certain project plans (DoD QSM) contain additional initial calibration acceptance criteria (e.g. CCC, SPCC). In these cases, the QAPP-specified criteria are used.

NOTE: Certain state or program protocols have specific procedures for calibration. This may include all or part of Method 8000C. The analyst must ensure that the correct procedures are used. Known uses of 8000C are as follows:

- The use of quadratic regression calibration is not allowed for projects (samples) originating from South Carolina and under the SC DHEC lab certification where historically that analyte responds in a linear manner.

11.4. Initial Calibration Verification

11.4.1. Following initial calibration, analyze an ICV standard. The ICV solution must contain all analytes in the calibration standards at a concentration in the middle of the range of the initial calibration. Calculate the concentration using the typical procedure used for quantitation. Calculate the percent difference (%D) from the ICV true value. The maximum allowed % Difference or % Drift is ±30%.

NOTE: DoD ELAP projects may use the acceptance criteria of ± 20%.

11.5. Continuing Calibration

11.5.1. Following an acceptable tune, a calibration standard, or standards, at mid-concentration containing all semivolatile analytes, and all required surrogates, must be analyzed every 12 hours during analysis.

Note: When analyzing samples subject to Wisconsin DNR regulations, a second CCV must be analyzed when second order (quadratic) calibrations are used. One will be analyzed at the lower end of the calibration range and one at a point where the curve can no longer be characterized as first order.

11.5.2. If the percent difference or percent drift for each compound is less than or equal to 20%, the initial calibration is assumed to be valid and the analysis of samples may begin.

Calculate the percent drift using:

$$\%\ Drift = \frac{C_1 - C_c}{C_1} \times 100$$

where:

C_1 = Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

11.5.3. If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the ≤ 20% criteria. If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.

11.5.4. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit.

11.5.5. Non-detected analytes can be reported from analyses when a CCV exhibit a positive bias (i.e., outside the upper control limit), no further documentation is required.

11.5.6. For situations when the CCV fails to meet the criterion in section 11.5.3, and a confirmed detection exceeds the MRL, the sample must be reanalyzed to ensure accurate quantification. If it is not possible to reanalyze the sample, the result must be reported as an estimated value.

11.5.7. The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as required. If the EICP area for any of the internal standards changes by a factor of two (50% to 200%) from that in the midpoint standard of the most

recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as appropriate. When corrective action is taken, reanalysis of samples analyzed while the system was malfunctioning is required. Update the reference spectra and retention times in the quantitation database for the instrument method or ID file. The initial calibration average RF or calibration curve is then used in the quantitation of subsequent analyses.

11.5.8. A blank (method blank, GPC blank, or solvent blank) should be analyzed after the CCV, or at any other time during the analytical shift, to prove the system is free of contaminants. If contaminants are found in a method blank or GPC blank, then a solvent blank should be analyzed to help isolate the source of contamination.

11.5.9. Each of the most common target analytes in the calibration verification standard should meet the minimum response factors noted in Table 6.

11.5.10. If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination of the front end of the analytical column, and active sites in the column or chromatographic system.

11.6. GC/MS Analysis

11.6.1. Evaluate FID screens if performed and make proper dilution (See FID screening SOP).

11.6.2. Spike the 1 ml extract obtained from sample preparation with 10 µL of the internal standard solution just prior to analysis. Use the same operating conditions as were used for initial calibration.

11.6.3. If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

11.6.4. Store the extracts at <-10˚C or less, protected from light in vials equipped with un-pierced Teflon lined septa. Archive extracts in freezer for 3 months after analysis in the instrument/date specific storage boxes.

NOTE: Client specific QAPPs may require extracts to be kept for a longer period of time.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

12.1.1. The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made. To do this, four clean matrix samples (water or solids) are spiked with the LCS spike solution, then prepared and analyzed.

12.2. Method Detection Limits and Method Reporting Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2. Calculate the average concentration found (x) in µg/L or mg/Kg, and the standard deviation of the concentrations (s) in µg/L or mg/Kg for each analyte. Calculate the MDL for each analyte. Refer to *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). The MDL study must be verified annually (or quarterly, if used for DOD work).

12.2.3. Limits of Quantification (LOQ)

12.2.3.1. The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within the LCS acceptance limits to verify the data reporting limit. Refer to *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011).

12.2.4. The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit. Current MDLs and LODs can be found in the laboratory Data Quality Objectives.

12.3. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). In general, these include:

12.3.1. Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps minimized. No target analytes should be detected above the MRL in the method blank. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants (phthalate esters, etc.).

Note: DoD requires no analytes detected at > ½ the RL or 1/10 the regulatory limit, whichever is greater. For common laboratory contaminates there should be no detection > the RL.

12.3.2. A lab control sample (LCS) must be extracted and analyzed with every batch of 20 or fewer samples. The LCS will routinely contain the entire target analyte list. The LCS is prepared by spiking a blank with the matrix spike solution, and going

through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

Acceptance criteria for lab control samples are listed in the laboratory Data Quality Objectives (DQO) tables. The accuracy of the analysis is controlled on a subset of target analytes. If the project analyte list is fewer than 20 analytes, all are considered control analytes. Analytes which are used for control analytes are listed in Table 7. For DoD projects all project target analytes are considered control analytes. If the LCS recovery for any control analyte fails acceptance limits, corrective action is required. If instrument corrective action is not applicable or ineffective, re-extraction of the associated samples is required. If any other analyte fails the advisory acceptance limits, the analyst must evaluate the impact on data quality and take any necessary corrective action, which may include re-extraction of the associated samples. Project-specific requirements may require all compounds to be treated as control analytes, or dictate use of project acceptance criteria.

12.3.3. A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples. The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

Where R1 = recovered concentration in the higher result
R2 = recovered concentration in the lower result

The acceptance limits for the MS/DMS recovery are listed in the laboratory Data Quality Objectives (DQO) tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken. The RPD acceptance limits are 30% for water and 40% for soils, sediments, and solids. Project-specific requirements may dictate the use of project acceptance criteria.

12.3.4. The acceptance limits for the surrogates are listed in the laboratory Data Quality Objectives (DQO) Tables. If any surrogate recovery is outside acceptance criteria,

the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be taken. The sample should be re-analyzed if instrument factors (calibration, injection port) are suspected. If not, re-extraction and re-analysis is required, except in cases of high recovery and no positive hits in the sample for the analyte class represented by the particular surrogate.

12.4. Additional QA/QC measures include control charting of QC sample results.

13. DATA REDUCTION AND REPORTING

13.1. Qualitative Analysis - The qualitative identification of compounds determined by this procedure is based on retention time, and comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the instrument and conditions used for the sample analysis. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

13.1.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

13.1.2. The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

13.1.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. Use professional judgment in interpretation where interferences are observed.

13.1.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is <50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.1.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks appear to represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification. When analytes co-elute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

13.2. For samples containing components not associated with the calibration standards, a library search may be made of the purpose of tentative identification. Refer to method 8270D for guidance on tentatively identified compound (TIC) identification and quantification.

13.3. Quantitation and Calculations

13.3.1. The GC/MS data stations, in current use, all use the H-P RTE Integrator to generate the raw data used to calculate the standards $\overline{RF_x}$ values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions.

When $\overline{RF_x}$ is used, calculate the extract concentration as follows:

$$C_{ex} = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF_x})}$$

Where: C_{ex} = the concentration in the sample extract (ppm);
$Resp_x$ = the peak area of the analytes of interest;
$Resp_{ISTD}$ = the peak area of the associated internal standard;
Amt_{ISTD} = the amount, in ppm, of internal standard added
$\overline{RF_x}$ = the average response from the initial calibration.

13.3.2. The concentration of analytes in the original sample is computed using the following equations:

Aqueous Samples: $$Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$$

Where Cex = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
Vs = Volume of sample extracted, liters

Non-aqueous Samples: $$Concentration\ (mg / Kg) = \frac{(Cex)\ (Vf)\ (D)}{(W)}$$

Where Cex = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
W = Weight of sample extracted in grams.

13.4. Tentative identification of compounds (TIC)

13.4.1. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The current library is NIST98.

13.4.2. After a visual comparison of sample spectra with the nearest library searches the analyst assigns a tentative identification. Guidelines for tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

13.5. Data Review

Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP for *Laboratory Data Review Process* (ADM-DREV) for details.

13.6. Reporting

13.6.1. Reports are generated in the ALS LIMS by compiling the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file that the Stealth reporting system uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.6.2. As an alternative, reports are generated using Excel© templates located in R:\SVM\forms. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The detected analytes, surrogates and matrix spikes are then transferred, by hand or electronically, to the templates.

13.6.3. Sample concentrations are reported when all QC criteria for the analysis have been met or the results are qualified with an appropriate footnote.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

15.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2. The method detection limit (MDL) is established using the procedure described in the SOP *Performing Method Detection Limit Studies and Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Environmental Health and Safety Manual.

16.3. This method uses Methylene Chloride and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and recycled off site.

16.4. This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of 3 months. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2. Training is documented following *ALS-Kelso Training Procedure* (ADM-TRAIN).

When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. Section 11.5.3, no limit defined in reference method, so lab assigned a limit of 40% based on CLP protocols.

19. REFERENCES

19.1. *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, Method 8270D, EPA Test Methods for Evaluating Solid Waste, SW-846, Final Update IV, February 2007.

19.2. *Determinative Chromatographic Separations*, Method 8000C, EPA Test Methods for Evaluating Solid Waste, SW-846, On-Line March 2003.

19.3. *Determinative Chromatographic Separations*, Method 8000B, EPA Test Methods for Evaluating Solid Waste, SW-846, Update III, December 1996.

20. CHANGES SINCE THE LAST REVISION

20.1. Updated QA Manager.
20.2. Minor grammatical and formatting revisions to improve readability.
20.3. Deleted duplicates in Tables 1A and 1B.

Table 1A – Routine Analytes and MRL/LOQ

ANALYTE	WATER MATRIX		SOIL/SOLID MATRIX	
	MRL/LOQ	Units	MRL/LOQ	Units
1,2,4-Trichlorobenzene	10	µg/L	0.33	mg/Kg
1,2-Dichlorobenzene	10	µg/L	0.33	mg/Kg
1,2-Diphenylhydrazine	10	µg/L	0.33	mg/Kg
1,3-Dichlorobenzene	10	µg/L	0.33	mg/Kg
1,4-Dichlorobenzene	10	µg/L	0.33	mg/Kg
2,3,4,6-Tetrachlorophenol	10	µg/L	0.33	mg/Kg
2,4,5-Trichlorophenol	10	µg/L	0.33	mg/Kg
2,4,6-Trichlorophenol	10	µg/L	0.33	mg/Kg
2,4-Dichlorophenol	10	µg/L	0.33	mg/Kg
2,4-Dimethylphenol	10	µg/L	0.33	mg/Kg
2,4-Dinitrophenol	25	µg/L	2	mg/Kg
2,4-Dinitrotoluene	10	µg/L	0.33	mg/Kg
2,6-Dinitrotoluene	10	µg/L	0.33	mg/Kg
2-Chloronaphthalene	10	µg/L	0.33	mg/Kg
2-Chlorophenol	10	µg/L	0.33	mg/Kg
2-Methyl-4,6-dinitrophenol	25	µg/L	2	mg/Kg
2-Methylnaphthalene	10	µg/L	0.33	mg/Kg
2-Methylphenol	10	µg/L	0.33	mg/Kg
2-Nitroaniline	25	µg/L	0.33	mg/Kg
2-Nitrophenol	10	µg/L	0.33	mg/Kg
3,3'-Dichlorobenzidine	25	µg/L	0.33	mg/Kg
3-Nitroaniline	25	µg/L	0.33	mg/Kg
4-Bromophenyl Phenyl Ether	10	µg/L	0.33	mg/Kg
4-Chloro-3-methylphenol	10	µg/L	0.33	mg/Kg
4-Chloroaniline	10	µg/L	0.33	mg/Kg
4-Chlorophenyl Phenyl Ether	10	µg/L	0.33	mg/Kg
4-Methylphenol	10	µg/L	0.33	mg/Kg
4-Nitroaniline	25	µg/L	2	mg/Kg
4-Nitrophenol	25	µg/L	2	mg/Kg
Acenaphthene	10	µg/L	0.33	mg/Kg
Acenaphthylene	10	µg/L	0.33	mg/Kg
Acetophenone	10	µg/L	0.33	mg/Kg
Aniline	25	µg/L	1	mg/Kg
Anthracene	10	µg/L	0.33	mg/Kg
Atrazine	10	µg/L	0.33	mg/Kg
Benz(a)anthracene	10	µg/L	0.33	mg/Kg
Benzo(a)pyrene	10	µg/L	0.33	mg/Kg
Benzo(b)fluoranthene	10	µg/L	0.33	mg/Kg
Benzo(g,h,i)perylene	10	µg/L	0.33	mg/Kg
Benzo(k)fluoranthene	10	µg/L	0.33	mg/Kg
Benzaldehyde	10	µg/L	0.33	mg/Kg
Benzoic Acid	25	µg/L	2	mg/Kg
Benzyl Alcohol	10	µg/L	0.33	mg/Kg
Biphenyl	10	µg/L	0.33	mg/Kg
Bis(2-chloroethoxy)methane	10	µg/L	0.33	mg/Kg
Bis(2-chloroethyl) Ether	10	µg/L	0.33	mg/Kg
Bis(2-chloroisopropyl) Ether	10	µg/L	0.33	mg/Kg

Table 1A - continued

Bis(2-ethylhexyl) Phthalate	10	µg/L	0.33	mg/Kg
Butyl Benzyl Phthalate	10	µg/L	0.33	mg/Kg
Caprolactam	10	µg/L	0.33	mg/Kg
Carbazole	10	µg/L	0.33	mg/Kg
Chrysene	10	µg/L	0.33	mg/Kg
Dibenz(a,h)anthracene	10	µg/L	0.33	mg/Kg
Dibenzofuran	10	µg/L	0.33	mg/Kg
Diethyl Phthalate	10	µg/L	0.33	mg/Kg
Dimethyl Phthalate	10	µg/L	0.33	mg/Kg
Di-n-butyl Phthalate	10	µg/L	0.33	mg/Kg
Di-n-octyl Phthalate	10	µg/L	0.33	mg/Kg
Fluoranthene	10	µg/L	0.33	mg/Kg
Fluorene	10	µg/L	0.33	mg/Kg
Hexachlorobenzene	10	µg/L	0.33	mg/Kg
Hexachlorobutadiene	10	µg/L	0.33	mg/Kg
Hexachlorocyclopentadiene	10	µg/L	0.33	mg/Kg
Hexachloroethane	10	µg/L	0.33	mg/Kg
Indeno(1,2,3-cd)pyrene	10	µg/L	0.33	mg/Kg
Isophorone	10	µg/L	0.33	mg/Kg
Naphthalene	10	µg/L	0.33	mg/Kg
Nitrobenzene	10	µg/L	0.33	mg/Kg
N-Nitrosodimethylamine	25	µg/L	2	mg/Kg
N-Nitrosodi-n-propylamine	10	µg/L	0.33	mg/Kg
N-Nitrosodiphenylamine	10	µg/L	0.33	mg/Kg
Pentachlorophenol	25	µg/L	2	mg/Kg
Phenanthrene	10	µg/L	0.33	mg/Kg
Phenol	10	µg/L	0.33	mg/Kg
Pyrene	10	µg/L	0.33	mg/Kg
Pyridine	25	µg/L	0.33	mg/Kg

Table 1B – Non-Routine Analytes and MRL/LOQ

ANALYTE	WATER		SOIL/SOLID	
	MRL/LOQ	Units	MRL/LOQ	Units
2-Picoline	10	µg/L	0.6	mg/Kg
N-Nitrosodiethylamine	10	µg/L	0.3	mg/Kg
Methyl Methanesulfonate	10	µg/L	0.3	mg/Kg
Pentachloroethane	10	µg/L	1	mg/Kg
N-Nitrosopyrrolidine	10	µg/L	0.3	mg/Kg
N-Nitrosomorpholine	10	µg/L	0.3	mg/Kg
N-Nitrosopiperidine	10	µg/L	0.3	mg/Kg
O,O,O-Triethyl Phosphorothioate	10	µg/L	0.3	mg/Kg
2,6-Dichlorophenol	10	µg/L	0.3	mg/Kg
Hexachloropropene	10	µg/L	0.3	mg/Kg
N-Nitrosodi-n-butylamine	10	µg/L	0.3	mg/Kg
p-Phenylenediamine	10	µg/L	0.3	mg/Kg
Safrole	10	µg/L	0.3	mg/Kg
1,2,4,5-Tetrachlorobenzene	10	µg/L	0.3	mg/Kg
Isosafrole	10	µg/L	2	mg/Kg
1,3-Dinitrobenzene	10	µg/L	0.3	mg/Kg
Pentachlorobenzene	10	µg/L	0.3	mg/Kg
1-Naphthylamine	10	µg/L	0.3	mg/Kg
2-Naphthylamine	10	µg/L	0.3	mg/Kg
2,3,4,6-Tetrachlorophenol	10	µg/L	0.3	mg/Kg
Diphenylamine	10	µg/L	0.3	mg/Kg
1,3,5-Trinitrobenzene	25	µg/L	2	mg/Kg
Phenacetin	50	µg/L	2	mg/Kg
4-Aminobiphenyl	10	µg/L	0.3	mg/Kg
4-Nitroquinoline N-Oxide	10	µg/L	2	mg/Kg
Total Aramite	50	µg/L	3	mg/Kg
3,3'-Dimethylbenzidine	25	µg/L	2	mg/Kg
7,12-Dimethylbenz(a)anthracene	10	µg/L	0.3	mg/Kg
Hexachlorophene	150	µg/L	5	mg/Kg
3-Methylcholanthrene	10	µg/L	0.3	mg/Kg
N,N-Dimethyl-1-phenethylamine	10	µg/L	20	mg/Kg
2-Acetylaminofluorene	10	µg/L	0.3	mg/Kg
o-Toluidine	10	µg/L	0.3	mg/Kg
Ethyl Methanesulfonate	10	µg/L	0.3	mg/Kg
1,4-Naphthoquinone	10	µg/L	0.3	mg/Kg
5-Nitro-o-toluidine	10	µg/L	0.3	mg/Kg
p-Dimethylaminoazobenzene	10	µg/L	0.3	mg/Kg
Pentachloronitrobenzene	50	µg/L	2	mg/Kg
Methapyrilene	100	µg/L	4	mg/Kg
Chlorobenzilate	10	µg/L	0.3	mg/Kg
2-sec-Butyl-4,6-Dinitrophenol (Dinoseb)	25	µg/L	1	mg/Kg
Diallate	10	µg/L	0.3	mg/Kg
Dimethoate	10	µg/L	0.3	mg/Kg
Disulfoton	10	µg/L	0.3	mg/Kg
Famphur	10	µg/L	0.3	mg/Kg
Isodrin	10	µg/L	0.3	mg/Kg
Kepone	100	µg/L	4	mg/Kg
Methyl Parathion	10	µg/L	0.3	mg/Kg

Table 1B - continued

Parathion	10	µg/L	0.3	mg/Kg
Phorate	10	µg/L	0.3	mg/Kg
Pronamide	10	µg/L	0.3	mg/Kg
Thionazine	25	µg/L	2	mg/Kg

TABLE 2
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-60% of mass 198
365	> 1% of mass 198
441	Present but <24 % of mass 442
442	Base peak, or > 50% of mass 198
443	15-24% of mass 442

Alternate tuning criteria (from Method 625, CLP OLM03.1, or manufacturer's specified criteria) may be used provided that method performance is not adversely affected and that method performance criterion is met. The criteria used must be the same for **all** ion abundance criteria checks associated with a given analysis. For example, initial calibration, continuing calibration(s), QC, and sample analyses for a given sample must all use the same criteria.

TABLE 3
8270 STANDARDS

CALIBRATION
Recommended: Supelco stock standards (or equivalent from other vendors*):

Supelco EPA CLP Semivolatile Calibration Mix
Supelco EPA 8270 Calibration Mix 4
Supelco EPA 8270 Benzidine Mix
Supelco n-Nitrosodiphenylamine
Absolute 2,3,4,6-Tetrachlorophenol
AccuStandard Method 8270 surrogate standard

Prepare 1 ml of each calibration point from purchased stock standards.
Calibration curve: 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 80 ppm, 100 ppm, 120 ppm, 160 ppm, and 200 ppm.
Add 10 µl internal standard (Z-014J) for each 1 ml calibration standard when curve is prepared. Store all calibration standards in 1 ml amber autosampler vials at -10°C. Expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

ICV
Recommended: AccuStandard catalog # (or equivalent from other vendors*):

CLP-HC-BN-R, 1ml x 2, 2000 ppm BN mix
Z-014E-R3, 1ml x 2, 2000 ppm Composite3 mix
Z-014F, 1ml x 2, 2000ppm Benzidines mix
CLP-HC-AR, 1ml x 2, 2000ppm Acid mix
M-8270-SS-PAK, 1ml x 5, 4000ppm Surrogates mix

Add 10 µl internal standard (Z-014J) for each 1 ml of ICV prepared.
Place in 1 ml amber autosampler vial, recap, and store at -10°C.
Expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

CCV & TUNE
Use the same solutions that were used for the calibration curve

Z-014J, 1ml x 5, 4000ppm Internal Standards mix
M-625C, 1ml x 3, 25000ppm DFTPP (added to CCV)
M-625-TS-20x, 1000ppm (separate tuning standard)

Prepare 1 ml of 80 ppm 8270 CCV standard, place in autosampler vial and cap with a crimp top seal. 80ppm is the nominal concentration. CCV concentrations must be varied periodically.
CCV expiration is set at 1 week from date prepared or expiration date of the parent standard(s), whichever is earliest. Tune standard expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

RECAP AND STORE IMMEDIATELY AFTER INJECTING
Store remaining stock solutions in 1 ml amber vials and store.
Expiration date is one year after ampoule is opened.
Order when down to one unopened ampoule.

* Vendor must be A2LA and/or ISO9000 certified.

TABLE 4
QC Standards

Supelco Parent	Initial Concentration	Dilution (mixed)*	Final Conc.
8270 Surrogate			
B/N Surrogate Mix (Absolute cat no. 23016)	5000 µg/mL	20mL to 1000mL in MeOH	100 µg/mL
Acid Surrogate Mix (cat no 86-1376)	10000 µg/mL	15mL to 1000mL in MeOH	150 µg/mL
PAH Surrogate Mix (cat no S8522)	5000 µg/ml	20 ml to 1000ml in MeOH	100 µg/ml
8270 Matrix Spike (mixed solution)			
CLP Semivolatile Mix (cat no. 5-06508)	1000 µg/mL	10mL to 100mL in MeOH	100 µg/mL
Benzidines Mix (cat no. 4-8467)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL
N-Nitrosodiphenylamine (cat no. 46702-U)	5000 µg/mL	2mL to 100mL in MeOH	100 µg/mL
8270 Cal Mix 4 (cat no. 86-1148)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL, 200 µg/mL Pyridine
2,3,4,6-Tetrachlorophenol (cat no. 79131)	1000 µg/mL	10mL to 100mL in MeOH	100 µg/mL
1-Methylnaphthalene (cat no. 4-8162)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL
Pyridine (cat. no. App-9-186-20x)	2000 µg/mL	5mL to 100mL in MeOH	200 µg/mL

* For surrogate solution, split the total volume made into 4 bottles for storage and use. To avoid waste, the quantity made can be varied as anticipated for workload.

Standards Expiration: 6 months from preparation date. Purchased standards may be retained past the expiration date for internal R&D, but must be physically separated from standards in active use by placing in a separate, labeled area. Prepared spiking solutions must not be retained past the expiration date. Sequester expired or concentrated spiking solutions in labeled drawers awaiting disposal.

TABLE 5
INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d4 Internal Standard		
N-Nitrosodimethylamine	1,2-Dichlorobenzene	2-Methylphenol
Aniline	1,3-Dichlorobenzene	3- and 4-Methylphenol (co-eluting)
2-Fluorophenol (surrogate)	1,4-Dichlorobenzene	2-Picoline
Bis(2-chloroethyl) Ether	N-Nitrosodi-n-propylamine	Bis(2-chloroisopropyl) Ether
Phenol-d6 (surrogate)	Hexachloroethane	N-Nitrosopyrrolidine
Phenol	Methyl Methanesulfonate	N-Nitrosomorpholine
2-Chlorophenol	N-Nitrosomethylethylamine	*o*-Toluidine
Benzyl Alcohol	Acetophenone	Ethyl Methanesulfonate
Nitrobenzene	N-Nitrosodiethylamine	Pentachloroethane
Pyridine	Nitrobenzene-d5 (surr.)	
Naphthalene-d8 Internal Standard		
	Hexachlorobutadiene	N-Nitrosodi-*n*-butylamine
	2-Methylnaphthalene	N-Nitrosopiperidine
Isophorone	2-Nitrophenol	N,N-Dimethyl-1-phenethylamine
Bis(2-chloroethoxy)methane	2,4-Dimethylphenol	O,O,O-Triethyl Phosphorothioate
1,2,4-Trichlorobenzene	Benzoic Acid	Hexachloropropene
Naphthalene	2,4-Dichlorophenol	*p*-Phenylenediamine
4-Chloroaniline	4-Chloro-3-methylphenol	Safrole
α,α-Dimethylphenethylamine	2,6-Dichlorophenol	1,2,4,5-Tetrachlorobenzene
Acenaphthene-d10 Internal Standard		
2-Fluorobiphenyl (surrogate)	2,4-Dinitrotoluene	1-Naphthylamine
Hexachlorocyclopentadiene	2,6-Dinitrotoluene	2-Naphthylamine
2-Chloronaphthalene	Diethyl Phthalate	2,3,4,6-Tetrachlorophenol
2-Nitroaniline	4-Chlorophenyl Phenyl Ether	Pentachlorobenzene
3-Nitroaniline	Fluorene	1,3-Dinitrobenzene
4-Nitroaniline	4-Nitrophenol	1,4-Naphthoquinone
Dimethyl Phthalate	2,4,6-Trichlorophenol	5-Nitro-*o*-toluidine
Acenaphthylene	2,4,5-Trichlorophenol	Thionazine
Acenaphthene	2,4-Dinitrophenol	Diphenylamine
Dibenzofuran	Isosafrole	2-Methyl-4,6-dinitrophenol
1,2-Diphenylhydrazine	N-Nitrosodiphenylamine	

TABLE 5 – continued

Phenanthrene-d10 Internal Standard		
4-Bromophenyl Phenyl Ether	Pentachlorophenol	Pentachloronitrobenzene
Hexachlorobenzene	1,3,5-Trinitrobenzene	Disulfoton
Phenanthrene	Phorate	2-sec-Butyl-4,6-Dinitrophenol (Dinoseb)
Anthracene	Phenacetin	Methyl Parathion
Di-n-butyl Phthalate	Diallate	4-Nitroquinoline N-Oxide
Fluoranthene	Dimethoate	Parathion
Carbazole	4-Aminobiphenyl	Methapyrilene
Sulfotep	Pronamide	Isodrin
2,4,6-Tribromophenol (surrogate)		
Chrysene-d12 Internal Standard		
Pyrene	Bis(2-ethylhexyl) Phthalate	Chlorobenzilate
Butyl benzyl Phthalate	Chrysene	Kepone
Benzidine	Terphenyl-d14 (surrogate)	3,3'-Dimethylbenzidine
3,3'-Dichlorobenzidine	Total Aramite	Famphur
Benz(a)anthracene	*p*-Dimethylaminoazobenzene	2-Acetylaminofluorene
Perylene-d12 Internal Standard		
Di-n-octyl Phthalate	Indeno(1,2,3-c,d)pyrene	Hexachlorophene
Benzo(b)fluoranthene	Dibenz(a,h)anthracene	3-Methylcholanthrene
Benzo(k)fluoranthene	Benzo(g,h,i)perylene	
Benzo(a)pyrene	7,12-Dimethylbenz(a)anthracene	

TABLE 6
Recommended Minimum Response Factor Criteria

Compound	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl) Ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitrosodi-n-propylamine	0.500
Hexachloroethane	0.300
Isophorone	0.400
Nitrobenzene	0.200
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2,-Nitroaniline	0.010
Dimethyl Phthalate	0.010
2,6-Dinitrotoluene	0.200

TABLE 6 (continued)

Compound	Minimum Response Factor (RF)
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

TABLE 6 (continued)

Compound	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

TABLE 7
Control Analytes for Non-DoD Projects

1,2,4-Trichlorobenzene
1,4-Dichlorobenzene
2,4-Dinitrotoluene
2-Chloronaphthalene
2-Chlorophenol
4-Bromophenyl Phenyl Ether
4-Chloro-3-methylphenol
4-Nitrophenol
Acenaphthene
Benzo(a)pyrene
Diethyl Phthalate
Hexachloroethane
N-Nitrosodi-n-propylamine
Pentachlorophenol
Phenol
Pyrene

TABLE 8

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C, EPA 8270D	ICAL	Prior to sample analysis	% RSD ≤ 20 COD ≥ 0.990	Correct problem then repeat ICAL
EPA 8000C, EPA 8270D	ICV	After ICAL	± 30% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8000C, EPA 8270D	CCV	Prior to sample analysis	± 20% Diff	Correct problem then repeat CCV or repeat ICAL
EPA 8000C, EPA 8270D	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 8000C, EPA 8270D	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO Table	If exceeds limits, re-extract and re-analyze
EPA 8000C, EPA 8270D	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO Table	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8000C, EPA 8270D	Matrix Spike Duplicates	Include with each analysis batch (up to 20 samples)	W: RPD ≤ 30 S: RPD ≤ 40	Re-homogenize and re-analyze if result is > 5 X the MRL

SOP 17
Organochlorine Pesticides by Gas Chromatography, EPA Method 8082Ar

ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY

ALS-KELSO

SOP ID:	SOC-8082Ar	Rev. Number:	18	Effective Date:	5/30/2017

Approved By: _____ Date: 5/3/17
Department Supervisor/Technical Director – Loren Portwood

Approved By: _____ Date: 5/3/17
QA Manager – Carl Degner

Approved By: _____ Date: 5/4/17
Laboratory Director – Jeff Grindstaff

Issue Date: _____ Doc Control ID#: _____ Issued To: _____

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date

ALS-Kelso SOP Annual Review Statement

SOP Code: SOC-8082AR
Revision: 19

An annual review of the SOP listed was completed on (date): _____

☐ The SOP reflects current practices and requires no procedural changes.

Supervisor: Date:

☒ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision
8.1.1.	Instrument GC27 routine matrix includes Water/Water-LL/Soil/Tissue		UA
11.5.2.	Figure 1: Standards 1-6 1016/1260/TCMX/DCB ICAL Standards		UA
Table 4	Single Point Calibration Standards. Aliquot of 200 ug/L Intermediate: 1000uL Final Volume:10 mL Final Concentration: 20 ug/L		UA
Table 4	ICV Standards: Aliquot: 100 uL Final Volume: 10 mL ICV Standards are then diltued with an aliquot of 20 uL to a final volume of 1 mL to get a final concentration of 20 ug/L		UA

ALS-Kelso SOP Annual Review Statement

SOP Code: SOC-8082AR

Revision: 19

Table 4	1016/1260 Initial Calibration Standards Aroclor 1016/1260 200 ug/L Intermediate: 50 uL Surrogate 20 ug/L Intermediate: 50 uL Final Volume: 10 mL Final Concentraion Aroclors: 1 ug/L Final Concentraion Surrogate: 0.1 ug/L Aroclor 1016/1260 200 ug/L Intermediate: 100 uL Surrogate 20 ug/L Intermediate: 100 uL Final Volume: 10 mL Final Concentraion Aroclors: 2 ug/L Final Concentraion Surrogate: 0.2 ug/L Aroclor 1016/1260 200 ug/L Intermediate: 250 uL Surrogate 20 ug/L Intermediate: 250 uL Final Volume: 10 mL Final Concentraion Aroclors: 5 ug/L Final Concentraion Surrogate: 0.5 ug/L Aroclor 1016/1260 200 ug/L Intermediate: 500 uL Surrogate 20 ug/L Intermediate: 500 uL Final Volume: 10 mL Final Concentraion Aroclors: 10 ug/L Final Concentraion Surrogate: 1 ug/L Aroclor 1016/1260 200 ug/L Intermediate: 1000 uL Surrogate 20 ug/L Intermediate: 1000 uL Final Volume: 10 mL Final Concentraion Aroclors: 20 ug/L Final Concentraion Surrogate: 2 ug/L * Aroclor 1016/1260 50 ug/mL Intermediate: 10 uL Surrogate 5 ug/mL Intermediate: 10 uL Final Volume: 10 mL Final Concentraion Aroclors: 50 ug/L Final Concentraion Surrogate: 5 ug/L Aroclor 1016/1260 50 ug/mL Intermediate: 20 uL Surrogate 5 ug/mL Intermediate: 20 uL Final Volume: 10 mL Final Concentraion Aroclors: 100 ug/L Final Concentraion Surrogate: 10 ug/L Aroclor 1016/1260 50 ug/mL Intermediate: 10 uL Surrogate 5 ug/mL Intermediate: 10 uL Final Volume: 10 mL Final Concentraion Aroclors: 200 ug/L Final Concentraion Surrogate: 20 ug/L		UA

ALS-Kelso SOP Annual Review Statement

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Revision: 18

An annual review of the SOP listed was completed on (date): _____

☐ The SOP reflects current practices and requires no procedural changes.

Supervisor: Date:

☒ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision
Signature Page	Clerical error occuring when overwriting a SOP format changing the title from: ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY to PCBS AS AROCLORS in the forthcoming revision.	12/11/18	CD

TABLE OF CONTENTS

PCBs AS AROCLORS

1. SCOPE AND APPLICATION

1.1. This procedure is used to determine the concentrations of PCBs as Aroclors using EPA Method 8082A. This procedure is typically applied to water, sediment, and soil matrices but may also be applicable to tissue or various miscellaneous waste samples. Tables 1 and 2 lists the analytes that are determined by this procedure and lists the method reporting limits (MRLs) for each compound in water and soil. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. MDLs may change as repeat studies are conducted.

2. METHOD SUMMARY

2.1. This procedure provides gas chromatographic conditions for the detection of parts-per-billion (ppb) levels of PCBs. The target PCBs are extracted from samples using the appropriate procedure for the sample matrix (see applicable SOP), analyzed, and reported as Aroclors.

2.2. An aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a fused silica capillary column. Compounds of interest are detected by an electron capture detector. Identification of the analytes of interest is performed by comparing the retention times of the analytes with the respective retention times of an authentic standard and by comparison of elution patterns to those of Aroclor standards. Quantitative analysis is performed by using the authentic standard to produce a calibration factor or calibration curve, and using the calibration data to determine the concentration of an analyte in the extract. The concentration in the sample is calculated using the sample weight or volume and the extract volume.

2.3. The sensitivity of this method usually depends on the level of interferences rather than on instrument limitations. If interferences prevent detection of the analytes, GPC, Florisil cleanup, sulfur cleanup, or concentrated sulfuric acid cleanups are used to eliminate interferences in the analysis. Refer to section 4.2 for cleanup procedure references.

2.4. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD) may supersede the requirements defined in this SOP.

3. DEFINITIONS

3.1. **Analysis Sequence** - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

3.2. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.2.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.2.2. Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.3. **Sample**

3.3.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.3.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.4. **Quality System Matrix** - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.4.1. Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.4.2. Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.4.3. Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.4.4. Nonaqueous Liquid - Any organic liquid with <15% settleable solids.

3.4.5. Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.4.6. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.4.7. Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.4.1 through 3.4.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.4.8. Miscellaneous matrices – Samples of any composition not listed in 3.4.1 – 3.4.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff,

mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.5. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.6. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.7. Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

3.8. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.9. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts of target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.10. Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.11. Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.12. Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.13. Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods,

institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4. INTERFERENCES

4.1. Interferences by phthalate esters can pose a major problem in PCB determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large, late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Phthalate contamination is not usually a problem in our laboratory operation.

4.2. Co-extractables such as lipids, waxes, etc., can be removed via GPC cleanup (SOC-3640A). Certain fractionation cleanups can be used to selectively remove organochlorine pesticides, aiding in Aroclor determination (SOC-3665). The presence of elemental sulfur will result in interferences for most Aroclors. If GPC cleanup is insufficient, cleanup via Method 3660 (SOC-3660) may be used for the removal of sulfur. If interferences from polar compounds is evident, cleanup using Florisil (EXT-FLOR) can be utilized.

4.3. A standard of the DDT analogs must be injected with each initial calibration to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

5. SAFETY

5.1. The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.2. Follow all applicable safety procedures as described in the ALS Kelso Chemical Hygiene Plan. A reference file of safety data sheets is available to all personnel involved in these analyses. ALS also maintains a file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Containers used to collect samples should be purchased pre-cleaned containers. Alternatively, containers may be soap and water washed followed by methanol (or isopropanol) rinsing. The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may not be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

6.2. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in

contact with the sampler (e.g., if an automatic sampler is used), run reagent water through the sampler and use the rinsate as a field blank.

6.3. Samples should be tested for residual chlorine at the time of sampling. For aqueous samples with residual chlorine present, add 3-mL 10% sodium thiosulfate solution per gallon (0.008%).

6.4. Water and soil samples must be iced or refrigerated at 4 ± 2ºC from time of collection until extraction. Tissue samples should be stored in accordance with project requirements, typically refrigerated or frozen.

6.5. There are no holding time requirements for this method.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

7.2. Solvents: Hexane, acetone, methylene chloride, isooctane, and methanol. Pesticide grade or equivalent. Solvents must be of sufficient purity to permit usage without lessening the accuracy of the determination or introducing interferences.

7.3. Stock Standard Solutions

7.3.1. Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials.

7.3.2. Stock standard solutions for each target Aroclor are purchased from AccuStandard at 1000 µg/mL. Other vendors may be used providing they meet the requirements in sec 7.3.1. Unopened stock standard solutions are stored as directed by manufacturer's recommendation. If no storage instructions are provided, the standards are stored at ambient and protected from light. Opened ampoules are stored in crimp-sealed vials at 4ºC ± 2ºC. The expiration date for unopened ampoules is the manufacturer's assigned expiration date. If the manufacturer does not assign a date, an expiration date of 1 year from receipt is assigned. Check opened stock standards frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.3.2.1. Intermediate calibration standard solutions are made for the following Aroclor mixtures by diluting 1000 µg/mL stock standards 1:20 in hexane:

- Aroclor 1016/Aroclor 1260
- Aroclor 1221/Aroclor 1254
- Aroclor 1232/Aroclor 1262
- Aroclor 1242/Aroclor 1268
- Aroclor 1248

7.3.2.2. Prepare calibration standards at a minimum of five concentration levels for each Aroclor by dilution of the intermediate standards with hexane. One of the concentration levels should be at or below a concentration representing the method reporting limit (MRL). The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. See Table 4 for preparation and concentrations. A calibration standard of Aroclor 1016/Aroclor 1260 and the surrogates at mid-range concentration is used for the CCV.

7.3.2.3. Calibration standard solutions are stored at 4 ± 2ºC and must be replaced after six months, or sooner, if comparison with check standards indicate a problem.

7.3.3. The independent calibration verification (ICV) standards for each target Aroclor are purchased from Ultra Scientific at 100 µg/mL. Other vendors may be used providing they meet the requirements in sec 7.3.1. Unopened stock standard solutions are stored as directed by manufacturer's recommendation. If no storage instructions are provided, the standards are stored at ambient and protected from light. Opened ampoules are stored in crimp-sealed vials at 4ºC ± 2ºC. The expiration date for unopened ampoules is the manufacturer's assigned expiration date. If the manufacturer does not assign a date, an expiration date of 1 year from receipt is assigned. Check opened stock standards frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.3.3.1. Working ICV standards at 1000 µg/L are prepared as described in Table 4. ICV Standards are stored at 4ºC ± 2ºC for up to six months.

7.3.4. Surrogate solutions are prepared from stock solutions of Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) purchased from Ultra Scientific at 200 µg/mL. Other vendors may be used providing they meet the requirements in sec 7.3.1.

7.3.4.1. An intermediate surrogate standard is prepared with the Aroclor 1016/Aroclor 1260 intermediate standard by diluting the 200 µg/mL surrogate stock 1:40 with hexane.

7.3.4.2. A surrogate spiking solution is prepared at 2 µg/mL by making a 1:100 dilution of the surrogate stock standard in acetone. The surrogate solution is stored in the refrigerator for up to six months.

7.3.5. Matrix spike solution: Prepare a spiking solution at 40 µg/mL containing both Aroclors 1016 and 1260 by diluting the 1000 µg/mL stock standards 1:25 with acetone.

8. APPARATUS AND EQUIPMENT

8.1. Gas Chromatograph (GC)

8.1.1. Analytical system complete with gas chromatograph suitable for splitless or split automated injection into a wide bore capillary column with an electron capture detector (ECD). Use of Large Volume Injection (LVI) is optional. Helium is used as the

carrier gas; argon/methane mixture is used for the detector makeup gas (auxiliary gas). Current instrumental systems are identified as follows:

Instrument I.D.	Analytical System	Routine Matrix
GC27	Agilent 6890	Water/Soil/Tissue
GC32	Agilent 6890	Water/Water-LL/Soil/Tissue

8.1.2. GC Autosampler: The GC system should be configured with a compatible autosampler for automated injection of standards, samples, and QC samples.

8.1.3. GC Columns - fused silica capillary columns
Column 1: DB-35MS, 30-m x 0.32mm, 0.25um film thickness, or equivalent.
Column 2: DB-XLB, 30-m x 0.32mm, 0.5um film thickness, or equivalent.

Note: Column diameter and film thickness varies depending on the column. Refer to the instrument maintenance logbook for the column used for a specific instrument configuration.

8.2. Data System - A computer data system must be interfaced to the GC/ECD. The system allows the continuous acquisition and storage on machine-readable media of chromatographic data obtained throughout the duration of the analysis program. The computer must have software that includes automated calibration, identification, and quantitation routines. The software must also be capable of integrating the chromatographic peaks abundances. The current version of the manufacturer's software is preferred (Target or HP ChemStation/EnviroQuant).

9. PREVENTIVE MAINTENANCE

9.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

9.2. Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

9.3. Gas Chromatograph

9.3.1. Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, ferrules, and autosampler syringe as needed. The liner should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners may be cleaned and re-used. Additionally, disassembly and sonication of the septum-less head may be performed if indicated.

9.3.2. Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and "clean" (uniform, without fragmentation) by using the proper column cutting tool.

9.3.3. Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in 8082A, is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. Sample Preparation

11.1.1. Water samples (1L) are extracted at a pH of 5-9 with methylene chloride, using either continuous liquid-liquid extraction (EPA Method 3520C, EXT-3520); solid phase extraction (EPA Method 3535A, EXT-3535) or by microextraction (SW-846 Method 3511, EXT-3511). Refer to the applicable extraction SOP. For extraction by 3535A, acidification of the sample prior to extraction may be allowable if project objectives and performance requirements of methods 3535A and 8082A are met. An ultra low-level water option may be used, where a 1 L sample amount and a final extract volume of 2 mL is used. Splitless injection is typically used for the ultra, low-level option.

Note: Project-specific or regulation-specific extraction methods may apply. For projects originating from South Carolina and under the SC DHEC lab certification, use the EPA Method 3520C extraction method only.

11.1.2. Soil/sediment samples are extracted using either a Soxhlet extraction (EPA Method 3540C, EXT-3540), automated Soxhlet extraction, (EPA Method 3541, EXT-3541), ultrasonic extraction (EPA Method 3550, EXT-3550) or by microwave extraction (SW-846 Method 3546, EXT-3546). Refer to the applicable extraction SOP. A low-level sediment option may be used where the sample weight of 40 g (20 g dry weight) and a final extract volume of 4 mL are used.

11.1.3. Waste samples (organic liquids) may be prepared using the waste dilution method (EPA Method 3580A, EXT-3580). Refer to the extraction SOP for specific parameters.

11.1.4. Additional sample cleanup procedures may be employed as appropriate for the samples. Refer to the section on interferences and the appropriate ALS SOP.

11.2. Calibration

Note: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL) are described as follows:

Note: Certain state or program protocols have specific procedures for calibration. The analyst must ensure that the correct procedures are used. Known exceptions are as follows:

- The use of quadratic regression calibration is not allowed for projects (samples) originating from South Carolina and under the SC DHEC lab certification.

Note: DOD QSM requires the quantitation for Aroclors must be performed using a 5-point calibration. Results may not be quantitated using a single point.

11.2.1. For each target Aroclor, select three to six characteristic peaks to use for quantitation. Choose peaks that are at least 25% of the height of the largest Aroclor peak and do not coelute with any of the DDT analogs. For each Aroclor, select at least one quantitation peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016 and Aroclor 1260 mixture, none of which should be found in both of these Aroclors. Establish the retention time window position using the mid-point of the ICAL range before processing the calibration curve.

11.2.2. Calibrate the system immediately prior to conducting any analyses. Refer to Table 3 for instrument conditions. Starting with the standard of lowest concentration, analyze each calibration standard and tabulate response (peak area) versus the concentration in the standard. Calculate the ratio of the response to the amount injected the (calibration factor) for each analyte at each standard concentration. The Relative Standard Deviation (RSD) must be less than 20% when average response factor is used.

11.2.3. The calibration of each Aroclor is verified by an independent source. Prepare an independent calibration verification standard (ICV) by dilution of a stock solution purchased from a different vendor and analyze immediately after each initial calibration. Calculate the concentration using the typical procedure used for quantitation. Calculate the percent difference (%D) from the ICV true value. Evaluate the ICV as described in *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL).

11.3. Calibration Verification

11.3.1. The working calibration curve or calibration factor must be verified on each analytical sequence by the analysis of one or more mid-range calibration standards (CCV) containing Aroclors 1016/1260 and the surrogates. A standard (CCV) must be injected at the start of each sequence and after each set of sample extracts (every 10 samples or every 12 hours, whichever is first) in the analysis sequence. Evaluate the CCV as described in SOC-CAL. The %D for Aroclor 1016 is a control for Aroclors 1016, 1221, 1232, 1242, and 1248. The %D for Aroclor 1260 controls for Aroclors 1254, 1260, 1262, and 1268.

Note: DOD projects require a CCV analysis every 10 field samples.

11.4. Retention Time Windows

11.4.1. Pattern recognition/matching and retention times are used for the identification of PCBs as Aroclors.

11.4.2. Establish retention time windows for the peaks used for quantitation with the GC system in acceptable operating condition. Make three injections of all analytes throughout the course of a 72 hour period. Serial injections over less than a 72 hour period may result in retention time windows that are too tight. Using retention times from these analyses, calculate retention time windows. Refer to EPA Method 8000C for detailed instructions.

11.4.3. Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. In those cases where the standard deviation for a particular standard is zero, the laboratory may use a default window of ± 0.03 minutes. If the peak width is > 0.06 minutes, use a default window of 0.1 minutes.

11.4.4. Calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. Retain this data in the method file.

11.5. Gas Chromatography

11.5.1. Set up an analytical sequence for the standards and samples to be analyzed. Calibrate the system as described in Section 11.2. Refer to Table 3 for typical instrument operating conditions. The same conditions must be used for samples as for calibration and QC analyses. Ensure that the instrument configuration is correct and that any necessary maintenance has been performed. Figure 1 shows a typical analysis sequence.

11.5.2. Evaluate the CCVs as indicated in Section 11.3. Use the standards interspersed throughout the sample analysis sequence to evaluate the qualitative performance of the GC system including positioning of the retention time window. If any retention time shift which would impede analyte identification is evident (as shown by Aroclor pattern irregularities or the surrogate falling outside of the retention time window), evaluate the chromatogram for possible causes such as carryover from a highly contaminated sample. If a problem related to GC system has been determined to be the cause of retention time shift, perform whatever maintenance is necessary before reanalyzing the CCV or recalibrating and proceeding with sample analysis. All samples that were injected after the sample exceeded the criteria must be reinjected if initial analysis indicated the presence of any analytes of interest.

FIGURE 1

Analysis Sequence

2,4'/4,4'-DDx Retention Time Marker	
Initial Calibration Blank	ICB
Standards 1-6	1016/1260/TCMS/DCB ICAL Standards
Standards 7-12	1221/1254 ICAL Standards
Standards 13-18	1232/1262 ICAL Standards
Standards 19-24	1242/1268 ICAL Standards
Standards 25-30	1248 ICAL Standards
Standards 31-39	ICVs for 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268
Continuing Calibration Verification	CCV
CCB	
Method Blank	
Laboratory Control Sample	LCS
Sample 1 - 8	
Matrix Spike	
Duplicate Matrix Spike	
Continuing Calibration Verification	CCV
Continuing Calibration Blank	CCB
Sample 9 - 18	
Continuing Calibration Verification	CCV
Continuing Calibration Blank	CCB

Note: For DOD projects, the CCB must be analyzed following the CCV. Instrument blanks and CCBs may not be analyzed prior to QC samples or standards.

11.6. Troubleshooting

11.6.1. Initial calibration – If the initial calibration fails to meet the criteria, or the ICV fails (indicating a calibration problem), the following steps may be taken, depending on nature of the problem.

- Recheck the information entered into the software used for calibration and quantitation. Verify the standard values are correct and data files are correct. If incorrect, repeat the calibration with the correct information.
- Recheck standards preparation to ensure that standards are correct. Re-prepare and reanalyze if needed.
- Ensure that proper preventive maintenance was performed. Repeat the preventive maintenance if necessary and reanalyze the calibration.
- If calibration problems persist or more substantial calibration problems exist, corrective maintenance or repair may be needed. This includes such measures as column changes, detector maintenance, or GC repair. This will depend on the nature of the problem. Following any such maintenance, repeat the calibration.

11.6.2. Continuing calibration – If the CCV analysis fails to meet the criteria, the following steps may be taken, depending on nature of the problem.

- Recheck the information entered into the software used for calibration and quantitation. Verify the standard values are correct and data files are correct. If incorrect, repeat the calibration with the correct information.
- Recheck standards preparation to ensure that standards are correct and that the correct standard is used as the CCV. Re-prepare and reanalyze if needed. Note that NELAC and DOD requirements apply when multiple CCVs are analyzed.
- Ensure that proper preventive maintenance was performed. Repeat the preventive maintenance if necessary and reanalyze the CCV.
- If calibration problems persist or more substantial calibration problems exist, corrective maintenance or repair may be needed. This includes such measures as column changes, detector maintenance, or GC repair. This will depend on the nature of the problem. Following any such maintenance, repeat analysis of the CCV and necessary samples. Major maintenance will require recalibration. Note that some samples may quickly deteriorate the system to the point that closing CCVs will not pass. This should be verified through a second run of the samples and documented..

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

12.1.1. The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made. To do this, four water samples are spiked with the LCS spike solution, then prepared and analyzed.

12.2. Method Detection Limits and Method Reporting Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2. Calculate the average concentration found (x) in µg/mL, and the standard deviation of the concentrations (s) in µg/mL for each analyte. Calculate the MDL for each analyte. Refer to *Performing Method Detection Limit Studies and Establishing Limits of detection and Quantification* (CE-QA011). The MDL study must be verified annually.

12.2.3. Limits of Quantification (LOQ)

12.2.3.1. The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis at the lowest point calibration level provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within 50% of the true values to verify the data reporting limit. Refer to *Performing Method Detection Limit Studies and Establishing Limits of detection and Quantification* (CE-QA011).

12.2.4. The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DOD ELAP must follow requirements defined in the DoD *Quality Systems Manual for Environmental Laboratories.* General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD). General QC Samples are:

12.3.1. Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps minimized. No target analytes should be detected above the MRL in the method blank.

12.3.1.1. If the method blank fails to meet the criteria, the sample data in the associated batch should be examined. If all samples and QC have hits for the analyte, samples and QC should be re-extracted and reanalyzed as necessary (samples with higher level hits may not need reanalysis). It should be verified through the analysis of instrument blanks that the problem is isolated to either the GC of the sample preparation. If the problem is isolated to the MB, the data may be flagged and narrated. Also refer to the QA Manual for additional corrective action.

12.3.1.2. The source of MB contamination should be isolated and corrected as soon as possible to prevent further failures.

Note: DOD projects require no analytes detected > ½ the RL or > 1/10 the regulatory limit.

12.3.2. A lab control sample (LCS) must be extracted and analyzed with every batch of 20 samples. The water LCS is prepared by adding 50 µL of the matrix spike solution to 1L of reagent water, resulting in a concentration of 2.0 µg/L. The soil LCS is prepared by adding 100 µL of spike solution to 20 g of sand, resulting in a concentration of 200 µg/kg. For project-specific low-level extractions, spiking amounts can be adjusted accordingly. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

Acceptance criteria for lab control samples are listed in Table 1.

12.3.3. Project-specific or program-specific acceptance criteria may supersede ALS criteria. For example, for samples requiring South Carolina DHEC certification the acceptance criteria are 70-130% recovery. If the lab control sample (LCS) fails acceptance limits for any of the compounds, the analyst must evaluate the system and calibration. If

no problems are found, corrective action must be taken. The acceptance criteria listed are current criteria, but are subject to change as control limits are updated.

12.3.4. A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples. The MS/DMS is prepared by adding the same volume of the matrix spike solution to the sample as listed for the LCS, then proceeding with the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
$X1$ = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where $R1$ = % recovery of the MS
$R2$ = % recovery of the DMS

Acceptance criteria for matrix spikes are listed in the DQO tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken. The acceptance criteria listed are current criteria, but are subject to change as control limits are updated.

12.3.5. Surrogate spike is added to every sample, blank and spike prior to extraction. Two surrogate standards (Tetrachloro-m-xylene and Decachlorobiphenyl) are added to each sample. For water, 100 µL of the surrogate spike is added to 1 L, resulting in 0.2 µg/L. For soil, 200 µL of the surrogate spike is added to 20 g, resulting in 20 µg/Kg. Calculate surrogate percent recovery (%R) as:

%R = S/V x 100
Where S = The amount of surrogate recovered

V = The amount spiked/final volume

Both surrogate recoveries must be within the acceptance limits listed in the DQO tables. If either (or both) surrogate is outside of acceptance limits for reasons other than matrix interferences, corrective action must be taken. Corrective actions include recalculation, reanalysis, or re-extraction and reanalysis. The acceptance criteria listed are current criteria, but are subject to change as control limits are updated.

12.3.6. Control charts should be maintained for QC results. The charts should be reviewed periodically for trends in results. Control limits for QC analyses may be determined using the control charts or similar mechanism on an annual basis.

13. DATA REDUCTION AND REPORTING

13.1. Identification of PCBs as Aroclors

13.1.1. To identify Aroclors, compare the chromatographic pattern of the sample to known Aroclor standards. Tentative identification of PCBs as Aroclors is made when the pattern of peaks in the sample chromatogram matches the pattern of peaks in the Aroclor standard itself. There also needs to be agreement between the retention times and response ratios of the 3-6 selected quantitation peaks in the sample chromatogram and the Aroclor standard.

13.1.2. Tentative identification of analytes must be confirmed using a second GC column of dissimilar phase. Identify the Aroclor by comparing the chromatographic pattern of the sample to known Aroclor standards analyzed on the same column. Confirmation of the Aroclor is made when the sample chromatogram matches the pattern of peaks in the Aroclor being confirmed. Quantitation results for the 2 columns must agree ($\leq$ 40%RPD) to confirm the identification. If interferences or other sample anomalies make the RPD value >40% but the analyst makes a positive identification, the basis of the identification must be documented and the data user notified of the discrepancy (see section 13.2).

13.2. Sample matrix difficulties

13.2.1. Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the pattern of a specific Aroclor so it does not closely match an Aroclor standard. The earlier eluting peaks will often diminish in comparison to the later eluting peaks. If this is observed, alternate peaks may be selected to aid identification to reduce quantitation bias.

13.2.2. Metabolism by organisms may also alter the pattern since individual PCB congeners are metabolized at different rates. When working with tissue samples, the 40% RPD criteria for confirmation may not be met.

13.2.3. Samples may also include mixtures of two or more Aroclors. To the extent possible, identify and quantify each Aroclor.

13.2.4. High amounts of organochlorine pesticides in the sample may interfere with identification. If this is observed, alternate peaks may be selected to aid identification and to reduce quantitation bias.

13.2.5. For all of these reasons a high level of analyst expertise is required to interpret complex chromatograms.

13.3. Quantitation of PCBs as Aroclors:

13.3.1. The quantitation of PCBs as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard or standards. All calibration acceptance criteria as described in section 11 must be met before reporting any results. Sample results should then be reported according to the organics confirmation SOP (SOC-CONF). Results may be reported from either column if all calibration acceptance criteria as described in section 11 are met.

13.3.2. Once the Aroclor pattern has been identified, compare the responses of 3 to 6 major peaks in the calibration standard of that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 6 peaks and the calibration model selected in section 11. The concentration is determined using the 3 to 6 characteristic peaks and then the concentrations are averaged to determine the concentration of the Aroclor. If there are interfering peaks with the 3 to 6 quantitation peaks that cause Aroclor average to be falsely overstated, then that interference peak is Q-deleted using the data system and the average is recalculated so that the average more truly represents the concentration in the sample. This often occurs when there are more than one Aroclor in a sample extract or if pesticides are present. Quantitation of mixed Aroclors will require the selection of peaks that are not shared in common by both Aroclors.

13.3.3. For samples with severe matrix interferences, the quantitation may be performed by measuring the total area of the PCB pattern and quantifying on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs should be subtracted from the total area. When the quantitation option is used, the sample problems should be described for the data user and quantification procedure documented.

13.3.4. Using the data system, calculate the concentration in the extract using the calibration model chosen for calibration (SOC-CAL).

13.3.5. Using the data system, calculate the concentration of each analyte in the sample extract (Cex) in µg/ml units using the calibration factor or calibration curve (Section 11). The sample concentration computed using the following equations:

Aqueous Samples:

$$Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$$

Where Cex = Concentration in extract in µg/ml
Vf = Final volume of extract in ml
D = Dilution factor
Vs = Volume of sample extracted, liters

Nonaqueous Samples:

$$Concentration\ (mg / Kg) = \frac{(Cex)\ (Vf)\ (D)\ x\ 1{,}000}{(W)\ x\ 1{,}000}$$

Where Cex = Concentration in extract in µg/ml
Vf = Final volume of extract in ml
D = Dilution factor

W = Weight of sample extracted. The wet or dry weight may be used, depending upon the specific client requirements.

13.4. Sample concentrations are reported when all QC criteria for the analysis have been met or the results are qualified with a footnote.

13.5. Data Review

13.5.1. Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to *Laboratory Data Review Process* (ADM-DREV) for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Manager to inclusion in the report narrative.

13.6. Reporting

13.6.1. Reports are generated using the STEALTH data reporting system which compiles the SMO login information. This compilation is then transferred to a file, which STEALTH uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.6.2. As an alternative, reports are generated using Excel© templates located in R:\SVG\forms. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The results for detected analytes, surrogate(s) and matrix spikes are then transferred, by hand or electronically, to the templates.

13.6.3. Sample concentrations are reported when all QC criteria for the analysis have been met or the results are qualified with an appropriate footnote. For Arizona projects the appropriate Arizona qualifier must be used.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Non Conformance and Corrective Action (*CE-QA008*)* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

15.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2. The method detection limit (MDL) is established using the procedure described in *Performing Method Detection Limit Studies and Establishing Limits of detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Kelso Chemical Hygiene Plan and the ALS Kelso Lab Waste Management Plan.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable SDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of 3 months. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2. Training is documented following the *ALS-Kelso Training Procedure* (ADM-TRAIN).

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

19. REFERENCES

19.1. Polychlorinated Biphenyls (PCBs) as Aroclors, Method 8082A, Revision 1, February 2007, EPA Test Methods for Evaluating Solid Waste, SW-846, Update IV

19.2. Determinative Chromatographic Separations, EPA SW846, Test Methods For Evaluating Solid Waste, On-Line, Method 8000C, Revision 3, March 2003.

19.3. 8000C Method criteria, Arizona DHS, 2/13/2007. Available online at http://www.azdhs.gov/lab/license/tech/8000cmethod.pdf

19.4. *DoD Quality Systems Manual for Environmental Laboratories,* Version 5.0.

20. CHANGES SINCE THE LAST REVISION

20.1. Section 11: Added references to EXT-3511 and EXT-3546, Change Request – 2/24/17.
20.2. Updated SOP and Manual references throughout.
20.3. Minor typographical, grammatical, and format corrections.
20.4. Updated DOD reference to current version of QSM.

TABLE 1
Target Analytes and Method Reporting Limits* - Water

Analyte	Standard Level (µg/L)	Low-Level (µg/L)	Ultra Low-Level (µg/L)
Aroclor 1016	0.20	0.020	0.0050
Aroclor 1221	0.40	0.040	0.010
Aroclor 1232	0.20	0.020	0.0050
Aroclor 1242	0.20	0.020	0.0050
Aroclor 1248	0.20	0.020	0.0050
Aroclor 1254	0.20	0.020	0.0050
Aroclor 1260	0.20	0.020	0.0050
Aroclor 1262	0.20	0.020	0.0050
Aroclor 1268	0.20	0.020	0.0050

TABLE 2
Target Analytes and Method Reporting Limits* – Soil/Sediment

Analyte	Standard Level (mg/Kg)	Low-Level (µg/Kg)
Aroclor 1016	0.10	10
Aroclor 1221	0.20	20
Aroclor 1232	0.10	10
Aroclor 1242	0.10	10
Aroclor 1248	0.10	10
Aroclor 1254	0.10	10
Aroclor 1260	0.10	10
Aroclor 1262	0.10	10
Aroclor 1268	0.10	10

* For some analytes, LOQs may vary slightly from MRLs due to program/project requirements.

TABLE 3
Gas Chromatograph Operating Conditions*

Gas Chromatograph:	Agilent 6890 or Equivalent w/ ECD
Injection Port Temperature:	Initial Temp 90ºC for 0.5 min., 250ºC/min ramp to 325ºC for 5.0 min., 20ºC/min ramp to 250ºC for 5.0 min.
Oven Temperature Program:	90˚C hold for 0.5min., 5˚C/min ramp to 230ºC for 0.5 min., 7ºC/min ramp to 315ºC, hold for 0.06 min.
Detector Temperature:	325˚C
Injection Volume:	1 µL
Column 1:	DB-35MS, 30 m, 0.32 mm ID, 0.25 µm film thickness or equivalent.
Column 2:	DB-XLB, 30 m, 0.32 mm ID, 0.50 µm film thickness or equivalent
Carrier Gas:	Hydrogen
Auxiliary Gas:	Nitrogen
Data System:	HP ChemStation (acquisition), Target (data processing)

* The above instrument temperatures may be modified depending on the instrument used. The GC column diameter and phase thickness depend on the instrument used. All conditions must be the same for initial calibration, continuing calibration, sample, and QC analysis.

TABLE 4
Calibration Standard Preparation

1016/1260 Initial Calibration Standards (prepared in hexane)

Aroclor 1260 50 µg/mL Intermediate	Surrogate 5 µg/mL Intermediate	Final Volume	Final Concentration Aroclors	Final Concentration Surrogates
12.5 µL	12.5 µL	25 mL	25 µg/L	2.5 µg/L
25 µL	25 µL	25 mL	50 µg/L	5.0 µg/L
250 µL	250 µL	25 mL	500 µg/L	50 µg/L
500 µL	500 µL	25 mL	1000 µg/L*	100 µg/L*
1000 µL	1000 µL	25 mL	2000 µg/L	200 µg/L
2500 µL	2500 µL	25 mL	5000 µg/L	500 µg/L

* CCV Standard

Single-Point Calibration Standards

Aliquot	Final Volume	Solvent	Final Concentration
25 µL	25 mL	Hexane	1000 µg/L
25 µL	25 mL		1000 µg/L
25 µL	25 mL		1000 µg/L
25 µL	25 mL		1000 µg/L
25 µL	25 mL		1000 µg/L
25 µL	25 mL		1000 µg/L
25 µL	25 mL		1000 µg/L

ICV Standards

Aliquot	Final Volume	Solvent	Final Concentration
250 µL	25 mL	Hexane	1000 µg/L
250 µL	25 mL		1000 µg/L
250 µL	25 mL		1000 µg/L
250 µL	25 mL		1000 µg/L
250 µL	25 mL		1000 µg/L
250 µL	25 mL		1000 µg/L
250 µL	25 mL		1000 µg/L
250 µL	25 mL		1000 µg/L
250 µL	25 mL		1000 µg/L

* As needed for projects requiring non-routine additional compounds, similar dilutions are prepared to obtain calibration standards for these compounds.

TABLE 5

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C EPA 8082A	ICAL	Prior to sample analysis	% RSD ≤ 20 R^2 COD ≥ 0.990	Correct problem then repeat ICAL
EPA 8000C EPA 8082A	ICV	After ICAL	± 20% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8000C EPA 8082A	CCV	Prior to sample analysis, every 10 samples or 12 hours	± 20% Diff	Correct problem then repeat CCV or repeat ICAL
EPA 8000C EPA 8082A	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 8000C EPA 8082A	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO	If exceeds limits, re-extract and re-analyze
EPA 8000C EPA 8082A	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8000C EPA 8082A	Matrix Spike Duplicates	Include with each analysis batch (up to 20 samples)	See DQO	Evaluate data to determine if the there is a matrix effect or analytical error

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

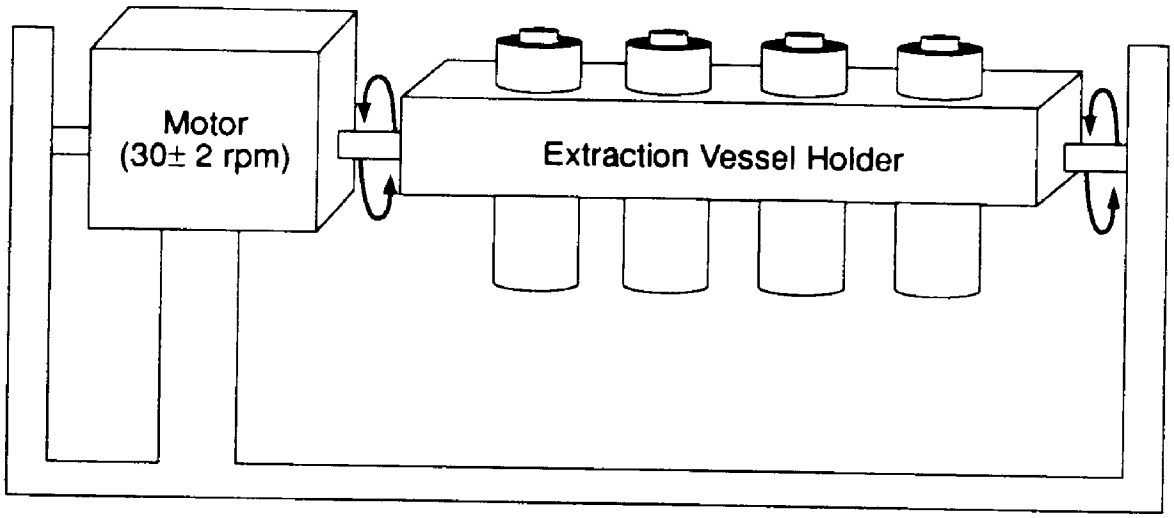


Figure 1. Rotary Agitation Apparatus

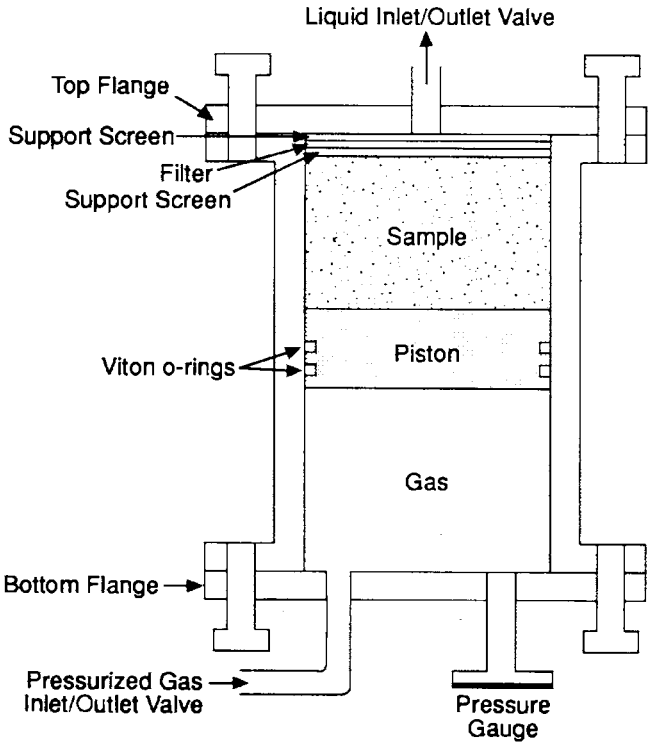
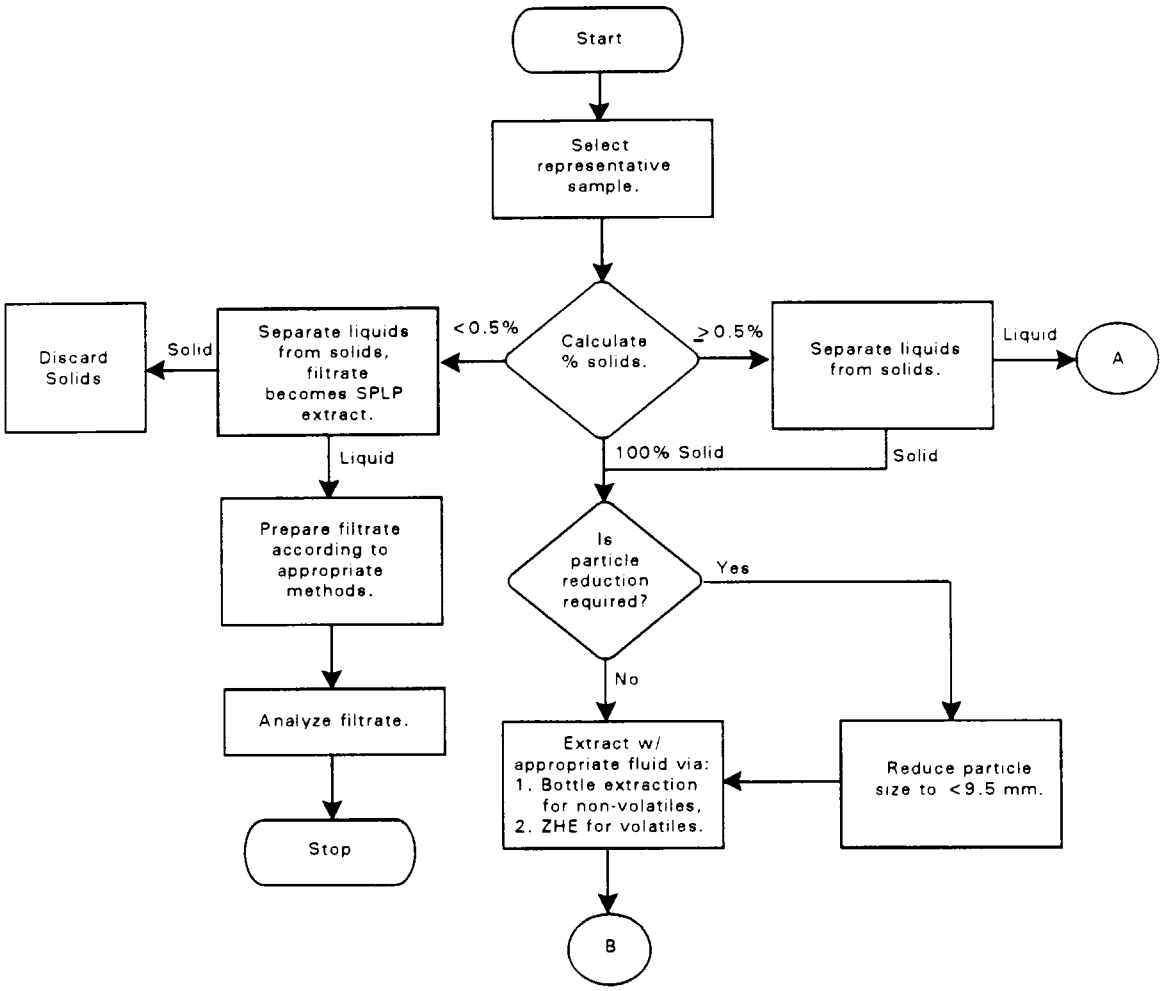
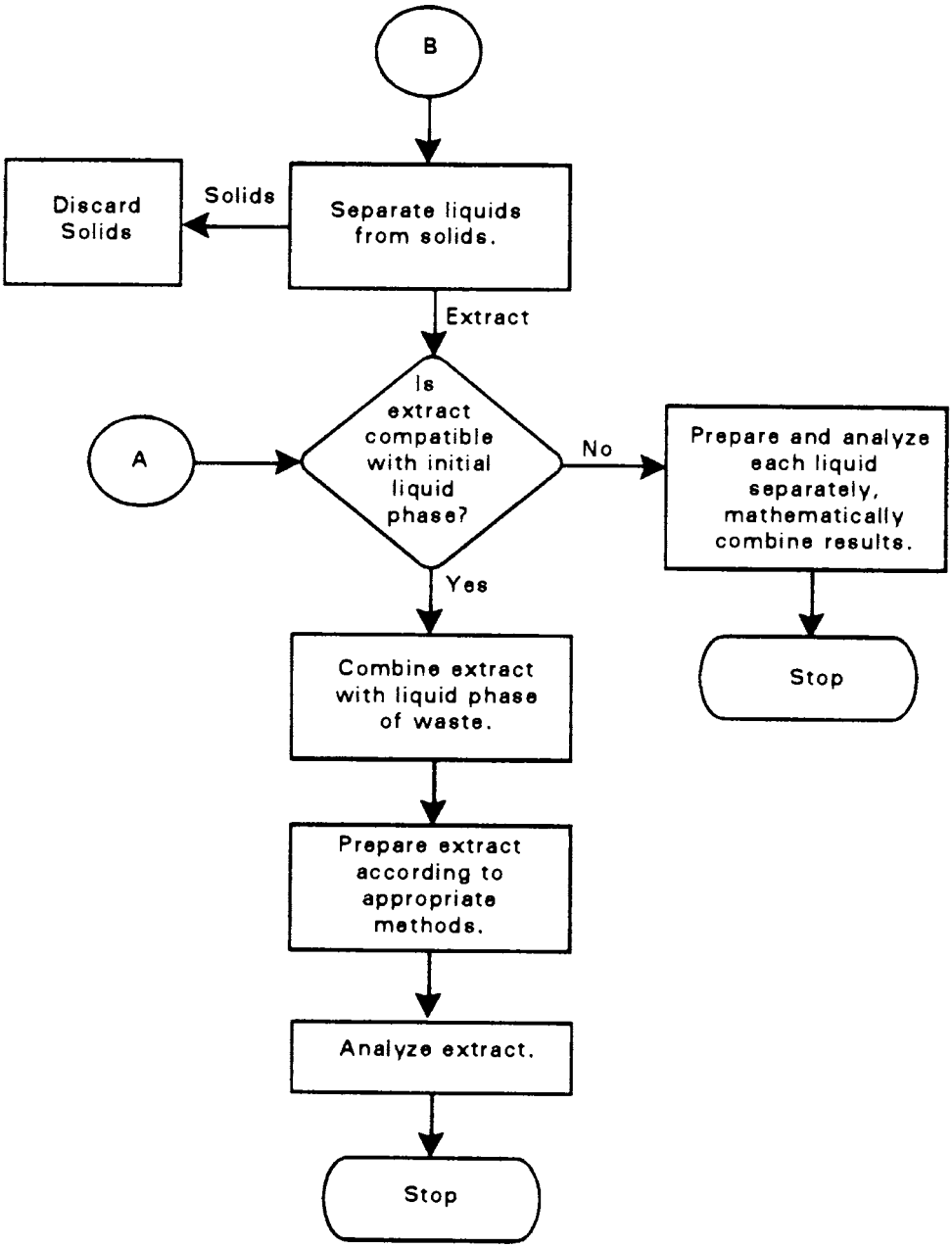


Figure 2. Zero-Headspace Extractor (ZHE)

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: _____