Final Revision 0.2

QUALITY ASSURANCE PROJECT PLAN

Technical Support for the Site Characterization and Monitoring Technical Support Center (SCMTSC)
Technical Directive 2-01 – Herbicide Passive Sampler Method Development

Prepared for:

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U.S. EPA Contract Number EP-C-11-038
Task Order 15

Battelle Project No. 100034455

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A. PROJECT MANAGEMENT

A1 Title and Approval Sheet

Final Revision 0.2
QAPP

TECHNICAL SUPPORT FOR THE SITE CHARACTERIZATION AND MONITORING TECHNICAL SUPPORT CENTER (SCMTSC), TECHNICAL DIRECTIVE 2-01 – HERBICIDE PASSIVE SAMPLER METHOD DEVELOPMENT

Prepared by:

Battelle
U.S. EPA Contract No. EP-C-11-038, Task Order 15

Battelle Project No. 100034455

REVIEW AND APPROVALS

Task Order Leader Battelle Thomas Kelly	Thomas Kelly	1/27/14
Technical Directive Manager Battelle Ian MacGregor		1/27/2014
Project Quality Assurance Officer Battelle Elizabeth Cutié	Elizabeth Cutié	1/27/2014
Task Order Manager U.S. EPA ORD William Hagel		1/27/2014
Task Order Technical Representative U.S. EPA Region 10 Elizabeth Allen	Elizabeth Allen	1/22/14
Task Order Regional Quality Assurance Manager U.S. EPA Region 10 Gina Grepo-Grove		1/22/2014
	Signature	Date

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A2 Table of Contents{ TC "**A2 Table of Contents**" \f C \l "2" **}**

FIGURES{ TC "FIGURES" \f C \l "1" }

TABLES{ TC "TABLES" \f C \l "1" }

A3 Distribution List{ TC "A3Distribution List" \f C \l "2" }

The final, approved document will be distributed to the following project participants:

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ACRONYMS AND ABBREVIATIONS{ TC "ACRONYMS AND ABBREVIATIONS" \f C \l "1" }

ASE	accelerated solvent extraction
CAL2	secondary source calibration verification
CFR	Code of the Federal Register
CON CAL	continuing calibration
DQI	data quality indicator
FB	field blank
ICAL	initial calibration
ID	identification
IDL	instrument detection limit
IS	internal standard
LCS	laboratory control spike
LRB	laboratory record book
MB	method blank
MDL	method detection limit
MQO	measurement quality objective
ORD	Office of Research and Development
PUF	polyurethane foam
QA	quality assurance
QC	quality control
QAO	Quality Assurance Officer
QAPP	quality assurance project plan
RL	reporting limit
RPD	relative percent difference
RSD	relative standard deviation
SB	solvent blank
SCMTSC	Site Characterization and Monitoring Technical Support Center
SMB	solvent method blank
S/N	signal-to-noise ratio
SOP	standard operating procedure
SPE	solid phase extraction
SRS	surrogate recovery standard
TD	technical directive
TDM	technical directive manager
TOL	task order leader
TOTR	task order technical representative

UHPLC/MS/MS	ultra-high pressure liquid chromatography/tandem mass spectrometry
U.S. EPA	United States Environmental Protection Agency

A4 Project and Task Organization{ TC "A4 Project and Task Organization" \f C \l "2" }

Figure 1 provides a project organization chart for the proposed activities. Table 1 describes the responsibilities and authorities of key personnel for this project. (Figures and tables are located at the end of the document). The reporting and communication pathways for key personnel are shown in the chart and the responsibilities and authority are defined in the table. The responsibilities and authorities of key Battelle personnel are summarized as follows:

- Battelle Task Order Leader (TOL) (Thomas Kelly): will review all project reports and deliverables, will provide guidance to the Technical Directive Manager (TDM), and will manage all aspects of overall project performance, including adherence to technical scope, cost and schedule.
- Battelle TDM (Ian MacGregor): will lead all technical aspects of this technical directive (TD) and will prepare all project reports and deliverables.
- Battelle Project Quality Assurance Officer (QAO) (Elizabeth Cutié): will verify that the project-specific and quality system requirements are met.
- Ultra high pressure liquid chromatography/tandem mass spectrometry (UHPLC/MS/MS) Analysis Lead (Larry Mullins): will lead all aspects of LC/MS/MS method establishment and evaluation, as well as analysis of extracted polyurethane foam (PUF) disks.
- Sample Preparation Lead (Martha McCauley): will oversee all aspects of accelerated solvent extraction (ASE) method development and PUF sample preparation.

A5 Problem Definition/Background{ TC "**A5 Problem Definition/Background**" \f C \l "2" **}**

A5.1 Problem Definition/Background{ TC "***A5.1 Problem Definition/Background***" \f C \l "3" ***}***

U.S. EPA Region 10 is working in collaboration with the Oregon Health Authority, the Agency for Toxic Substances and Disease Registry, and the Oregon Department of Environmental Quality on an investigation to assess exposures related to current timber industry herbicide application practices. At this time, air sampling is possible only for atrazine and 2,4-D via U.S. EPA Method TO-4A, and there are no available methods to evaluate exposure to other herbicides currently used by timber companies in western Oregon. In addition, many of the residences in the area are fairly remote; it is impractical to deploy either large, high-volume air samplers or battery-powered devices due to the associated costs and limitations of these instruments. A passive air sampling methodology for determining air concentrations of herbicides has been determined to be the most practical method. This task will develop and evaluate the performance of a passive sampling approach to assess ambient air concentrations of herbicides in areas where such chemicals are applied on a broad scale.

This Quality Assurance Project Plan (QAPP) defines procedures for the development and evaluation of a method to extract and analyze target herbicides from PUF passive sampling media. The target herbicides are listed in Table 2.

A5.2 Project Objectives{ TC "***A5.2 Project Objectives***" \f C \l "3" ***}***

This task has two objectives. The first is to develop and qualify extraction and analysis techniques that enable the measurement of target herbicides on PUF disks used as a passive sampling medium. The second objective is to experimentally establish the efficiency with which target herbicides may be

recovered from the PUF, and determine the PUF's effective sampling rate by measuring the loss of target herbicides over time under controlled conditions.

The two objectives above will be addressed in two phases, Phase I and Phase II.

Phase I involves (i) developing and optimizing the UHPLC/MS/MS method to analyze the target herbicides, including an initial rudimentary estimation of instrumental detection limits (IDLs) for the various herbicides; and (ii) evaluating and optimizing a method for extracting the target herbicides from the PUF sampling media, using ASE, and refining the herbicide IDLs based on any analysis method optimization that is performed.

Phase II involves (i) measuring recoveries of target herbicides from PUF disks spiked at low, medium, and high concentrations and establishing method detections limits (MDLs); and (ii) conducting a deployment study under controlled indoor conditions to determine the sampling rate of the passive sampler by measuring the loss of target herbicides over time.

Given the method development nature of these tasks, all quality control (QC) criteria set forth in this QAPP are targets, desirable for establishing and qualifying an analytical method. Actual QC criteria that are attainable will become evident as analytical work progresses, and method development results as they relate to these targets will be discussed with U.S. EPA in a timely manner so that the effect of any changes in QC criteria from the QAPP target criteria can be taken into account. If needed, revised QC criteria will be established prior to Phase II through a QAPP amendment. A final set of QC criteria recommendations, based on the outcome of Phases I and II, will be included in the final report.

A5.3 Schedule of Milestones and Deliverables{ TC "*A5.3 Schedule of Milestones and Deliverables*" \f C \l "3" *}*

Table 3 lists the schedule of milestones and deliverables for this project.

A5.4 Reports{ TC "*A5.4 Reports*" \f C \l "3" *}*

Battelle will provide electronic copies or access to all deliverables for this project. This will include a report describing the test procedures, instrument parameters for the UHPLC/MS/MS analysis and method evaluation results. No hardcopies of these deliverables will be provided. The report will be delivered in draft version for U.S. EPA review and comment. Battelle will incorporate one iteration of review comments into one final version before submittal to U.S. EPA.

Battelle will also share with U.S. EPA analytical data packages at various project milestones; these data packages will be provided in electronic format and will contain a summary of analytical results, calculations of various QC parameters (spike recoveries, method blanks, duplicate samples, etc.), and chromatograms. Battelle will make reasonable revisions to the content and format of these electronic data deliverables so as to align with U.S. EPA's expectations.

Battelle will not publish or otherwise release, distribute, or disclose any work product generated under this contract without obtaining U.S. EPA's express advance written approval.

A6 Project/Task Description{ TC "A6 Project/Task Description" \f C \l "2" }

This project consists of two phases, which are described in detail below. Before beginning the technical work, Battelle will prepare and submit a QAPP (this document) for the work to be performed. Performance of the technical work will not begin until U.S. EPA approves this QAPP.

Phase I: Develop and evaluate a method to extract and analyze the target herbicides from PUF media.

A UHPLC/MS/MS analysis method based on information provided by U.S. EPA will be established on a Waters Acquity UHPLC system coupled to a Waters Xevo TQ mass spectrometer or similar. Battelle will optimize the analysis method for the simultaneous identification and sensitive quantification of all of the target herbicides (Table 2), as well as two surrogate recovery standards (SRSs), and two internal standards (ISs). At present, Battelle assumes that the ISs will be dicamba-d_3 and simazine-d_5 and the SRSs will be 4,4'dibromobiphenyl and atrazine-C_{13}; the final selection of these four compounds will take into account EPA input, if any, similarity of their chromatographic and detector response behavior as compared to the targets, and compound availability. Battelle will explore instrument response in both positive and negative ionization modes, and anticipates that all analyses will be performed in one of the two modes. An initial calibration curve will be prepared to investigate response linearity and chromatography, and an initial rudimentary estimate of each herbicide's IDL will be calculated based on consideration of signal-to-noise (S/N) ratios. Results will be discussed with the U.S. EPA TOM and TOTR via phone conference or e-mail so that any effect on future activities based on outcome of the method setup can be initiated.

Extraction of target herbicides from PUF media will be performed with a Dionex ASE, and the ASE method will be optimized. All PUFs will be pre-cleaned before use; a baseline ASE method will be established for pre-cleaning the PUFs based on Battelle's experience and guidance from U.S. EPA (see Section B4). PUFs will be dried following pre-cleaning, if necessary, under a low flow of ultrahigh purity nitrogen. Three sets of three pre-cleaned PUFs will then be spiked at a mid-level amount of the target herbicides (i.e., approximately 10 times the IDL estimated from the initial analysis work, above); appropriate QC samples will also be prepared (specific types of QC samples are described in more detail in future sections of this document). Three sets of spiked PUFs (and QC samples) will then be extracted with one of three different ASE methods: the baseline method, and two methods anticipated to use different solvents. All extracts will be concentrated (likely using a Kuderna-Danish technique; actual technique selected will be based on guidance, if any, received from U.S. EPA, and on facility of execution of the Kuderna-Danish method relative to other potentially appropriate alternate methods), and the extracts will be analyzed using the UHPLC/MS/MS instrumental method established as above. The best of the three ASE extraction methods will be selected for further use, based on, for instance, minimization of imprecision and bias of analyte recoveries, chromatographic performance, assessment of chromatographic interferences, etc. Results will be discussed with U.S. EPA via phone conference or e-mail so that any effect on future activities based on outcome of the ASE extraction optimization can be initiated.

The UHPLC/MS/MS analysis method will be finalized for use in Phase II based on the results of the above extraction study, including final refinement/optimization of method parameters and performance of a second IDL study, with IDLs estimated using the procedure adapted from the Code of the Federal Register (CFR).

Phase II: Determine the efficiency with which herbicides may be extracted from the PUFs, and the effective rate at which herbicides are taken up onto the PUF disks.

The recovery of target herbicides at low, medium, and high concentrations on the PUF sampling medium will be measured. Three sets of three precleaned PUFs will be spiked with approximately 3, 10, and 30

times, respectively, the IDL mass as determined from the second IDL study at the conclusion of Phase I. Along with each set of triplicate spikes, appropriate method QC samples will be prepared (as described in subsequent sections of this QAPP). All samples will be extracted using the optimal ASE method and analyzed using the final UHPLC/MS/MS method determined from Phase I. The extraction efficiency for each herbicide at each of the three concentration levels will be calculated, and the MDL for each herbicide will be estimated from the recoveries of the triplicate lowest observable spikes. Results will be discussed with U.S. EPA via phone conference or e-mail so that any effect on future activities based on outcome of the extraction efficiency and MDL determination can be initiated.

Battelle will then conduct a deployment study/sampling rate experiment in which 27 precleaned disks will be spiked with 10 times the MDL mass for each herbicide. Within three days of spiking the disks, the study will begin and the initial spike mass [M_0] will be verified on the start day by extracting three of the disks along with appropriate QC samples (as described in subsequent sections of this QAPP). The remaining 24 disks along with eight unspiked disks (field blanks, FBs) will be placed in a 17.3 m^3 stainless steel chamber and purged with ambient air at a controlled rate of approximately one air change per hour. A minimum distance of approximately 1 ft will be maintained between disks. The time of deployment will be denoted as T_0. The chamber temperature and relative humidity will be monitored and recorded. At the following eight intervals, three spiked and FB PUF disks will be removed from the chamber and analyzed along with appropriate QC samples: 14, 28, 42, 56, 70, 84, 98, and 112 days post deployment.

After analyzing the samples collected from the 28-day deployment time, a conference call will be held with the U.S. EPA TOM and TOTR to discuss the results up to that point in the study so that any issues can be addressed before proceeding with analysis of the next deployment set.

A7 Quality Objectives and Criteria{ TC "**A7 Quality Objectives and Criteria**" \f C \l "2" }

Quantitative and qualitative measurement quality objectives (MQOs) for the various data quality indicators (DQIs) such as completeness, accuracy, comparability, etc., have been established for this project to define target data quality for measurement data. Given the method development nature of this project, these objectives are target values, subject to change as methods are developed and qualified. All final MQOs will be detailed in the final report. Target MQOs for accuracy and precision are given in Table 4. The laboratory IDLs and MDLs will be determined as part of Phase I of this project. The working definitions for the project MQOs for the various DQIs are as follows:

- Completeness: the completeness MQO is established as 100%, i.e., all PUF disks that are spiked are successfully extracted and analyzed, with results reported. However, it is estimated that the project will not be compromised if 90% of the samples collected are analyzed with acceptable quality.
- Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components. Accuracy will be expressed as percent recovery and will include recovery of spiked analytes as well as spiked internal and surrogate standards.
- Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision will be expressed as relative percent difference (RPD) or relative standard deviation (RSD).
- Comparability: a measure of the confidence with which one data set can be compared to another. This is a qualitative assessment that has been addressed primarily in sampling

design through use of comparable extraction, analysis, and reporting procedures for all samples processed in Phase II.

- Representativeness: the degree to which data accurately and precisely represent a characteristic of a population. This is a qualitative assessment and has been addressed primarily in the sample design, through the selection of procedures that reflect the project goals and environment being sampled. It will be ensured during Phase II through proper sampling and sample handling procedures (those that conform to this QAPP).
- Sensitivity: the capability of a test method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. Sensitivity has been addressed primarily through the selection of appropriate analytical methods, equipment, and instrumentation. It will be monitored through the establishment and achievement of IDLs and MDLs, instrument calibration, and various QC blanks.
    - Instrument detection limits: the minimum concentration of a substance measurable, in the absence of the sampling matrix, with 99% confidence that the analyte concentration is greater than zero. The data qualifier "U" will be appended to results for analyses lacking the PUF disk matrix where analytes were not detected above IDLs.
    - MDLs: the minimum concentration of a substance measurable, in the presence of the sampling matrix, with 99% confidence that the analyte concentration is greater than zero. The data qualifier "U" will be appended to results for analyses of PUF disks where analytes were not detected above MDLs.
    - Reporting Limits (RLs): the minimum concentrations of an analyte that can be reliably identified, measured, and reported with complete confidence that the analyte concentration is greater than zero, and where method quality control criteria such as precision and accuracy may be routinely met. For this project the RLs will be assigned nominally as three times the MDL and will be adjusted on a sample-specific basis for sample dilution.

A8 Special Training/Certification

{ TC "**A8 Special Training/Certification**" \f C \l "2" **}**

All personnel who perform technical activities for this project will have sufficient training and experience to complete their tasks independently. Analysts and data management personnel will have experience or direct training in the procedures that they will be performing for this project. In addition, individuals implementing this QAPP must receive, at a minimum, orientation to the project's purpose, scope, and methods of implementation. This orientation is the responsibility of the Battelle TDM or his designee, and will be completed as part of a project kickoff meeting.

A9 Documentation and Records

{ TC "**A9 Documentation and Records**" \f C \l "2" **}**

A9.1 Document Control

{ TC "***A9.1 Document Control***" \f C \l "3" ***}***

It is critical that project personnel have the most current versions of this QAPP and Standard Operating Procedures (SOPs). Version control is maintained for these documents through the document header blocks, which identify the document, version, and effective date.

A9.2 Documentation Standards{ TC "***A9.2 Documentation Standards***" \f C \l "3" ***}***

Any records generated for this project must be able to withstand challenges to their validity, accuracy, and legibility. To meet this objective, records will be generated in standardized formats and in accordance with prescribed procedures. Project documentation must meet the following minimum requirements:

- Data must be documented directly, promptly, and legibly. All reported data must be uniquely traceable to the raw data. All data reduction formulas must be documented.
- Handwritten data must be recorded in ink. All original data records include, as appropriate, a description of the data collected, units of measurement, unique sample identification (ID), name (signature or initials) of the person collecting the data, and date of data collection.
- Any changes to the original (raw data) entry must be made with a single line cross out so as not to obscure the original entry. The change must be initialed and dated by the person making the change.
- The use of pencil, correction fluid, and erasable pen is prohibited.

Other specific documentation requirements are discussed throughout this QAPP.

A9.3 Storage and Disposal{ TC "***A9.3 Storage and Disposal***" \f C \l "3" ***}***

Storage of project data must ensure that the integrity and traceability of data are maintained. Storage locations must be appropriate for the media (paper or electronic) and limited access or availability of the data.

At Battelle, electronic data files will be stored in the network project folder, one that is backed-up periodically, not on individual computers. Hard-copy records will be maintained by the Battelle TDM. Once the project is complete, Battelle will archive all project files with Battelle's Records Management Office, including project management files and electronic copies of deliverables, for at least 10 years.

B. DATA GENERATION AND ACQUISITION { TC "B. DATA GENERATION AND ACQUISITION" \f C \l "1" }

B1 Sampling Process Design (Experimental Design){ TC "B1 Sampling Process Design (Experimental Design)" \f C \l "2" }

Phase I involves the establishment of analytical methods as described in B4.

- Multi-point initial calibration (ICAL) and secondary source calibration verification (CAL2) standards will be analyzed per the method described in Section B7. By inspection of the response of the low-level ICAL standard, a preliminary IDL for each herbicide will be determined by way of Equation 1 (Section B5).
- For the ASE method development study, 12 PUF disks will be precleaned using the method given in Section B4. Nine will be spiked with 10 times the IDL of each herbicide; all 12 will be spiked with 10 times the IDL of the selected SRSs – the three PUF spiked with only SRS will serve as method blanks (MBs). One spike check and three solvent method blanks (SMBs) will be prepared by spiking the same concentrations of herbicides and SRSs, and only SRSs, respectively, into solvent only. One MB, one SMB, and three spiked PUFs will be extracted using each of the three ASE methods given in Section B4. All extracts will be volume-reduced to 1 mL per Section B4, diluted at least 1:1 with reagent-grade water, and this final solution will be fortified to achieve a concentration approximately 10 times the IDL of the two ISs. Extracts will be analyzed per the analytical sequence as described in Section B7.
- Following review and inspection of these results, the best ASE method will be selected for further use based on assessment of accuracy (average percent recovery of the triplicate extractions), precision (%RSD of the triplicate extractions), sensitivity (MDLs estimated using Equation 1 [Section B5]), and chromatographic performance. Finally, the UHPLC/MS/MS will be modified, if necessary, to account for any matrix affects that may impact the method. If significant modifications are made to the analytical method, another IDL study will be performed by preparation and analysis of seven low level standards, followed by workup of the data per Equation 2 (Section B5).

In Phase II, Battelle will verify the extraction and analysis method performance and conduct a deployment study such that the effective sampling rates of the PUFs for each of the target herbicides may be empirically determined. Specifically, in Phase II, Battelle will:

- Measure the recovery of each of the target herbicides at low, medium, and high concentrations on the PUF sampling medium. A total of 14 PUFs will be precleaned; three sets of three precleaned PUFs will be spiked with approximately three, 10, and 30 times, respectively, the IDL mass determined for each herbicide at the conclusion of Phase I of the work, along with 10 times the IDL levels for the SRSs. Along with these triplicate spikes, appropriate QC samples will be prepared: two laboratory control spikes (LCSs; precleaned PUFs spiked at 10 times the IDL with herbicides and SRSs); three method blanks (precleaned PUFs spiked with only SRSs); one solvent method blanks (solvent spiked with only SRS); and three spike checks (solvent spiked with herbicides and SRSs). The nine spiked PUFs, two LCSs, three MBs, and one SMB will be subjected to ASE with the method determined from Phase I of the work (nominally as described in Section B4), and analyzed using the optimized UHPLC/MS/MS method established during Phase I (for analysis QC requirements,

see Section B4). The extraction efficiency for each herbicide at each of the three concentration levels (mean ± standard deviation at each spike level) will be calculated. The MDL for each herbicide will be estimated from the recoveries of the triplicate lowest observable spikes (likely at the lowest of the three spike levels), using either Equation 1 or 2 (Section B5).

- Conduct a deployment study/sampling rate experiment.
    - A total of 56 PUF disks will initially be precleaned. Twenty-seven PUF disks will be spiked with 10 times the MDL mass for each herbicide. The remaining 29 precleaned PUF disks will be used for QC samples, as follows: three as 'cleaned blanks' and eight for FBs (for a total of 11 field QC samples); nine for MBs and nine for LCSs (for a total of 18 laboratory QC samples).
    - The deployment study will begin within three days of preparation of spiking the 27 sample disks. At the commencement of the study, three spiked PUF, the three 'cleaned blanks', one MB and one LCS will be set aside and each spiked with 10 times the MDL of the SRSs; also, one SMB (10 times MDL SRS only) and one spike check (10 times MDL herbicides and SRS) will also be prepared. This batch of samples will be immediately extracted and the triplicate spiked PUF results will serve to determine the initial spiked mass [M_0] of each herbicide.
    - On the same day as those three disks are extracted, the eight FB and 24 remaining spiked PUF disks will be deployed by hanging them in Battelle's 17.3 m^3 stainless steel, ventilated chamber. The chamber will be purged with ambient air at a controlled rate of approximately 1 air change per hour. A minimum distance of approximately 10 cm will be maintained between disks. The time of deployment will be denoted as T_0. The chamber temperature and relative humidity will be monitored and recorded, and is anticipated to range between approximately 20 and 25°C and 30 to 70% relative humidity.
        - When operated as per the above, with the disks separated by 10 cm, the advective air speed in the chamber will be approximately 10 times greater than the speed by which compounds may move by diffusion; thus back diffusion should not be of concern. See calculations in Appendix B.
    - At 14, 28, 42, 56, 70, 84, 98, and 112 days post deployment, three spiked and one unspiked FB PUF disks will be removed from the chamber. The collected PUF disks will be stored as per Section B3 for no more than five days, or will be immediately processed and extracted. For processing, these and one MB, LCS, and SMB and will be spiked (spiked PUFs, FB, MB and SMB: SRSs only; LCS: herbicides and SRSs), extracted and analyzed together.

B2 Sampling Methods{ TC "**B2 Sampling Methods**" \f C \l "2" }

PUF disks used in Phases I and II will be obtained from Tisch Environmental (or another suitable vendor) and will be 14 cm in diameter x 1.35 cm thick with a total approximate surface area of 365 cm^2. Similar PUF disks will be deployed to remote locations for passive collection of herbicides from ambient air.

B3 Sample Handling and Custody{ TC "**B3 Sample Handling and Custody**" \f C \l "2" }

Success of the study is dependent on samples that are carefully prepared and handled. Sample integrity can be compromised by contamination from outside sources (e.g., equipment, atmosphere) and other

samples (cross contamination). Throughout sample collection activities, care will be taken to avoid sample contamination. This will be accomplished through careful sample handling procedures.

- Nitrile (or equivalent) gloves will be worn during sample handling.
- All glassware will, at a minimum, be washed in warm soapy water, triple rinsed in reagent water (≥ 18 MΩ), and allowed to air dry. Glassware used for solvent volume reduction is typically muffled.
- Amber jars and aluminum foil used to hold samples will be purchased precleaned and muffled prior to use.
- If storage of precleaned PUFs is necessary, each will be individually wrapped in precleaned aluminum foil, or enclosed in a Petri dish, and placed in individual labeled zip-lock bags. Alternatively, precleaned PUFs may be stored in muffled amber glass jars. Unspiked PUFs may be stored as per the above at room temperature; spiked PUFs will be stored at -20°C.
- All samples will be tracked by way of using unique identification codes, such as the nine digit codes assigned when using Battelle laboratory record books (LRBs): five digit LRB number, two digit LRB page number, two digit line number.
- Tracking of all samples will be performed by way of recording their location and storage conditions in the LRB. Staff members assuming possession of samples, whether for extraction, analysis, deployment, etc., will inspect the integrity of the samples for leaks, cracks, mislabeling and other conditions that may cause samples to be unusable and report any problems or concerns to the TDM.
- PUF media will be discarded after extraction and analysis are complete (after data have undergone quality assurance [QA] and technical review).
- Standards and sample extracts will be stored separately and refrigerated at 4°C ± 3°C. High level stock solutions prepared in solvent (methanol, acetone, etc.) will be assigned a 6 month expiration date. Calibration standards or any other solutions prepared in water will be assigned a 1 month expiration date. Neat solvents and standards will be stored per manufacturer guidance, separately from standards and sample extracts.

B4 Analysis, Extraction and Cleanup Methods{ TC "B4 Analysis, Extraction and Cleanup Methods" \f C \l "2" }

A Waters UHPLC/MS/MS system (detailed in Section A6) will be used to analyze PUF media extracts for herbicides. The developed method will be informed by technical memoranda previously provided by U.S. EPA as guidance (See Appendix A) and will be optimized during Phase I. The analysis method will initially be developed using the following parameters, which are subject to change as needed to improve method performance:

- Mobile Phase A: Reagent water with 0.05% formic acid
- Mobile Phase B: High performance liquid chromatography grade methanol with 0.05% formic acid
- UHPLC Column: Agilent ZORBAX RRHD SB-Phenyl, 2.1 × 50 mm, 1.8 µm
- Column Temperature: 40-65 °C
- Flow Rate: 0.5 mL/min
- Mass Resolution: unit

All PUF disks will be precleaned, and herbicides will be extracted from PUF with ASE. A Dionex ASE with cells having an internal volume of approximately 33 mL will be used. Each PUF will be rolled along its diameter into the shape of a cylinder then inserted into individual ASE cells. No filtration material (sand, a cellulose filter, etc.) will be added to the cell.

The baseline ASE method will be as follows:

- Pressure = 2000 psi
- Temperature = 100°C
- 2 cycles
- 120 second purge time
- 60% flush.

Precleaned PUFs will subsequently be dried in a glovebox under a flow of dry nitrogen. During Phase I, three different ASE methods will be evaluated. It is anticipated that the three methods will use three different solvents – acidic methanol, acidic acetonitrile, and acidic acetone – but identical operating conditions. The PUF extracts will be concentrated likely using the Kuderna-Danish technique, heating at 60°C until the solvent is evaporated to 1 mL.

All standards and solvents will be purchased from Sigma-Aldrich, Chemservice, Thermo Fisher, or other vendor known to supply chemicals of known high quality and purity. Certificates of Analysis will be maintained in the project file.

B5 Quality Control{ TC "**B5 Quality Control**" \f C \l "2" }

The required QC checks and samples for the analytical measurements along with target acceptance criteria are listed in Table 4. Given the method development nature of this project, target acceptance criteria may be modified between Phase I and Phase II. A final set of recommended QC criteria will be included in the final report, and any deviations from the target criteria in this QAPP will be discussed in the final report.

IDL/MDL (S/N method)
IDL = 3 · concentration of the standard analyzed/observed S/N ratio) Equation (1)

IDL/MDL (CFR method)
$IDL/MDL = t_{99\%} \cdot s$ Equation (2)

where: $t_{99\%}$ is the one-sided Students-t statistic for the (N-1) degrees of freedom ($t_{99\%}$ = 3.143 for N=7); and s = standard deviation of the N replicate measurements performed.

$$\text{Absolute Percent Difference (APD)} = \frac{|\text{concentration or amount observed} - \text{concentration or amount expected}|}{\text{concentration or amount expected}} \times 100\ \%$$ Equation (3)

$$\text{Percent Recovery (\%R)} = \frac{\text{concentration or amount observed}}{\text{concentration or amount expected}} \times 100\%$$ Equation (4)

$$\text{Relative Percent Difference (RPD)} = \frac{|\text{concentration or amount in sample 1} - \text{concentration or amount in sample 2}|}{\text{Average concentration or amount in samples 1 and 2}} \times 100\ \%$$

Equation (5)

$$\text{Relative Standard Deviation (RSD)} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\ \%$$

Equation (6)

B6 Instrument/Equipment Testing, Inspection, and Maintenance{ TC "**B6 Instrument/Equipment Testing, Inspection, and Maintenance**" \f C \l "2" **}**

Routine laboratory equipment will be operated and maintained as described in the following Battelle SOPs:

- ENVS-3-189 SOP for Calibration, Maintenance, and Operation of Electronic Balances;
- ENVS-3-191 SOP for the Operation, Calibration, and Maintenance of Adjustable Volume Pipettes;
- ENVS-3-192 Use of Refrigerators and Freezers; and
- ENVS-3-193 SOP for the Operation, Calibration, and Maintenance of Digital, Glass, and Infra-red Thermometers.

General operation and maintenance of the UHPLC/MS/MS instrumentation will be covered under the following Battelle SOPs:

- CAC-RDTE IV-057 Operation and Maintenance of Liquid Chromatographs; and
- KAC I-011 The General Use and Maintenance of Mass Spectrometer Systems.

B7 Instrument/Equipment Calibration and Frequency{ TC "**B7 Instrument/Equipment Calibration and Frequency**" \f C \l "2" **}**

Routine laboratory equipment will be calibrated as described in the following Battelle SOPs:

- ENVS-3-189 SOP for Calibration, Maintenance, and Operation of Electronic Balances,
- ENVS-3-191 SOP for the Operation, Calibration, and Maintenance of Adjustable Volume Pipettes,
- ENVS-3-192 Use of Refrigerators and Freezers, and
- ENVS-3-193 SOP for the Operation, Calibration, and Maintenance of Digital, Glass, and Infra-red Thermometers.

Calibration requirements for the UHPLC/MS/MS instrument will be determined during Phase I method development and includes both analyte calibration and mass calibration of the spectrometer. Battelle will explore instrument response in both positive and negative ionization modes, and anticipates that all analyses will be performed in one of the two modes. Mass calibration of the spectrometer will be performed using the appropriate reference solution (polyethylene glycol, NaRbI, or similar reference

solution) and will cover the full range of analyte masses. Nominally, mass calibration will be performed prior to the start of each analytical sequence. Acceptance criteria for mass calibration are given in Table 4. The analyte calibration sequence will begin with a system blank (neat solvent), an ICAL containing a minimum of three, but preferably six calibration points, spanning a nominal range of 3 to 300 times the IDL, followed by analysis of a secondary source calibration verification standard (CAL2; sourced from a different vendor) at 10 times the IDL, followed by analysis of a system blank. Acceptance criteria for these calibration QC samples are given in Table 4. On a continuing basis after analysis of every 10 samples and at the start of a day subsequent to the initial calibration when analyses are performed, a mid-level calibration solution (nominally 10 times the IDL) will be analyzed as a continuing calibration check (CON CAL). Target acceptance criteria for the CON CAL are noted in Table 4. Before analysis of the on-going (every tenth sample) CON CAL, a system blank will be analyzed to decrease the probability that sample carryover will preclude verification of continuing system calibration. The CAL2 will also be analyzed following the CON CAL on days subsequent to the ICAL when calibration requires confirmation. The method IDL is anticipated to be approximately 1 ng mL^{-1} (= µg L^{-1}), or lower. Note that due to the method development nature of this project, the concentration ranges and acceptance criteria in Table 4 are targets and all are subject to change based on the outcome of Phase I. Actual acceptance criteria will be discussed with U.S. EPA and documented in the final report.

B8 Inspection/Acceptance of Supplies and Consumables{ TC "**B8 Inspection/Acceptance of Supplies and Consumables**" \f C \l "2" **}**

Prior to use, supplies and consumables will be inspected and tested, if appropriate, to ensure that they conform to the required level of quality. The TDM is responsible for ensuring that supplies meet the following standards:

- Containers for analytical chemistry samples must be free of defects (chips, cracks, etc.) and lids must be Teflon®-lined without flaws (cracks, tears). Certified clean containers (I-Chem or equivalent) will be used as sample containers. Prior to use, containers will be inspected. Any defective material will be replaced before the sampling event begins.
- Reagents and chemicals must be pesticide grade or better, with percent purity of at least 96%. Any exceptions will be documented and any impact on data quality will be determined before use.
- Standards used to calibrate equipment must be within expiration date, have an assigned lot number and purity, and be continuously stored to maintain integrity. The quality of stock standards will be documented by the supplier and supplier certificates of analysis received with the standards will be retained in the project records.

B9 Non-Direct Measurements{ TC "**B9 Non-Direct Measurements**" \f C \l "2" **}**

Not applicable to this project.

B10 Data Management{ TC "**B10 Data Management**" \f C \l "2" **}**

The Battelle TDM will maintain all project data and information as described in Section A9.3. As part of the data review, the TDM, or designee, will evaluate any QA/QC data generated with the data set for outliers or other reasons that specific data points should be excluded or flagged. Additionally, any data transferred from instrument output to other software packages (such as Microsoft® Excel) for further calculations will receive a data audit as described in C1.1 to ensure transfer accuracy and the completeness and accuracy of any additional calculations. All computer hardware used for this project

must use Intel-based Pentium or compatible processors running a Microsoft® operating system so that documents can be transferred between organizations.

C. ASSESSMENTS AND OVERSIGHT{ TC "C. ASSESSMENTS AND OVERSIGHT" \f C \l "1" }

The following subsections identify planned assessment and oversight activities for this project. The Battelle Project QAO and/or the TDM may identify additional assessment activities to be performed during the course of this project, based upon findings of the planned assessment activities described below. These individuals are authorized to stop work for cause if data quality or staff safety are threatened.

C1 Assessment and Response Actions{ TC "C1 Assessment and Response Actions" \f C \l "2" }

C1.1 Quality Assurance Performance Audits, System Audits, and Frequency{ TC "C1.1 Quality Assurance Performance Audits, System Audits, and Frequency" \f C \l "3" }

QA audits are both organizational and project-specific. Each organization must have an internal audit program to monitor the degree of adherence to its own quality system. The internal audit program at Battelle includes systems audits, performance evaluations, data audits, and laboratory inspections.

Quality systems audits are performed at least annually at Battelle. Systems audits evaluate conformance to, and effective implementation of, the requirements of the quality system.

Data audits verify the accuracy and traceability of reported data. Once the existing data have been transferred into the proper electronic format, they will be reviewed for accuracy and completeness by the person transferring the data. After the primary data transfer has been checked for accuracy and acceptability, the data will be available for further evaluation. After all further evaluation is complete, the Battelle project QAO or designee will conduct a data audit prior to delivery of the final report to U.S. EPA. This audit will assess the following:

- Accuracy of existing data transcribed or imported for further evaluation
- Completeness and accuracy of calculations conducted as part of the further evaluation
- Accuracy and completeness of the draft and final deliverable.

The results of each assessment will be documented and reported to the person directly responsible for the task (for correction) and the Battelle TDM. The QAO or designate will verify that corrections are complete and address any errors identified.

Auditors will be independent of the activities audited and will have the technical expertise required to conduct a meaningful audit. The results of all QA audits and inspections will be reported to management. The Battelle project QAO will receive copies of all QA audit reports generated for this project as part of the project records.

C1.2 Corrective Action Procedures{ TC "C1.2 Corrective Action Procedures" \f C \l "3" }

An effective quality system requires prompt and thorough correction of non-conformance conditions that can affect quality. Rapid and effective corrective action minimizes the possibility of questionable data or documentation. Corrective actions for this project depend on the severity of the non-conformance condition. If immediate and complete corrective action is implemented by project personnel, the corrective action will be documented in an e-mail communication to the appropriate task leader, TDM and QAO.

*C1.3 Corrective Action Responsibilities{ TC "**C1.3 Corrective Action Responsibilities**" \f C \l "3" }*

Corrective action items may be specific to this project or generic to an organization. The responsibility for addressing project-specific corrective action items is assigned based on the specific issue and action item. The Battelle TDM is responsible for investigating and implementing project-level corrective actions to address errors or deviations in data evaluation. The TOL is ultimately responsible for ensuring that corrective action is completed such that impacts to data quality are minimized and that reported results are accurate and defensible.

C2 Reports to Management{ TC "**C2 Reports to Management**" \f C \l "2" }

For this project internal reports will be prepared for management as part of Battelle's quality system.

Internal reports to management at Battelle will be prepared by the Project QAO and submitted to project management (the TOL) and line management. These include:

- Results of systems or data audits (Section C1.1)
- Any practices or incidents that do not comply with the project QAPP or Battelle's quality system
- Results of report reviews.

D. DATA VALIDATION AND USABILITY{ TC "D. DATA VALIDATION AND USABILITY" \f C \l "1" }

D1 Data Review, Verification and Validation{ TC "D1 Data Review, Verification and Validation" \f C \l "2" }

Data verification is defined as the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements. Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine the analytical quality of a specific data set. Data validation includes both "data usability" and data validation.

Data generated in the method development Phase I will be reviewed by the TDM. For Phase II, data verification and validation will include a data audit by the Project QAO or designee as described in C1.1. Any suspect data will be flagged as necessary, based on the typical U.S. EPA Region 10 flagging scheme. When more than one quality issue is noted, the most restrictive qualifier is attached to the data.

U	The analyte was not detected at or above the MDL.
J	The identification of the analyte is acceptable; however, the reported value is an estimate.
UJ	The analyte was not detected at or above MDL. The reported value is an estimate.
NA	Note applicable; the parameter was not included in the analysis, or there is no analytical result for this parameter. No value is reported with this qualification.
R	The presence or absence of the analyte cannot be determined from the data due to severe quality control problems. No value is reported with this qualification.

D2 Validation and Verification Methods{ TC "D2 Validation and Verification Methods" \f C \l "2" }

The following criteria must be met in order for a peak to be reported as detected:

- Peaks must be present with ≥ 3:1 S/N for both the quantification and qualification ion transitions
- Peak retention times must track with appropriate positive control samples (such as LCSs)
- The peak shapes of the monitored ion transitions must approximately comaximize
- Ion ratios (the ratio of the quantification ion area to the qualification ion area) must be within 50% of the average ratio (obtained from the average of all ICAL/CON CAL/CAL2 standards).

Once an analyte has met the criteria listed above, the quantification of that analyte will be based upon calibration curves derived from the primary (most abundant) precursor-ion to product-ion transition. If the instrument response for a detected analyte exceeds the range of the calibration curve, or if interferences are observed in the blank samples, the TDM will be notified to determine how to proceed. Options include, for example, dilution and reanalysis or selection of an alternative quantification ion.

Once all detections have been determined and quantified, the data will be submitted to a trained UHPLC-MS/MS operator for technical peer review. The peer reviewer will check the data to determine that all criteria given in this QAPP were met and that detections were properly integrated and quantified. Once peer and QA review are complete, the data will be submitted for review and finalization by the TDM.

D3 Reconciliation with User Requirements{ TC "**D3 Reconciliation with User Requirements**" \f C \l "2" **}**

The data generated for this project will be evaluated against the target MQOs listed in Table 4 and any subsequent revisions to these MQOs that result from Phase 1 method development.

The TDM will attempt to correct or minimize any limitations on data usability. At a minimum the impact of data limitations will be discussed in the final report, including any recommendations such as caveats on data use or suggestions for data re-collection.

E. REFERENCES{ TC "E. REFERENCES" \f C \l "1" }

Battelle SOP ENVS-3-189-03, SOP for Calibration, Maintenance, and Operation of Electronic Balances. July 19, 2013.

Battelle SOP ENVS-3-191-02, SOP for the Operation, Calibration, and Maintenance of Adjustable Volume Pipettes. April 26, 2013.

Battelle SOP ENVS-3-192-01, Use of Refrigerators and Freezers. May 10, 2013.

Battelle SOP ENVS-3-193-03, SOP for the Operation, Calibration, and Maintenance of Digital, Glass, and Infra-red Thermometers. May 14, 2013.

Battelle SOP CAC-RDTE IV-057 Operation and Maintenance of Liquid Chromatographs.

Battelle SOP KAC I-011 The General Use and Maintenance of Mass Spectrometer Systems.

FIGURES

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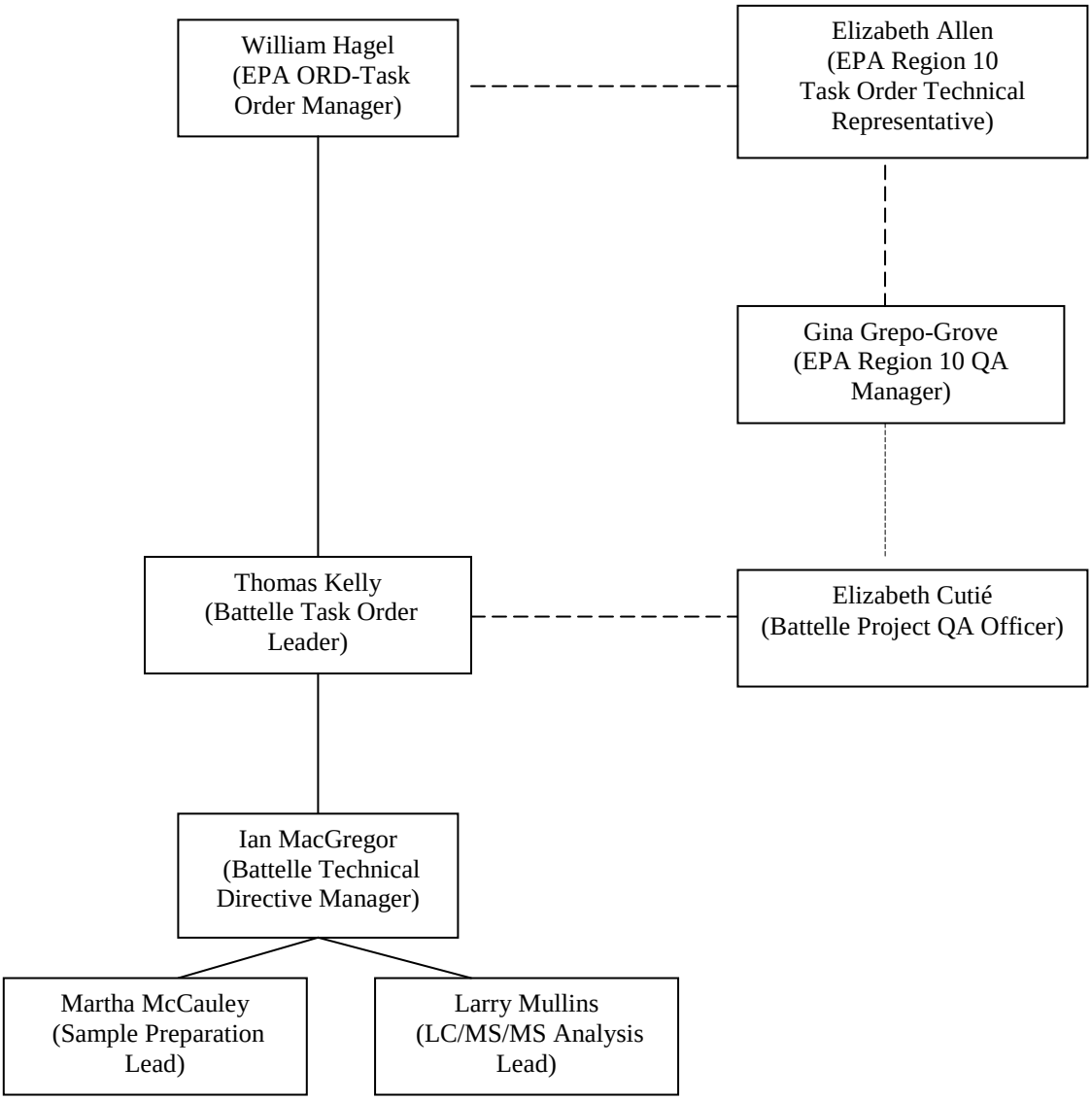

Figure 1. Project Organizational Chart{ TC "Figure 1. Project Organizational Chart" \f F \l "1" }

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TABLES

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Table 1. Task Order Personnel and Responsibilities{ TC "Table 1. Task Order Personnel and Responsibilities" \f D \l "1" }

Position	Responsibilities	Authority
U.S. EPA ORD Task Order Manager William Hagel	• Ultimate TO responsibility • Overall management of the TO • Assignment of personnel • Liaison with Contracting Officer/CO Representative • Monitoring and control of cost, schedule, and QC	Authorized to suspend work if data quality or project objectives are jeopardized
U.S. EPA Region 10 Quality Assurance Manager Gina Grepo-Grove	• Oversight of QA issues for entire program • Review and approval of the QAPP and all other QA/QC documents • Review of design process • Review of data validation • Communication of issues to the U.S. EPA Region10 Task Order Technical Representative	Authorized to suspend work if data quality or project objectives are jeopardized
U.S. EPA Region10 Task Order Technical Representative Elizabeth Allen	• Oversight of the TO • Approval of the release of study reports • Oversight of data evaluation activities • Communication with the Battelle QA Officer	Authorized to suspend work if data quality or project objectives are jeopardized
Battelle Task Order Leader Thomas Kelly	• Management of budget and scheduling • Review and approval of QAPP • Reporting and planning • Recommendation/justification for change order	Approve all technical deliverables, including the QAPP Authorized to suspend work if data quality or project objectives are jeopardized
Battelle Project Quality Assurance Officer Elizabeth Cutie	• Approval of QAPP and QA/QC requirements • Interaction with EPA Region 10 QA Officer	Authorized to suspend work for cause if data quality is threatened
Battelle Technical Directive Manager Ian MacGregor	• Communicate project requirements to any staff supporting this task • Conduct method development and validation according to the QAPP and SOPs • Track TO progress • Review all data packages • Communicate issues to the Battelle TOL • Prepare the QAPP and draft/final reports	Allocate budget among tasks as identified in the TO Approve all labor, materials, and equipment charges to the project Assign technical and operational staff to the project Recommend acceptance or rejection of data submissions or evaluations
Sample Preparation Lead Martha McCauley	• Conduct sample preparation according to instructions from TDM and this QAPP • Purchase all supplies related to sample preparation • Receive samples and properly document receipt • Ensure preparation equipment receives proper maintenance and calibration	Notify the TDM of any issues related to sample preparation
LC/MS/MS Analysis Lead Larry Mullins	• Conduct sample analysis according to instructions from TDM and this QAPP • Purchase all supplies related to sample analysis • Receive sample extracts and properly document receipt • Ensure LC/MS/MS instrumentation receives proper maintenance and calibration.	Notify the TDM of any issues related to sample analysis

Table 2. Target Herbicides{ TC "Table 2. Target Herbicides" \f D \l "1" }

Triazines	Pyridines	Phenoxy acids
Atrazine	Imazapyr	2,4-D
Hexazinone	Clopyralid	
	Aminopyralid	
	Picloram	
	Triclopyr	

Table 3. Anticipated Schedule of Milestones and Deliverables for Technical Directive 2-01{ TC "Table 3. Proposed Schedule of Milestones and Deliverables for Technical Directive 2-01" \f D \l "1" }

Milestone/Deliverable	Estimated Date
Draft project-specific QAPP	November 18, 2013
Final project-specific QAPP	January 3, 2014[(a)]
Phase I commences	January 6, 2014
Phase II commences	January 27, 2014
Deployment study begins	February 28, 2014
Data review conference call after 28 day deployment testing time point	April 9, 2014[(b)]
Draft report	July 30, 2014[(c)]
Final report	August 28, 2014[(d)]

(a) Within 10 working days of receipt of U.S. EPA review comments on the draft QAPP; assumes 10 working days for U.S. EPA review.
(b) No later than 40 calendar days after start of deployment testing.
(c) No later than 150 calendar days after start of deployment testing.
(d) Within 15 working days of receipt of U.S. EPA review comments on the draft report; assumes 15 working days for U.S. EPA review.

Table 4. Method Quality Control Checks and Target Acceptance Limits{ TC "Table 4. Method Quality Control Checks and Target Acceptance Limits" \f D \l "1" }

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
The ASE and LC/MS/MS are checked to verify that the correct methods are loaded and that the operating parameters are correct.	Before extraction batch (ASE) or each analytical sequence (LC/MS/MS)	Parameters will be specified in the methods developed as part of Phase I.	If parameters are changed or are out of specifications, the operator discusses with TDM.
Mass Calibration	Prior to each analytical sequence	All reference ions must be detected and the mass accuracy (residuals) must be ± 0.2 amu.	Verify instrument parameters and perform instrument maintenance if needed. For repeated failures, inform TDM.
System/Solvent blanks	At the beginning of each analytical sequence, once after the ICAL/before sample analysis, and before a CON CAL that follows 10 samples.	If two or more blanks are run consecutively (for instance, at the beginning of a sequence), only the last check must be acceptable. Analyte concentrations must be ≤ ½ the IDL.	Flag affected data and repeat blank analysis. If the blank still exceeds criteria then discuss appropriate actions with TDM.
Method Blank (MB) and Solvent Method Blank (SMB)	As per Section B2. To be analyzed after a solvent blank and before any test samples	Analyte concentrations must be ≤ ½ the MDL.	Flag affected data and repeat blank analysis. If the blank still exceeds criteria then discuss appropriate actions with TDM.
Initial Calibration Curve (ICAL)	Either at the beginning of each analytical sequence or at the beginning of a given study	For multipoint calibrations, the mean absolute percent difference across the ICAL is ≤ 10 %. Also, the percent difference for any single ICAL point from its known concentration must be ≤ 30%.	Repeat calibration. If still out of calibration, then inform TDM to determine what corrective maintenance to perform.
Continuing calibration verification (CON CAL) with mid level calibration standard	Minimally at the end of each analytical sequence and every 24 hours of analysis following successful ICAL. If more than 10 samples are analyzed, the CON CAL, followed by a solvent blank, should be repeated every 10 samples.	Calculated concentration of CON CAL using ICAL must be within 30 % of known concentrations (percent difference ≤ 30%).	Flag data and repeat analysis. If still outside of criteria, inform TDM.
Analysis of secondary source calibration standard (CAL2)	Once for every sequence	Calculated concentration of secondary source using ICAL must be within 30 % of known concentrations (percent difference ≤ 30%).	Flag data and repeat analysis. If still exceeds criteria then discuss appropriate actions with project leader.

Table 4. Method Quality Control Checks and Target Acceptance Limits (Continued)

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCS)	As per Section B1	70-130% recovery of spiked analytes	Flag data. Discuss with TDM to determine if repeat analysis is required.
Recovery of Internal Standards (IS)	For all analyses performed in a sequence	Must be within 50% of the mean IS response for the ICAL (or for the CON CAL if ICAL was not run during the last 24 hours).	Flag data. Discuss with TDM to determine if corrective action is required.
Recovery of Surrogate Recovery Standards (SRS)	For all analyses performed in a sequence	Must be within between 50 and 150 %.	Flag data. Discuss with TDM to determine if repeat analysis is required.
Field blanks (FB) and 'cleaned blanks'	As per Section B1.	Analyte concentrations must be $\leq$ ½ the MDL.	Flag affected data.
Compound Identification	All analyses performed in a sequence	For positive identification, analytes and IS compounds must exhibit a signal-to-noise ratio (S:N) of 3:1 or greater for at least two precursor-ion to product-ion transitions, monitored ion transitions must track one another (peaks must comaximize), and peak retention time should track with the appropriate positive control sample(s) (LCS). For compounds calculated to have concentrations above their IDL, the ion ratio must be within 50% of average of the ion ratios across the ICAL, CON CAL, and CAL2.	Flag affected data.

APPENDIX A

Technical Memoranda: LC/MS/MS analysis methodologies provided by US EPA

Acquisition Method Report

Acquisition Method Info

Method Name O031513A POS MRM AIR HRB.m
Method Path D:\MassHunter\methods\O031513A POS MRM AIR HRB.m
Method Description

Device List
h-ALS
Bin Pump
Column
DAD
MS QQQ

QQQ Mass Spectrometer

Ion Source ESI
Tune File atunes.tune.xml
Stop Mode No Limit/As Pump
Stop Time 3.5
Time Filter On
Time Filter Width 0.07

Time Segments

Time Seg #	Time	Scan Type	Ion Mode	Div Valve	Delta EMV	Store
1	0	MRM	ESI	To MS	400	☑

Time Segment 1

Scan Segments

Compound Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Dwell	Frag (V)	CE (V)	Polarity
Metsulfuron methyl	☐	382	Unit	167	Unit	50	120	15	Positive
Metsulfuron methyl	☐	382	Unit	141	Unit	50	120	15	Positive
Sulfometuron methyl	☐	365	Unit	199	Unit	50	100	20	Positive
Sulfometuron methyl	☐	365	Unit	150	Unit	50	100	15	Positive
Imazapyr	☐	262	Unit	217	Unit	50	120	20	Positive
Imazapyr	☐	262	Unit	202	Unit	50	120	25	Positive
Hexazinone	☐	253	Unit	171	Unit	50	120	15	Positive
Hexazinone	☐	253	Unit	71	Unit	50	120	35	Positive
Picloram	☐	243	Unit	197	Unit	50	80	20	Positive
Picloram	☐	241	Unit	195	Unit	50	80	20	Positive
Atrazine	☐	216	Unit	174	Unit	50	140	15	Positive
Atrazine	☐	216	Unit	104	Unit	50	140	30	Positive
Aminopyralid	☐	209	Unit	163	Unit	50	100	20	Positive
Aminopyralid	☐	207	Unit	161	Unit	50	100	20	Positive
Simazine-d5	☐	207	Unit	129	Unit	50	120	20	Positive
Clopyralid	☐	192	Unit	174	Unit	50	80	10	Positive
Clopyralid	☐	192	Unit	146	Unit	50	80	20	Positive

Source Parameters

Parameter	Value
Gas Temp (°C)	300
Gas Flow (l/min)	11
Nebulizer (psi)	35
Capillary (V)	4000

Acquisition Method Report

Chromatograms

Chrom Type	Label	Offset	Y-Range
TIC	TIC	0	10000000

Instrument Curves

Actual

#N/A

Wellplate Sampler

Name h-ALS **Model** G1367B
Ordinal # 1 **Options**

Stop Time (min) As Pump **Post Time (min)** Off

Injection Type	Standard Injection	**Injection Volume**	1
Overlap Time	Disable Overlapped Injection	**Draw Position**	0
Draw Position Detection	0	**Draw Speed**	200
Eject Speed	200	**Flush Out Factor**	5
Automatic Delay Volume Reduction	No	**Equilibration Time**	0
Wash Vessel	N/A	**Wash Location**	N/A
Wash Time	N/A	**Wash Cycles**	N/A
Ready Temp. Range		**Temp.**	

Contact 1 0
Contact 2 0
Contact 3 0
Contact 4 0

Injector Program
Signals Selected
Contacts Time Table

Binary Pump

Name Bin Pump **Model** G1312A
Ordinal # 1 **Options** SSV

Stop Time (min) 11 **Post Time (min)** 7

Flow (ml/min) 0.4 **Pressure Min (bar)** 0

Pressure Max (bar) 400 **Max Flow Gradient (ml/min)** 100

Solvent A	water + 0.05% formic acid	**Solvent B**	methanol + 0.05% formic acid
Solvent Ratio A	45	**Solvent Ratio B**	55
Compress. A (*10-6/bar)	50	**Compress. B (*10-6/bar)**	115
Stroke A	Auto	**Stroke B**	Auto

Contact 1 0
Contact 2 0
Contact 3 0
Contact 4 0

Acquisition Method Report

Pump Time Table

Time	Flow	Pressure	Solv Ratio B
0	0.4	400	55
1	0.4	400	55
15	0.4	400	100

Signals Selected
Contacts Time Table

Thermostated Column Compartment

Name Column **Model** G1316A
Ordinal # 1 **Options** CSV

Stop Time (min) As Pump **Post Time (min)** Off

Left Temp. 25 **Right Temp.** Same as left
Left Ready When Temp Within Set Point +/- 0.8 **Right Ready** When Temp Within Set Point +/- 0.8
Valve Position 0

Contact 1 0
Contact 2 0
Contact 3 0
Contact 4 0

Temperature Time Table
Signals Selected

Description
Temperature of left heat exchanger
Contacts Time Table

Diode Array Detector

Name DAD **Model** G1315B
Ordinal # 1 **Options**

Stop Time (min) As Pump **Post Time (min)** Off **Delay Time (min)** 0

Store Spectra None **Threshold** 10
Pre-Run Balance Yes **Post-Run Balance** No
Balance Mode 1 **Margin for -ve absorbance** 100
Peak Width2 GT 0.1 min (2.0s) **Slit** 4

Output Zero Offset1 (%) 5 **Output Zero Offset2 (%)** 5
Ouput Attenuation1 1000 **Output Attenuation2** 1000
UV Lamp No **Vis Lamp** No
From 190 **To** 400
Step 2
Contact 1 0
Contact 2 0

Acquisition Method Report

Contact 3 0
Contact 4 0

Signal Time Table
Signals Selected
Contacts Time Table

Wavelength Settings

Channel	Sample WL	Sample BW	Ref. WL	Ref. BW	Ref. On
A	250	4	0	0	Off
B	254	16	0	0	Off
C	210	8	0	0	Off
D	230	16	0	0	Off
E	280	16	0	0	Off
F	280	16	360	100	Off
G	280	16	360	100	Off
H	280	16	360	100	Off

Acquisition Method Report

Acquisition Method Info

Method Name O031513A NEG MRM AIR HRB.m
Method Path D:\MassHunter\methods\O031513A NEG MRM AIR HRB.m
Method Description

Device List
h-ALS
Bin Pump
Column
DAD
MS QQQ

QQQ Mass Spectrometer

Ion Source ESI
Tune File atunes.tune.xml
Stop Mode No Limit/As Pump
Stop Time 3.5
Time Filter On
Time Filter Width 0.07

Time Segments

Time Seg #	Time	Scan Type	Ion Mode	Div Valve	Delta EMV	Store
1	0	MRM	ESI	To MS	400	☑

Time Segment 1

Scan Segments

Compound Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Dwell	Frag (V)	CE (V)	Polarity
Triclopyr	☐	256	Unit	198	Unit	100	80	5	Negative
Triclopyr	☐	254	Unit	196	Unit	100	80	5	Negative
Picloram	☐	241	Unit	197	Unit	100	80	5	Negative
Picloram	☐	239	Unit	195	Unit	100	80	5	Negative
Dicamba-d3	☐	222	Unit	178	Unit	100	50	0	Negative
2,4-D	☐	221	Unit	163	Unit	100	80	5	Negative
2,4-D	☐	219	Unit	161	Unit	100	80	5	Negative
Aminopyralid	☐	207	Unit	163	Unit	100	80	5	Negative
Aminopyralid	☐	205	Unit	161	Unit	100	80	5	Negative
Clopyralid	☐	192	Unit	148	Unit	100	80	5	Negative
Clopyralid	☐	190	Unit	146	Unit	100	80	5	Negative

Source Parameters

Parameter	Value
Gas Temp (°C)	300
Gas Flow (l/min)	11
Nebulizer (psi)	35
Capillary (V)	4000

Chromatograms

Chrom Type	Label	Offset	Y-Range
TIC	TIC	0	10000000

Instrument Curves
Actual
#N/A

Wellplate Sampler

Acquisition Method Report

Name h-ALS **Model** G1367B
Ordinal # 1 **Options**

Stop Time (min) As Pump **Post Time (min)** Off

Injection Type	Standard Injection	**Injection Volume**	1
Overlap Time	Disable Overlapped Injection	**Draw Position**	0
Draw Position Detection	0	**Draw Speed**	200
Eject Speed	200	**Flush Out Factor**	5
Automatic Delay Volume Reduction	No	**Equilibration Time**	0
Wash Vessel	N/A	**Wash Location**	N/A
Wash Time	N/A	**Wash Cycles**	N/A
Ready Temp. Range		**Temp.**	

Contact 1 0
Contact 2 0
Contact 3 0
Contact 4 0

Injector Program
Signals Selected
Contacts Time Table

Binary Pump

Name Bin Pump **Model** G1312A
Ordinal # 1 **Options** SSV

Stop Time (min) 11 **Post Time (min)** 7

Flow (ml/min) 0.4 **Pressure Min (bar)** 0

Pressure Max (bar) 400 **Max Flow Gradient (ml/min)** 100

Solvent A	water + 0.05% formic acid	**Solvent B**	methanol + 0.05% formic acid
Solvent Ratio A	45	**Solvent Ratio B**	55
Compress. A (*10-6/bar)	50	**Compress. B (*10-6/bar)**	115
Stroke A	Auto	**Stroke B**	Auto

Contact 1 0
Contact 2 0
Contact 3 0
Contact 4 0

Pump Time Table

Time	Flow	Pressure	Solv Ratio B
0	0.4	400	55
1	0.4	400	55
15	0.4	400	100

Signals Selected
Contacts Time Table

Acquisition Method Report

Thermostated Column Compartment

Name Column **Model** G1316A
Ordinal # 1 **Options** CSV

Stop Time (min) As Pump **Post Time (min)** Off

Left Temp. 25 **Right Temp.** Same as left
Left Ready When Temp Within Set Point +/- 0.8 **Right Ready** When Temp Within Set Point +/- 0.8
Valve Position 0

Contact 1 0
Contact 2 0
Contact 3 0
Contact 4 0

Temperature Time Table
Signals Selected

Description
Temperature of left heat exchanger
Contacts Time Table

Diode Array Detector

Name DAD **Model** G1315B
Ordinal # 1 **Options**

Stop Time (min) As Pump **Post Time (min)** Off **Delay Time (min)** 0

Store Spectra	None	**Threshold**	10
Pre-Run Balance	Yes	**Post-Run Balance**	No
Balance Mode	1	**Margin for -ve absorbance**	100
Peak Width2	GT 0.1 min (2.0s)	**Slit**	4
Output Zero Offset1 (%)	5	**Output Zero Offset2 (%)**	5
Ouput Attenuation1	1000	**Output Attenuation2**	1000
UV Lamp	No	**Vis Lamp**	No
From	190	**To**	400
Step	2		

Contact 1 0
Contact 2 0
Contact 3 0
Contact 4 0

Signal Time Table
Signals Selected
Contacts Time Table

Wavelength Settings

Acquisition Method Report

Channel	Sample WL	Sample BW	Ref. WL	Ref. BW	Ref. On
A	250	4	0	0	Off
B	254	16	0	0	Off
C	210	8	0	0	Off
D	230	16	0	0	Off
E	280	16	0	0	Off
F	280	16	360	100	Off
G	280	16	360	100	Off
H	280	16	360	100	Off

APPENDIX B

Chamber Diffusion Calculations

Calculation of diffusivities of herbicides in air and comparison to expected advective flow rate in chamber during passive sampler deployment study
STREAMS II Task Order 15 TD 2-01, Herbicide passive sampler method development

Ian MacGregor Battelle 12/17/2013 100034455-TD2F01QAPP

See Schwarzenbach, Gschwend and Imboden, "Environmental Organic Chemistry" Wiley, 1993, Chapter 9.

T	298	K
P	1	atm
m_{air}	28.97	g mol^{-1}
$Vbar_{air}$	20.1	cm^3 mol^{-1}
$v_{advection}$	0.14	cm s^{-1}
Distance between PUF discs	10	cm

Volume contribution, cm^3 mol^{-1}						
C	H	O	N	Cl	S	rings
16.50	2.00	5.50	5.70	19.50	17.00	-20.20

				Number of moieties											
Herbicide	**MW**	**CAS**	**formula**	**C**	**H**	**O**	**N**	**Cl**	**S**	**rings**	**Molar vol, cm^3 mol^{-1}**	**Da, cm^2 s^{-1}**	**Diffusion t, s**	**$V_{diff+eff}$ cm s^{-1}**	**v_{adv}/v_{diff}**
Atrazine	215.683	1912-24-9	$C_8H_{14}ClN_5$	8	14	0	5	1	0	1	187.8	0.0593	843	0.012	**12**
2,4D	221.037	94-75-7	$C_8H_6Cl_2O_3$	8	6	3	0	2	0	1	179.3	0.0605	827	0.012	**12**
Hexazinone	252.3128	51235-04-2	$C_{12}H_{20}N_4O_2$	12	20	2	4	0	0	1	251.6	0.0514	973	0.010	**14**
Imazapyr															
Sulfometuron Methyl															
Metsulfuron Methyl															
Clopyralid															
Triclopyr	256.471	55335-06-3	$C_7H_4Cl_3NO_3$	7	4	3	1	3	0	1	184.0	0.0593	843	0.012	**12**
Aminopyralid															
Picloram	241.459	1918-02-1	$C_6H_3Cl_3N_2O_2$	6	3	2	2	3	0	1	165.7	0.0623	802	0.012	**11**
check of calc for benzene															
78.1118		71-43-2	C6H6	6	6	0	0	0	0	1	90.8	0.0894	560	0.018	**8**