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Quality Assurance Project Plan for

IN-VIAL PRESERVATION OF SOIL VOCs

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by
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A. Project Management

1. Project Organization

The project organization and names of responsible individuals are given in Figure 1. The Work Assignment Manager (WAM), Brian Schumacher, of the Environmental Protection Agency (EPA) Environmental Sciences Division-Las Vegas (ESD-LV), is responsible for direction and oversight of this project. George Brilis, ESD-LV Quality Assurance Manager, will ensure that the project conforms to the quality standards set by the EPA.

The Lockheed Martin (LM) Quality Assurance (QA) Officer, Marianne Faber, will verify that the Quality Assurance Project Plan (QAPP) is comprehensively developed and implemented. Ms. Faber will provide a technical on-site audit of the data collection, tracking, and analytical operations during the study and notify the LM managers and the Task Lead of any major QA problems or insufficiencies.

The Task Lead, Marti Minnich, will be responsible for ensuring that the QAPP is implemented, that procedural documentation is regularly reviewed, that the project schedule is followed, and that deliverables meet the goals of the project. Dr. Minnich will review all data with the Analytical Lead and make decisions for any necessary adjustments or clarifications to procedures during implementation. She is responsible for all communications with the WAM, including reports of any major problems, required modifications to the QAPP, and draft and final reports.

Jan Kilduff, the Organic Analytical Lead, will supervise and conduct the analytical sample flow, instrument maintenance, instrument and procedural trouble shooting, and data reduction activities. He will insure that all QA/QC procedures are followed and that the chromatography software is utilized in an appropriate manner.

Figure 1. Project Organization Chart

2. Problem Definition

Preservation of soil samples destined for analysis of volatile organic compounds (VOCs) has two broad components with respect to sample integrity: to prevent analyte degradation and to prevent analyte vapor loss. Analyte degradation in soil is predominantly microbially mediated. Abiotic degradation reactions on mineral surfaces are reported to be extremely slow under typical environmental temperatures (Voudrias and Reinhard, 1986). Naturally occurring compounds are more readily degraded in soil than are synthetic compounds (Kobayashi and Rittmann, 1982). With respect to VOCs on EPA's target compound list, the naturally occurring aromatic compounds (e.g., benzene, toluene, ethylbenzene, and xylene [BTEX]) are more easily degraded than the halogenated solvents (e.g., trichloroethylene and carbon tetrachloride). Therefore, techniques that effect soil sterilization, or at least inhibit the activity of soil microbes, will foster preservation of soil VOCs and, in particular, will help preserve petroleum-derived analytes.

The volatilization losses during soil sample collection, storage, and handling have long been identified as the major source of negative bias in soil VOC data (Siegrist and Jenssen, 1990). The vapor loss problem resulting from analytical transfer steps has been resolved by the SW-846 Method 5035, in which 1 to 5 g of soil is sealed in the analytical vial, either in the field or by extrusion from an air-tight container (e.g., the EnCore™ sampler). Therefore, successful storage/preservation techniques must halt or slow biological degradation of VOCs in soil.

2.1 Background--Soil VOC Preservation Research

Biologically mediated degradation is generally inhibited by storing the soil samples at 4 ^{o}C. Chilling has the added advantage of decreasing the vapor pressure, therefore suppressing vapor losses. Hewitt (1997) isolated the contribution of VOC degradation losses by following VOC concentrations in moist, contaminated soil samples stored in sealed ampules. The ampules were placed in 40-mL vials which were sealed before the ampules were open. In this manner, VOC

losses from volatilization were virtually eliminated and any VOC losses found could be attributed solely to degradation. Samples stored at room temperature (22 ºC) were analyzed after 1, 2, 3, and 5 days. Samples stored at 4 ºC were analyzed after 5, 13, 21, and 28 days. Samples acidified with sodium bisulfate ($NaHSO_4$), were stored at 22 ºC and analyzed after 5, 13, 21, and 28 days.

After 5 days at 22 ºC, benzene, toluene, ethylbenzene, and p-xylene decreased from initial concentrations of approximately 11, 9, 8, and 7 mg/kg, respectively, to 0.3 mg/kg or less. Chilling to 4 ºC delayed the degradation of these compounds. Concentrations in the chilled samples after 13 days were within 8% of the initial value for all compounds except benzene, which decreased by approximately 60%. The samples preserved with $NaHSO_4$ and stored at 22 ºC exhibited virtually no degradation over 28 days. A minor point of concern with the $NaHSO_4$ treatment is the decrease in o- and p-xylene concentrations. Data for days 5, 13, and 21 indicated that the decreases were slow, but steady, implying that something other than spurious results had been observed.

Hewitt (1997) provides evidence that acidification with $NaHSO_4$ inhibits microbial degradation of the BTEX compounds in at least some soils for up to 28 days. Hewitt notes that acidification of a carbonate-rich soil may be untenable. Furthermore, microbial degradation of the chlorinated compounds trans-dichloroethene (trans-DCE), trichloroethene (TCE), and tetrachloroethene (PCE), were not observed, even when samples were stored at 22 ºC for 28 days. In another experiment (Experiment 2), no degradation was observed for seven other chlorinated compounds. These results confirm the premise that naturally occurring compounds are more readily degraded than synthetic compounds.

Freezing samples to inhibit microbial degradation and retard vapor loss has been tried with mixed success. King (1993) reported that gasoline concentrations in soil (fine sand) remained constant for 13 days when stored in a cooler with dry ice (author estimates -70 ºC). Maskarinec et al. (1988) looked at VOC losses after freezing three types of soils for up to 56 days. No

specific descriptions of the soil types or composition of the soils were provided. They found essentially no loss during 56 days at -20 ºC for the USATHAMA reference soil. The Tennessee soil showed a loss of some of the analytes over the 56 day storage, but data were erratic with respect to time (e.g., TCE concentrations on days 0, 3, 7, 14, 28, and 56 were 75, 81, 66, 72, 54, and 40, respectively). The third soil, "Mississippi topsoil," exhibited a steady loss of 17 out of 19 analytes over the 28 day storage period.

In both on-site and laboratory studies, methanol has been shown to be the most effective preservative by many researchers. Perhaps the largest methanol preservation study reported to date compared 50 soil sample pairs collected from two fuel-contaminated U.S. Air Force sites in the Pacific northwest (Liikala et al., 1996). The collocated samples were collected as (1) bulk samples sent to the laboratory for subsampling and analysis by EPA SW-846 Proposed Method 8211 and (2) preserved in methanol in the field, analyzed by EPA Method 502.2. Concentrations of benzene and toluene observed in methanol-preserved samples were one to three orders of magnitude greater than concentrations observed in bulk samples that were subsampled at the laboratory. Lesser differences were observed for xylenes and ethylbenzene, analytes for which higher concentrations were occasionally observed by the bulk method. The authors noted that the magnitude of compound losses was inversely related to the vapor pressures. Additionally, Liikala et al. (1996) investigated the preservation of soil samples which were spiked with six chlorinated solvents at 100 and 200 ppb [sic], immersed in 10 mL methanol, sealed in VOA vials, and stored at 4 ºC for 82 days. Recoveries of all compounds after 82 days were greater than 80% with an average recovery of 84%.

2.2 Background--Containers Used to Transport Soil

Hewitt and Lukash (1996) demonstrated that soil containing VOCs cannot be sealed in core liners for transport to a laboratory without loss of analyte. It may be convenient for field samplers to cover and tape the ends of core liners as retrieved from a split-spoon sampler and transport these to the laboratory for subsampling. One might suppose that by opening and

sampling the core only once, the losses would be comparable to vapor losses that occur during field sampling. However, Hewitt and Lukash (1996) observed losses whether TFE Teflon or aluminum foil were inserted before capping the cores. Small brass cores, 3.6-cm i.d. x 5.1-cm long, were removed from a prepared area of contaminated field soil. After 5 and 10 days in cold storage, soil was sampled and analyzed. VOC concentrations were at least 90% less on day 5 than observed on day 0. By day 10, cores sealed with aluminum-lined caps showed better recovery than cores sealed with Teflon-lined caps, although toluene contamination was also observed in the aluminum-lined cores. Thus, vapor-tight seals can not be achieved on the ends of the core-liners with current technology.

Hewitt (1997a) compared the trichloroethene (TCE) concentrations of soil collected by a truncated pipette and placed into methanol with soil collected in an EnCore sampler (En Chem, Inc., Green Bay, WI), stored cold for 2 and 7 days, and then transferred into methanol. Two early designs of the sampler showed TCE losses, but the third-generation EnCore™ sampler demonstrated no measurable loss of TCE even after samples were stored for 7 days in the sampler before transferring to methanol. TCE is not likely to degrade and, therefore, the study demonstrated that volatile losses during the storage and transfer were not measurable. The main disadvantage of the sampler is that it has not been designed for, nor tested in, soils that contain a significant portion of gravel or rock fragments. Soil replicates in the Hewitt (1997a) study were collected in a silty clay soil with presumably few coarse fragments.

3. Project Description

This study will compare analyte concentrations of laboratory-spiked soils after storage under various preservation treatments. The study has three parts: (1) screening of potential pharmaceutical products for effects on the preservation and analysis of soil VOCs, (2) a comprehensive comparison of in-vial soil VOC preservation options, and (3) a comparison of VOC recovery from soils stored in the 5-g EnCore™ sampler versus methanol storage. Four soils will be included in parts 2 and 3 of the study encompassing low and high concentrations of

organic matter, different types and proportions of clays, and different pH values. Dry soil will be spiked with the analytes because dry soil is relatively easy to spike accurately, mix, and divide into homogeneous replicates (Minnich et al., 1996). Eight compounds will be included in the study: benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, 1,1-dichloroethene, TCE, and PCE. Section 6 provides the procedural details; an overview of the study tests is provided below.

Part 1-- Seven non-traditional environmental soil sample preservatives have been tentatively selected for this study to determine how effective they are in mitigating the biological degradation of VOCs in soil. Five of these are over-the-counter antiseptics, Bactine™, Betadine™, Chloraseptic™ mouthwash, Gold Bond Powder™, and Hibiclens™. The other two are wintergreen oil, a linament and pH 10 buffer. Novel chemical preservatives will be screened for background contamination, recovery of VOCs, and effectiveness as a soil VOC preservative (Section 6.1). First, background contamination and recovery check samples (without soil) will be evaluated for each prospective preservative. Then, a preliminary effectiveness test will be performed in the presence of soil and results will be evaluated after the 14-day storage test (criteria given in Section 6.5).

Part 2--VOC recovery from four different soils will be compared using preservatives selected based on the results of the Part 1 evaluation. In addition, the following preservation treatments will be studied: methanol, sodium bisulfate ($NaHSO_4$), copper sulfate ($CuSO_4$), frozen storage, and 4 ^oC (control). Samples will be sealed in 40-mL vials and analyzed at 0, 7, 14, and 28 days (Section 6.2).

Part 3--VOC recovery from the four different soils will be evaluated for spiked soil stored chilled at 4 ^oC in 5-g EnCore™ samplers for 0, 2, 7, and 14 days, and for soil stored frozen at 12 ^oC in 5-g EnCore™ samplers for 28 days. After the designated storage time, samples will be extruded into methanol in 40-mL vials and stored in methanol 1 to 14 days before analysis (Section 6.3).

Samples for all three parts of this study will be analyzed by purge-and-trap/gas chromatography/ mass spectrometry (PT/GC/MS) in accordance with SW-846 Methods 5035 and 8260 (Section 7). Surrogates and internal standards will be added by the autosampler immediately before

analysis. Methanol extracts, when used, are opened and an aliquot transferred to a 40-mL vial. The aliquot is then analyzed in the same manner as the unopened vials.

3.1 Measurements

All VOC measurements are critical. An approximate number of measurements can be anticipated, based on the assumption that three of the novel preservatives from Part 1 are included in Part 2. If this is the case, the total number of samples to be analyzed in all three study parts would be 485 (calculations given in Section 6.4). In addition, a minimum of two blanks and two continuing calibration samples would be included for quality control (QC) purposes every 16 samples analyzed, adding at least 121 more samples. The detection limit study (Section 8) will add 7 samples and establishing the calibration curve will require analysis of a minimum of 18 more samples. Thus, a minimum of 146 QC samples will be analyzed under the described scenario.

3.2 Schedule

The VOC analyses by PT/GC/MS) will either be subcontracted to a local Las Vegas laboratory or the necessary analytical instruments will be leased and analyzed by LM chemists in the Pilot Road Laboratory. If instruments are leased, this will require approximately six weeks for contract negotiations, delivery, set up, and stabilization of the instruments. If the analyses are performed under subcontract, approximately a three-week lead time is required.

The schedule of laboratory sample preparation and analysis is given in Table 5. Part 1 is expected to take 5 weeks to complete. Part 2 will require at least three months. Part 3, the EnCore™ sampler study, is expected to begin concurrent with the Part 2 tests. In total, the analytical work is estimated to require approximately 19 weeks or 5 months with no analytical down time. Instrument maintance and quick repairs will be crucial to meet the rigorous schedule. More than three days of instrument down time during a busy week may cause us to

repeat sample preparation through timed analysis steps. Therefore, the schedule provided represents optimal circumstances and 6 to 7 months is a more realistic estimate of the time needed to complete the laboratory analyses.

Results will be summarized in a letter report with all data attached. The report will be delivered within 3 months of the completion of the data collection activities. A draft report or study status report is to be completed by September 30, 1998.

4. Data Quality Objectives

4.1 Project Quality Objectives

The project objective is to quantify differences in VOC concentrations as a result of different preservation options for various soils. Options are sought that will preserve soil VOC sample integrity to the extent that no significant changes in VOC concentrations are observed after 28 days of storage. These data are intended to be used to support government and private decision makers who select and approve appropriate field sampling and sample preservation methods for the analysis of VOCs in soil.

4.2 Measurement Performance Criteria

Precautions have been incorporated to ensure that any differences in VOC concentrations observed between treatments is truly the result of natural processes that change the sample concentrations rather than artifacts in the equipment, design, or instrument performance. The experimental design incorporates numerous QC samples including a detection level test, continuing calibration checks, and frequent blank checks. System monitoring compounds are added to every sample, blank, and standard. Acceptance criteria for the QC samples are described in Section 8. Data evaluation will incorporate statistical methods using a significance level of $\alpha = 0.05$. Interpretation of the results will discuss any differences among the compounds

or among the soils.

As is the nature of any repeated measures study, any significant instrument problems will need to be resolved within a few days or sample preparation and analyses may need to be repeated. This is the nature of a timed study. We will accept data generated as much as three days late for day-7 analyses and as much as 5 days late for day-14 or day-28 analyses.

5. Documentation and Records

All data will be generated in electronic and hard copy formats via the instrument-associated software. The software will record the sample identification numbers, date and time of sample analysis, and associated raw data (area counts). Instrument data (i.e., sample identification and ng of analyte) will be transferred to electronic spreadsheets for analysis and presentation. All records of the study will be maintained by Lockheed Martin for up to two years after the final report is accepted and then transferred to the EPA WAM for storage.

B. Data Acquisition

6. Experimental Design

The study will consist of three parts. Part 1 will screen some potentially effective pharmaceutical antiseptic products plus pH 10 buffer for use as soil VOC preservatives. Part 2 will compare five existing storage/preservation treatments plus the use of any of the preservatives from Part 1 that meet minimum criteria (Section 6.5). Part 3 will investigate the recovery of soil VOCs as a function of time of storage (chilled or frozen) in the EnCore™ sampler, as compared with storage in methanol at room temperature.

6.1 Part 1 -- Sample Preparation

The preservatives tentatively selected for study are: Bactine™, Betadine™, Chloraseptic™ mouthwash, Hibiclens™, Gold Bond Powder™, wintergreen oil, and pH 10 buffer. The liquid antiseptics will be employed as purchased (full strength). The powder will be mixed at 1-g powder per 4-g soil or per 5-mL water. The wintergreen oil is considered an extractant and used in the same manner as methanol. The VOCs are expected to partition into the wintergreen oil and therefore, only 100 µL will be transferred to 5 mL water for purging.

Preparation steps are as follows:

- For each of the liquid antiseptics, 5 mL will be pipetted into a 40-mL vial. The Gold Bond Powder (1 g) will be weighed into a 40-mL vial and 5 mL of distilled water will be added. For the wintergreen oil, 100 µL will be added to 5 mL of distilled water. All vials will be sealed immediately after preparation.
- Another two sets of vials will be prepared, as above, except that 5 mL of the wintergreen oil will be used. The eight target VOCs will be added to each vial at 250 ng each. This will come from dilutions of two certified reference standards. The 1000 µg/mL standard containing benzene, toluene, chlorobenzene, 1,1-dichloroethene, and TCE, and the 5000 µg/mL standard containing ethylbenzene, o-xylene, and PCE, will be each be diluted to 10 µg/mL with water. A 25 µL aliquot of each standard will supply each target compound at 250 ng. All samples will be mixed by hand. An aliquot of the wintergreen oil will be placed in 5 mL water for analysis. The control sample will be a spiked water sample.
- A third set of vials will be prepared after the results of the previous two tests are evaluated. Charleston soil (described below) will be moistened 10 days before the experiment to promote biological activity. Treatments, prepared in duplicate, will be: each of the preservatives alone (blanks), each preservative + soil + VOC spike (test), and spiked soil with no preservative (control). The spike will be accomplished as described above, using freshly prepared solutions. Only the control soil will be refrigerated; all

other samples will be stored at room temperature. Samples will be analyzed after 14 days.

Finally, during Part 1, each of the soils will be mixed with water and $NaHSO_4$, capped, and the pH will be monitored. Soil (4 g) will be mixed with 5 mL of water and 1 g $NaHSO_4$ in a 40-mL vial; a second sample (4 g) will be mixed with water and 2 g $NaHSO_4$. The pH of each sample will be checked using a pH meter and semi-micro combination pH electrode after 1 h, 7 days, and 14 days. The amount of $NaHSO_4$ to be used in Part 2 will be soil specific, 1 or 2 g, whichever generated a pH of 2 or below without excessive pressurization by CO_2.

6.2 Part 2 -- Sample Preparation

VOC recovery from four different soils will be compared under the following preservation treatments: (1) control, 4 ^oC, no water added; (2) acidification with $NaHSO_4$ at 1 or 2 g $NaHSO_4$ /4 g soil; (3) 20mM $CuSO_4$; (4) freezing at $^-$12 ^oC, no water added; (5) methanol immersion; and (6, 7, and 8) any preservatives from Part 1 that meet the criteria outlined in Section 6.5. Biologically active, moist soil will be mixed with dry, VOC-spiked soil (1:1 mixture) and treatments will be sealed in individual 40-mL vials. Samples will be stored at room temperature unless otherwise indicated. Three replicates will be prepared for each treatment for each day that samples are to be analyzed (days 0, 2, 7, 14, and 28) generating a total of 12 samples per treatment per soil type.

6.2.1 Soils -- Soils, tentatively selected to be used in this study, are described in Table 1. A soil with pH 8 or above, organic carbon less than 1%, and clay greater than12% will be substituted for the New England C soil, if possible.

6.2.2 Moist Soil-- To simulate field soil with an active microbial population, uncontaminated soil will be moistened and incubated aerobically at room temperature for at least 10 days. For each of the above soil types, 500 g of air-dried (uncontaminated) soil will be moistened to

achieve 10% to 20% gravimetric water content, based on observation, in order to obtain moist, but not wet soil. The moistened soil will be mixed in a 1-L bottle, on an end-over-end mixer, for 1 hr. The moist

TABLE 1. Selected Characteristics of Soils.

Soil Designation	Horizon	sand (%)	silt (%)	clay (%)	organic C (%)	pH (0.01 *M* $CaCl_2$)
Hayesville	B	46	22	32	0.2	4.4
Charleston	A	61	31	8	3.8	7.3
New England A	A	47	48	5	4.2	4.4
New England C	C	96	3.5	0.5	0.12	4.8

soil will then be incubated aerobically at room temperature in a loosely covered container for at least 10 days as a means of reviving the native soil microbial population. After the 10 days, the moist soil will be weighed and the moisture content will either be brought back to the initial moisture content or recorded "as is" to permit calculations of soil portions on a dry-weight basis. The jar will be sealed and refrigerated at 4 ºC until used. (Note: after refrigeration, the jar will be opened briefly to insure proper aeration every two to three days.)

6.2.3 Dry VOC-Spiked Soil-- For each of the soil types in Table 1, 500 g of soil will be desiccator-dried for 24 hr. The desiccator-dried soil will be spiked with concentrated methanolic solutions of the eight target VOCs to achieve soil spiked with the target analytes at 500 ng/g (Table 2). All standards will be certified standards from a commercial supplier (e.g., Supleco). The compounds listed as 1000 µg/mL standards will be added as a mixture of five compounds (i.e., one 0.25-mL addition). The 5000 µg/mL standards will be added individually (i.e., three 0.05-mL additions). The dry VOC-spiked soil will then be sealed in a 1-L wide-mouthed jar with a septum-seal and mixed on an end-over-end mixer for 2 to 3 hr. It will then be stored at room temperature in the sealed jar for 10 days. After 10 days, the spiked soil will be refrigerated to lower the vapor pressure of the headspace before samples are scooped from the jar.

TABLE 2. VOC spike additions to add to 500 g soil. Soil will contain 500 ng/g, each analyte.

Compound	Standard Concentration (µg/mL)	Volume to be added (mL)
benzene	1000	0.25
toluene	1000	0.25
ethylbenzene	5000	0.05
o-xylene	5000	0.05
chlorobenzene	1000	0.25
1,1-dichloroethene	1000	0.25
TCE	1000	0.25
PCE	5000	0.05

6.2.4 Treatments-- After the soils have incubated, replicate 40-mL vials will be prepared for each of the preservation/storage treatments. Replicates will be prepared in rounds. This means that one vial of each treatment for a given soil will be prepared before preparing the next replicate, and so on until all 12 replicates have been prepared. Moreover, only 4 rounds for a given soil will be prepared the first day and 8 rounds will be prepared the next day. Therefore treatment preparation for each soil requires two days. In each vial, approximately 2 g moist soil (dry soil basis) will be added, followed by the preservative. The VOC-spiked soil is added last and the vial is sealed immediately after the VOC-spiked soil addition.

The procedure will be as follows:

- Vials plus stirring bars will be tared on a balance; moist soil will be added to the vials and the weight will be recorded.
- The liquid preservative (5 mL) or the powder (1 g plus 5 mL water) will be added, depending on the treatment. (No addition here for chilled control or frozen preservation.) The vial weight will be recorded.

- To minimize potential bias caused by volatilization during the addition of dry VOC-spiked soil, vials will then be organized and the spike soil addition will be completed in rounds. Round 1 starts by adding the spiked soil to Treatment 1, then adds spiked soil to the other treatments in order. Round 2 starts with Treatment 2, etc.
- Not only are the individual vials prepared to minimize bias, but the twelve treatment rounds are assigned to the four analysis days as follows:

TABLE 3. Part 2 Study--Assignment of Sample Rounds to Analysis Days

Part 2 Analysis Day	Round No.	
	Prep Day 1	Prep Day 2
0	2	5, 12
7	3	6, 9
14	4	7, 10
28	1	8, 11

- Dry VOC-spiked soil will be scooped and poured into the vials using a glass weighing spoon. Vials will be sealed and the vial weights will again be recorded.
- Vials will be mixed by hand with an end-over-end motion.
- Chilled and frozen soils will be transferred to the refrigerator or freezer approximately 30 minutes after preparation. Day 0 samples will be prepared for analysis approximately 2 hr after sample preparation has been completed.

6.3 Part 3 -- Sample Preparation

The same soils and preparation of moist and dry VOC-spiked soils described above (Section 6.2.1, 6.2.2, and 6.2.3) will be used for this experiment. However, the experimental units will be prepared from single, large-batch mixtures for each soil rather than mixed in individual vials.

Dry VOC-spiked soil (100 g) and moist soil (50 g, dry wt basis) will be placed in a wide-mouth jar (250 mL) a with septum seal. The jar will be rotated on the end-over-end mixer for 4 hr. The soils will be chilled for at least 4 hr before opening to remove sample replicates. The resulting soil spike will be approximately 333 ng/g. This slightly higher soil concentration will be used because inadvertent (unavoidable) VOC losses are anticipated during the replicate preparation step.

Soil aliquots will be collected in the EnCore™ sampler by pressing the sampler into the soil as prescribed by the manufacturer. Any soil adhering to the sealing edges of the sampler will be removed before capping the sampler. The EnCore™ samples will be sealed and stored in the refrigerator at 4 ^{o}C or in the freezer at $^{-}$12 ^{o}C. For each soil, 3 replicates for each of 5 analysis days will be prepared. Treatments will be assigned to the 15 replicates as follows:

TABLE 4. Part 3--Assignment of Sample Replicates to Treatment Groups

Part 3 Treatments	Analysis Day	Replicate No.
1 hr refrigerated	17	4, 9, 14
2 days, refrigerated	17	5, 10,15
7 days, refrigerated	17	1, 6, 11
14 days, refrigerated	17	2, 7, 12
28 days, frozen	31	3, 8, 13

After the designated storage time, the spiked soil will be extruded into a 40-mL vial containing 5 mL of methanol. Vials will be mixed by hand for 30 seconds each. The previously refrigerated samples will remain immersed in the methanol at room temperature until 15 to 17 days after the start of the experiment. At that time, methanol aliquots will be drawn and analyzed. The frozen samples will be extruded into methanol after 28 days storage and shaken by hand. Samples will be extracted in methanol at room temperature for 1 to 3 days, and then aliquots will be taken and analyzed.

6.4 Laboratory Schedule and Sample Count

An overview of the laboratory schedule is presented in Table 5. Part 1 test 1 will require 23 samples including the preservatives alone (7 samples), spiked water (2 samples), and preservative plus spike samples (14 samples). The number of samples in the Part 1 soil screening test will depend on the number of preservatives that pass the background check. If all 7 preservatives are still considered viable, then 30 samples will be generated (14 preservative duplicates, 2 control soil + spike, 14 soil + spike + preservative duplicates). This would generate a total of 53 samples in Part 1. It is expected to take 5 weeks to complete Part 1 including the 10-days hold time for moist soil and the 14-day sample hold time. We will also check the effect of sodium bisulfate on soil pH during Part 1.

Part 2 is anticipated to require 12 weeks. It is anticipated that at most only 3 of the 7 novel preservatives will be included in Part 2. Assuming this, Part 2 would then have eight treatments. If we prepare 3 replicates of each treatment for each of the four sample analysis days, 96 samples per soil for a total of 384 samples would be required. Sample preparation will be metered in order to accommodate the sample throughput capacity of the purge-and-trap procedure of 16 samples per day maximum. Each soil type will be prepared over two days time and a maximum of two soils can be prepared per week, creating 4 days of sample preparation per week and the corresponding 4 days of sample analyses per week. The weekly analytical schedule will consist of 8 samples on the first day (one replicate of each treatment), 16 samples on the second day (2 replicates of each treatment), which is then repeated for another soil type on the next 2 days.

Preparation of Part 3 samples will be scheduled to begin during the Part 2 “rest” weeks that fall between sample analyses days 14 and 28 (Table 5). Part 3 will generate a total of 48 samples (3 replicates for each of 4 analysis days, times 4 soils). The analysis of methanol extracts from samples transferred to methanol on days 0, 2, and 14 will be batched for two soils at a time. This creates 18 samples in the batch (3 replicates times 3 days times 2 soil types). Analysis of the frozen, day 28 samples will be conducted between days 29 and 31 (6 samples per batch).

TABLE 5. Nominal Laboratory Schedule for Completion of Study

Week	Activity	Days after sample preparation				
		Part 1	Part 2 A,B	C,D	Part 3 A,B	C,D
1	Prepare moist soil for Part 1; Prepare soil +$NaHSO_4$ for pH check					
2	Prepare and analyze Part 1 preservatives					
3	Prepare Part 1 soil + preservatives	0				
4	Prepare moist soil and dry VOC-spike soils A&B for Part 2					
5	Analyze Part 1 soil + preservatives	14				
6	Prepare treatments and analyze soils A&B Part 2		0			
7	Analyze soils A&B Part 2		7			
8	Analyze soils A&B Part 2		14			
9	Prepare soils A&B Part 3; Transfer soils A&B Part 3				0, 2	
10	Analyze soils A&B Part 2; Transfer soils A&B Part 3		28		7	
11	Prepare treatments and analyze soils C&D Part 2; Transfer soils A&B Part 3			0	14	
12	*Analyze soils C&D Part 2; Analyze soils A&B Part 3			7	17	
13	Analyze soils C&D Part 2; Transfer soils A&B Part 3			14	28	
14	Prepare soils C&D Part 3; Transfer soils C&D Part 3; Analyze soils A&B Part 3				31	0,2
15	Analyze soils C&D Part 2; Transfer soils C&D Part 3			28		7
16	Transfer soils C&D Part 3					14
17	Analyze soils C&D Part 3					17
18	Transfer soils C&D Part 3					28
19	Analyze soils C&D Part 3					31

* The number of analytical samples is expected to exceed the capacity of our system on this

week. Methanol samples (Part 3) will be analyzed late in the week and on into the next week.

6.5 Rationale

The following criteria will be used to select preservatives from Part 1 to be used in Part 2.

- Background contamination of a candidate preservative is expected to be less than 5 ng/mL of any target VOC or no more than 2x the water blank value if the water blank is above 5 ng/mL for any target compound.
- Recovery of a 50-ng/mL spike for all target compounds is expected to be at least 70% of the control concentrations (obtained from the same spike added to acidified water).
- An effective preservative is expected to demonstrate VOC recoveries at least 30% higher than the control treatment concentrations for at least two of the compounds susceptible to rapid degradation (BTEX), and no artifact condition for any of the target compounds.
- Finally, any unusual purge behavior, such as excessive foaming, will be unacceptable.

The experiment is designed to look at the preservation of representative VOCs on varied soils, with the understanding that the population of interest is all VOCs on EPA's target compound list for all potentially contaminated soils and sediments. This study is expected to demonstrate any gross differences among the preservation methods. Results from this study may point to more specific future study needs with respect to the effect of compound or soil properties. Furthermore, a need for field studies to verify and refine the results obtained in this study is anticipated.

The VOC concentration to be studied was set by practical constraints of achieving values within the same calibration curve for both water and methanol extracts. The spike concentration for Part 2 of the study was determined as follows: by mixing 2 g of 500 ng/g soil with 2 g of uncontam-inated soil, the final soil concentration will be 250 ng/g, capable of generating a nominal 1000 ng on detector for all but the methanol treatments. The methanol aliquot will contain a maximum of 250 ng/mL, resulting in only 25 ng on detector if 0.1 mL is analyzed, or 50 ng on detector if 0.2 mL of the extract is purged from 10 mL of water. Part 3 soil

concentrations will be 333 ng/g, to be measured only on methanol extracts, generating a potential 33 ng on the detector if 0.1 mL of methanol is analyzed and 66 ng on the detector if 0.2 mL of methanol is analyzed.

6.5 Measurement Error Assumptions

We assume that, in general, batch-to-batch variability will be greater than within batch variability. By segregating soil types into separate batches that include all treatments in each batch, the primary focus is on the effect of treatment. Differences in analyte recoveries among the soils are of lesser concern than any differences in how the treatments affect recoveries. Analyte concentrations may vary among the soils because the extractability of the various analytes is expected to differ based on soil properties (such as pH, proportion and type of clays, and organic carbon content).

7. Analytical Methods

Samples will be analyzed by closed-system purge-and trap introduction (SW-846 Method 5035) into a gas chromatograph with mass spectrometer detector (SW-846 Method 8260, calibrated only for the analytes of interest). The Varian Archon Purge & Trap autosampler will be plumbed into an Tekmar 3000 Sample Concentrator with a Vocarb 3000 trap. A Hewlett-Packard 5890 Series II gas chromatograph with a Hewlett Packard Model 5973 MSD will be used to analyze the samples. The system will be equipped with a 60-m, 0.25-mm, RTX Volatilization/RTX 5022 fused silica capillary column. HP software will be used to analyze the chromatography. The instrumental operating conditions are specified below.

Purge-and-Trap Operating Conditions

Helium purge gas	40 mL/min.
Purge time	10 min.
Purge temperature	40 ˚C
Desorb time	4 min.

Desorb temperature	250 ˚C
Bake time	10 min.
Bake temperature	260 ˚C
Transfer line temperature	125 ˚C

External line temperature	125 ˚C
Valve temperature	125 ˚C

GC Operating Conditions

Linear flow rate	20 cm/sec
Split ratio	40:1
Initial temperature	35 ˚C
Initial hold time	0
Ramp rate-1	13 ˚C/min
Final temperature	150 ˚C
Ramp rate-2	20 ˚C/min
Final temperature	250 ˚C
Final hold time	2 min
Injection port temperature	200 ˚C

MSD Operating Conditions

Solvent delay	3.00 min
Low mass	35
High mass	300
Plot type	total ion

8. Quality Control

Purge-and-trap is an inherently “noisy” analytical procedure. Internal standards are added to every blank, standard, and sample to correct for electronic noise in the mass spectrometer detector. System monitoring compounds (SMCs) are added to every blank, standard, and sample as a check on the purge efficiency. The use of frequent water blanks monitors for contamination within the purge lines, trap, or water. The direct injection of the tuning standard, 4-bromofluorobenzene (BFB) monitors fluctuations or drift in the detector electronics.

The types of QC samples, analysis schedule for these samples, and acceptance criteria for each are given in Table 6.

TABLE 6. QC Samples: Schedule and Corrective Actions

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Continuing calibration	every 16 samples	%D ≤ 25% for all sample analytes	reanalyze up to 3 times; run new calibration curve
Instrument blank	every 16 samples	below analyte IDL or sample values >5X instrument blank	run blanks or instrument check until corrected
SMC recovery	each sample, blank, and standard	%R =100%±25%	reanalyze standard or blank, flag data
IDL	determined during start-up phase	SMC %R = 100%±25%	reanalyze until 7 samples meet criteria

8.1 Replicates

Soil VOC measurements will be repeated in triplicate (Section 6.2 and 6.3). From these replicates, one can estimate the measurement precision with respect to the spiking and analyzing of the soil. Four replicate measurements of the mid-range calibration standard will be used to quantify the precision of the analytical determination. Acceptance criteria will be and RSD ≤ 25%.

8.2 Continuing calibration

Bias or systematic instrument drift which may occur during a run will be checked by an ongoing calibration standard at the beginning and end of each run, or at a minimum after 16 samples. The calibration check will consist of a mid-range concentration standard. Instrument response must be within 25 percent difference (% D) of the initial calibration response for the target compounds.

8.3 Instrument Blanks

An instrument blank, consisting of deionized water with the internal standards and SMCs, will

be analyzed after every 16 samples. Instrument blanks will monitor any contamination from reagents, glassware, or analyte carryover within the instruments. Blank concentrations are expected to be below IDLs. Analyses will not be conducted if the initial blank is contaminated with more than one compound above its IDL.

8.4 System Monitoring Compound

Bias in individual samples will be checked by following the recovery of SMCs in each sample. If the percent recovery (%R) of the SMCs exceed a window of 75 to 125%, analytes associated with that SMC for the affected samples will be flagged.

8.5 Instrument Detection Limit

The instrument detection limit (IDL) for the target compounds will be determined as three times the standard deviation of seven replicate blank measurements. Seven replicate deionized water samples containing the SMCs will be analyzed. If SMC recoveries are not within the 75-125% window, IDL analyses will be repeated. Our IDL for each compound is anticipated to be 10 ng on column.

9. Instrument Calibration and Frequency

9.1 Initial Calibration Standards

Calibration standards will be prepared in methanol from ampulated 1000 µg/mL stock of the target analytes. A six-point calibration curve(5 points plus blank) will be generated at 0, 25, 100, 250, 500, and 900 ng on-column. A coefficient of linear determination (r^2) greater than or equal to 0.99 will be acceptable for this study, allowing calibration by the mean response factor (RF), where:

RF = mass of analyte (ng) ÷ peak area.

9.2 Continuing Calibration Standards/Instrument Blanks

A calibration check will be performed before and after every 16 samples. The calibration check will consist of a mid-range concentration standard (250 ng on-column). Instrument response must be within 25% D of the initial calibration response for any of the target compounds. An instrument blank will be analyzed prior to each continuing calibration standard to demonstrate instrument integrity and the absence of reagent/system contamination. The instrument blank consists of 5 mL of deionized water and the SMCs.

10. Data Management

Analytical data in ng on-column will be converted to soil concentrations of ng/g as described below. For each analyte, the ng on-column for samples (excluding methanol and wintergreen oil samples) will be divided by the mass of soil in the vial (g), yielding soil concentrations in ng/g. Analysis of the methanol or wintergreen oil extracts will generate the ng of each analyte derived from 0.2 mL of the extract. The ng on-column will be divided by the amount of soil represented by the extract aliquot, "D," to yield ng analyte/g soil. The mass of soil represented, D, is the total mass of soil in the vial, divided by the total volume of methanol in the extract times the aliquot volume:

$$D = \frac{mass\ of\ soil\ extracted\ (g)}{total\ volume\ of\ methanol\ (mL)}\ x\ volume\ of\ methanol\ aliquot\ (mL)$$

C. Assessment/Oversight

11. Assessment and Response Actions

Problems that may arise will likely be unanticipated qualitative or quantitative analytical results or equipment failures. Corrective actions for nonroutine problems often require an assessment of the problem with respect to the project objectives and cost considerations. LM management will be involved if problems require additional resources. The WAM will be consulted if any major modifications to or significant deviations from this QAPP are needed.

12. Reports to Management

The Task Lead is responsible for monthly progress reports to the ESD-LV WAM and by written communications regarding any modifications to this QAPP. The draft report will include a project summary, a description of the methods, results, and a discussion of the results. Appendices will include: (1) all data and observations and, (2) the QA/QC report which outlines the results of QA procedures and discusses these results with respect to the initial QA objectives.

D. Data Validation and Usability

13. Data Review, Validation, and Verification Requirements

Data will be considered valid for an analyte if the associated instrument blanks and continuing calibration standards meet the acceptance criteria, and the SMC recovery is within the 25%R window. Any datum with QC violations will be flagged and discussed in the QA/QC report. Justification for the inclusion or exclusion of qualified data in the data analysis steps will be based in context with the entire data set.

14. Reconciliation of Data Quality Objectives

The reconciliation of data with the DQOs will use the parameters and equations described below. Statistical evaluation of information will be utilize tools as described in *Guidance for Data Quality Assessment* (EPA QA/G-9).

14.1 Precision

Instrument precision will be monitored by continuing calibration check standards after every 10 samples or, at a minimum, at the beginning and end of each day that samples are analyzed. The percent difference (%D) from the initial calibration response will be calculated as follows:

$$\%D = |(R1 - R2)|/R1 \times 100,$$

where "R1" is the initial calibration peak area count and "R2" is the subsequent or daily peak area count. The instrument precision DQO is a %D of ≤ 25. If the %D for two or more compounds in a daily calibration standard is greater than 25%, new standards and/or instrument recalibration will be necessary before proceeding. If the second calibration standard in a run has a %D ≥ 25%, the data will be flagged and the SMC recoveries within the run will be scrutinized for indications of erratic instrument performance.

The precision of sample duplicates for VOCs will be calculated as the relative percent difference (RPD):

$$RPD = \frac{(C1 - C2) \times 100\%}{(C1 + C2)/2}$$

where, $C1$ = larger of the two observed values

$C2$ = smaller of the two observed values.

14.2 Bias

Percent recovery (%R) of the SMC compound added to each sample, blank, and standard will be calculated as follows:

$$\%R = 100\ (S/C_{sa})$$

where S is the measured concentration and C_{sa} is the concentration of the SMC spike addition.

14.3 Instrument Detection Limits

The instrument detection limit (IDL) is defined as follows:

$$IDL = t_{(n-1,1-\alpha=0.99)}\ sd$$

where sd is the standard deviation of the replicate blank analyses and $t_{(n-1,1-\alpha=0.99)}$ is the Student's t-value for a one-sided 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

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