Quality Assurance Project Plan

for the

Multi-Laboratory Verification of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry

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Approvals:

ORD Technical Research Lead:	/s/ Brian Schumacher, Branch Chief, ESD/ECB	2-12-13 Date
ESD Division Director:	/s/ Randall Gentry, Division Director, ESD	2/13/13 Date
ESD Quality Assurance Manager:	/s/ George Brilis, QAM, ESD	2/13/2013 Date

Concurrences:

EPA/ORD/NERL/MCEARD ESD Quality Assurance Manager:	/s/ Margaret Vazquez, MCEARD	2-14-13 Date
EPA/Region 3 ESD Quality Assurance Manager:	/s/ Jill Bilyeu, Region 3	03-05-13 Date
EPA/Region 5 ESD Quality Assurance Manager:	/s/ Angela Ockrassa, Region 5	02/22/2013 Date

NOTICE:
The non-EPA participants in this study were assembled in an *ad hoc* manner. All non-EPA organizations in this study verbally agreed to perform these analyses with the affirmation that there is no expectation of extrinsic compensation for expenditure of the resources used for this study, and that there is no pre-conceived intent to immediately use participation in this study as a marketing tool ("immediately" means - "within 30 days of submission of the "study" results). Further, all non-EPA organizations in this study indicated that their primary intent for participation is to enhance HF-related chemical analyses for the general scientific community.

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EPA
Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources
Required Front Matter for Quality Assurance Project Plans

Disclaimer:
EPA does not consider this internal planning document an official Agency dissemination of information under the Agency's Information Quality Guidelines because it is not being used to formulate or support a regulation or guidance, nor does it represent a final Agency decision or position. This planning document describes the overall quality assurance approach that will be used during the research study. Mention of trade names or commercial products in this planning document does not constitute endorsement or recommendation for use. Non-Federal participants understand and agree that there will be no extrinsic compensation for the resources expended during this study.

The EPA Quality System and the HF Research Study
EPA requires that all data collected for the characterization of environmental processes and conditions are of the appropriate type and quality for their intended use. This is accomplished through an Agency-wide quality system for environmental data. Components of the EPA quality system can be found at http://www.epa.gov/quality. EPA policy is based on the national consensus standard ANSI/ASQ E4-2004 *Quality Systems for Environmental Data and Technology Programs: Requirements with Guidance for Use*. This standard recommends a tiered approach that includes the development and use of Quality Management Plans (QMPs). The organizational units in EPA that generate and/or use environmental data are required to have Agency-approved QMPs. Programmatic QMPs are also written when program managers and their QA staff decide a program is of sufficient complexity to benefit from a QMP, as was done for the study of the potential impacts of hydraulic fracturing (HF) on drinking water resources. The HF QMP describes the program's organizational structure, defines and assigns quality assurance (QA) and quality control (QC) responsibilities, and describes the processes and procedures used to plan, implement and assess the effectiveness of the quality system. The HF QMP is then supported by project-specific QA project plans (QAPPs). The QAPPs provide the technical details and associated QA/QC procedures for the research projects that address questions posed by EPA about the HF water cycle and as described in the *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (EPA/600/R-11/122/November 2011; www.epa.gov/hydraulicfracturing). The results of the research projects will provide the foundation for EPA's 2014 study report. This EPA Quality Level I QAPP provides information concerning all portions of the HF water cycle as found in Figure 1 of the HF QMP and as described in HF Study Plan.

LIST OF ABBREVIATIONS

ADQ	Audit of Data Quality
CAS	Chemical Abstracts Service
CCV	Continuing Calibration Verification
COC	Chain-of-Custody
ECB	Environmental Chemistry Branch
EPA	Environmental Protection Agency
ESD	Environmental Sciences Division, Las Vegas, NV
DI	Deionized
DQI	Data Quality Indicator
DQO	Data Quality Objective
GWERD	Ground Water and Ecosystem Restoration Division, Ada, OK
HF	Hydraulic Fracturing
LC	Liquid Chromatography
LCS	Laboratory Control Sample
MCEARD	Microbiological & Chemical Exposure Assessment Research Division, Cincinnati, OH
MDL	Method Detection Limit
MS	Mass Spectrometry
NERL	National Exposure Research Laboratory
NRMRL	National Risk Management Research Laboratory
ORD	Office of Research and Development
PARCC	Precision, Accuracy, Representativeness, Completeness, and Comparability
%R	Percent Recovery
PI	Principal Investigator
QA	Quality Assurance
QAM	Quality Assurance Manager
QAR	Quality Assurance Representative
QATS	Quality Assurance Tracking System
QC	Quality Control
QCCS	Quality Control Check Sample
QAP	Quality Assurance Professional
QAPP	Quality Assurance Project Plan
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SOP	Standard Operating Procedure
TSA	Technical System Audit

SECTION A. PROJECT MANAGEMENT

A3 Distribution List

EPA, ORD, NERL, ESD

Patrick DeArmond	(702) 798-2102
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Brian Schumacher	(702) 798-2242
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EPA, ORD, NERL, IO

Michelle Henderson	(513) 569-7353

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Angela Ockrassa	(312) 353-3521

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Jill Bilyeu	(410) 305-2638

EPA, ORD, NRMRL, GWERD

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Stephen Watkins	(202) 564-3744

EPA, ORD, NERL, MCEARD

Jody Shoemaker	(513) 569-7298
Margie Vazquez	(513) 569-7182

Eurofins Lancaster Laboratories

Charles Neslund	(717) 556-7231
Dorothy Love	(717) 556-7327

TestAmerica, Incorporated

Karen Kuoppala	(303) 736-0100
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Teresa Williams	(303) 736-0121

Metropolitan Water District of Southern California

Rich Yates	(909) 392-5398

Philadelphia Water Department

Earl Peterkin	(215) 685-1439
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A4 Project/Task Organization

The *Multi-laboratory Verification of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry* study is a special project designed to determine the efficacy of a method developed by US EPA Region 3 for the determination of glycols in drinking waters derived from drinking water wells. This project is associated with the hydraulic fracturing study being conducted by the U.S. EPA. The special project will be managed and implemented by the Environmental Sciences Division (ESD) in Las Vegas, NV, of the EPA Office of Research and Development (ORD). Brian Schumacher is the Technical Research Lead. For the verification/validation of the method, a minimum of eight analytical laboratories will participate in the analyses of a series of samples. It is anticipated that the following EPA laboratories will be participating in this study:

1. National Exposure Research Laboratory (NERL), Environmental Sciences Division, Las Vegas, NV,

2. National Exposure Research Laboratory, Microbiological & Chemical Exposure Assessment Research Division (MCEARD), Cincinnati, OH,

3. Region 3 Environmental Science Center, Fort Meade, MD, and

4. Region 5 Chicago Regional Laboratory, Chicago, IL.

The verification study has been expanded to include non-EPA laboratories. The non-EPA laboratories represent two commercial environmental testing laboratories and two metropolitan water district laboratories. These laboratories, who are participating in this study *a gratis*, are:

1. Eurofins Lancaster Testing Laboratories, Lancaster, PA (commercial laboratory),

2. TestAmerica, Inc, Arvada, CO (commercial laboratory),

3. Philadelphia Water Department, Philadelphia, PA (water district laboratory), and

4. Metropolitan Water District of Southern California, La Verne, CA (water district laboratory).

Table 1 summarizes individual responsibilities for the special study activities. **Figure 1** illustrates the individual and organizational interactions of all involved parties.

A5 Problem Definition/Background

Hydraulic fracturing (HF) has become increasingly prevalent as a method of extracting energy resources from "unconventional" reservoirs, such as coalbeds, shales, and tight sands. One concern that has been identified associated with the hydraulic fracturing process is the potential for chemicals used during the hydraulic fracturing process to enter ground water aquifers that may be used as drinking water sources. Of concern for this special project are diethylene glycol (CAS #111-46-6), triethylene glycol (CAS #112-27-6), tetraethylene glycol (CAS #112-60-7), 2-butoxyethanol (CAS #111-76-2), and 2-methoxyethanol (CAS #109-86-4). In response to this concern, the US EPA Region 3 Environmental Science Center in Fort Meade, MD (to be referred to as Region 3) has developed a quick method for the determination and quantification of these compounds. This method needs to be verified to determine its efficacy in determining these compounds in laboratory and drinking water matrices.

Table 1. Main Study Activities and Responsible Organizations.

Study Activities	Responsible Party
Design, implementation, and management of the study	Brian Schumacher, ESD
Quality Assurance Project Plan (QAPP) Preparation	Lawrence Zintek, Region 5; Brian Schumacher, ESD
Drinking well water collection	Multiple sources
Water sample preparation and spiking	Lantis Osemwengie, ESD; Jade Morgan, ESD; Don Betowski, ESD
Method testing	Patrick DeArmond, ESD; Lawrence Zintek, Region 5; Jennifer Gundersen, Region 3; Jody Shoemaker, MCEARD; Charles Neslund, Eurofins Lancaster Laboratories; Charlie Carter, TestAmerica Inc.; Earl Peterkin, Philadelphia Water District; Rich Yates, Metropolitan Water District of Southern California
Data verification and data analysis; report development	Patrick DeArmond, ESD; Brian Schumacher, ESD; Maliha Nash, ESD
Data storage, management, and access	Patrick DeArmond, ESD
Ensure the quality assurance (QA) and quality control (QC) activities described in the QAPP are being implemented	George Brilis, ESD; Angela Ockrassa, Region 5; Margie Vazquez, MCEARD; Jill Bilyeu, Region 3; ; Dorothy Love, Eurofins Lancaster Laboratories; Teresa Williams, TestAmerica; Robert Eppinger, Philadelphia Water District
Data QA and QC review	Participating Laboratory's Quality Assurance Manager
QA oversight, problem resolution assistance, and tracking corrective action	Michelle Henderson, HF PQAM

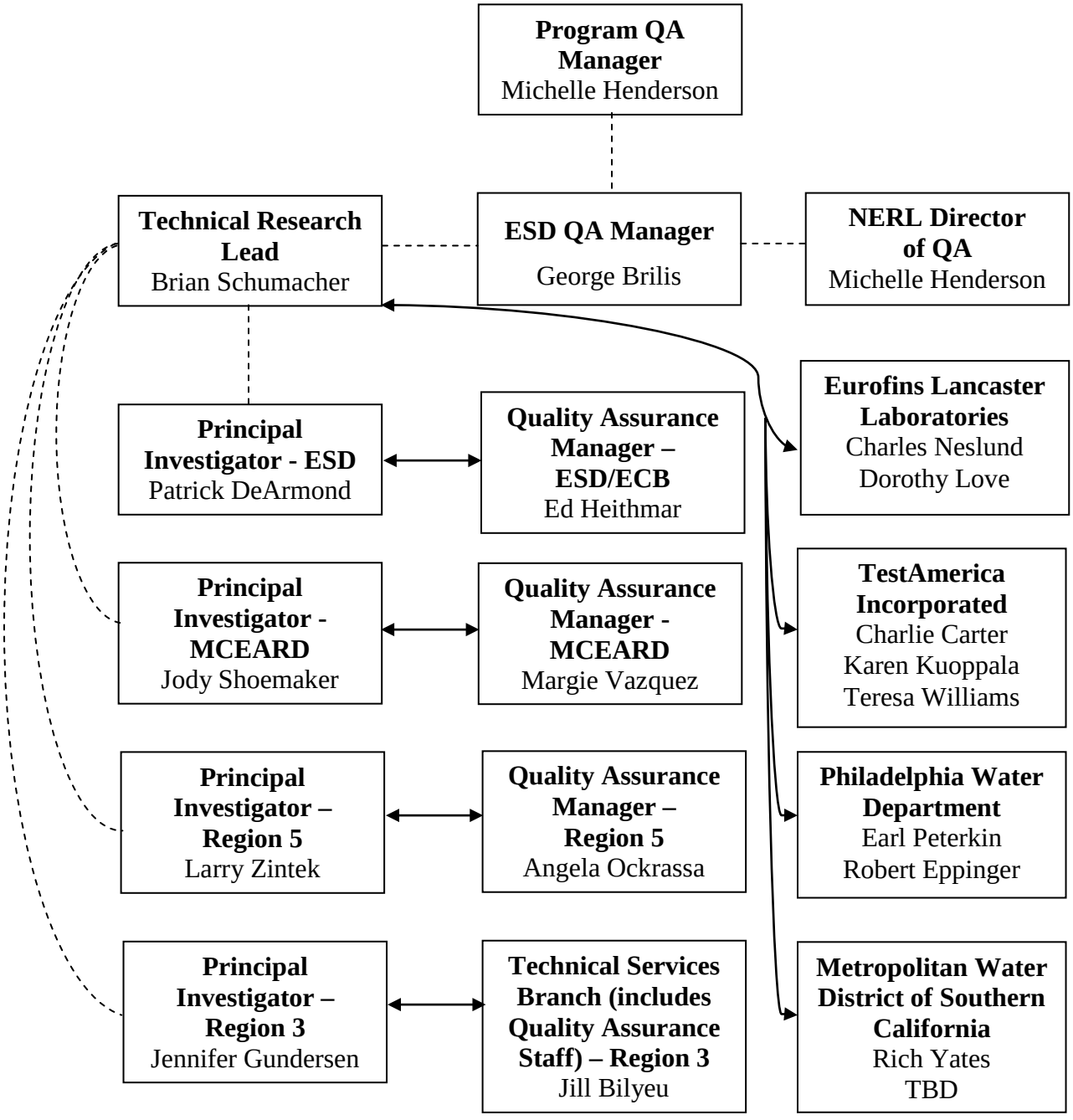

Figure 1. Organizational Flowchart for Glycol Method Study.

A6 Project/Task Description

The primary objective of this study is to verify the performance of the Region 3 draft Standard Operating Procedure (SOP) in multiple laboratories.

Verification for this study will be performed through the submission of multiple blind samples (spiked and unspiked) in multiple matrices (e.g., laboratory waters and drinking well waters) to each participating laboratory for analysis. The quality assurance/quality control (QA/QC) procedures for this project will follow the QA/QC procedures specified in this QAPP.

To ensure that these study objectives are met, all participating laboratories shall strictly adhere to the requirements that:

- Each laboratory will verify and optimize the liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) conditions in sections 10 and 11 of the Region 3 draft SOP on their instrumentation to meet Region 3 reporting limits or determine the reporting limits on their LC/MS/MS systems.
- Each laboratory must follow all analytical and quality control procedures in this QAPP.
- Any laboratory that wishes to deviate from the procedures in the Region 3 draft SOP or this QAPP shall obtain prior approval of the changes from the Technical Research Lead and document those approved changes in detail.
- All data produced are capable of being verified by an independent person reviewing the analytical data package.
- Each laboratory must have a verifiable QA program, equal to or exceeding EPA requirements, in place and operating throughout the study. This QA program will ensure that the data produced are of appropriate and documented quality. The laboratory's quality management plans shall be made available to the Technical Research Lead for review against requirements noted above, by the ESD QAM.

A7 Quality Objectives and Criteria for Measurement Data

The Data Quality Objective (DQO) for this study is that the results from four groups of samples should have their variance determined and the variance among the laboratories should agree to within 30% of the established known concentrations. If this criterion is met, then the method is considered to be robust, precise, and acceptable for normal use. If the variance falls between 30 and 50%, the root cause of the unexpected variance will be investigated, documented, and a possible re-analysis of that group of samples may be requested if a viable cause can be determined. If the variance exceeds 50%, the method will need further evaluation for systematic errors and method re-development may be undertaken.

Data quality indicators (DQIs) are typically assessed by evaluating the precision, accuracy, representativeness, comparability, and completeness (PARCC) parameters of all aspects of the data collection.

Precision is defined as the degree of mutual agreement among individual measurements and provides an estimate of random error. Precision for determination of response factors and of target analytes in the samples will be expressed as relative standard deviation (RSD) for replicates of three or more or as the relative percent difference (RPD) for duplicates.

Accuracy refers to correctness of the data and is the difference between the population mean of the determination and the true value or assumed true value. Bias is the systematic error inherent in the method or caused by an artifact in the measurement process.

Representativeness expresses the degree to which data accurately and precisely represent a measured characteristic of a condition of a population or a process. For the verification study, representativeness of the starting materials (i.e., water samples) will be ensured as only the ESD laboratory will prepare and send the samples and a known concentration standard to the participating laboratories for analysis.

Completeness may be defined as the amount of data collected during the measurement process that is valid relative to the total amount of collected data.

Comparability is the relative confidence that one data set can be compared to another. Comparability will be ensured by all the participating laboratories receiving the same samples (i.e., samples from the same source) and following the Region 3 draft SOP for the analysis of the samples.

The data quality indicators (DQIs) for precision, accuracy, and completeness for each major measurement parameter are summarized in **Table 2**.

A8 Special Training/Certification

To achieve the stated quality objective and indicators, only analysts trained and experienced in the use of liquid chromatography/tandem mass spectrometry will carry out measurements.

A9 Documents and Records

Laboratory activities must be documented according to the appropriate record keeping policy of the laboratory performing the analyses. These policies generally require the use of laboratory notebooks and the management of lab records, both paper and electronic, such that the data acquisition may continue even if a researcher or an analyst participating in the project leaves the project staff.

Electronic copies of this QAPP, SOPs, and any associated audit reports, will be kept on the shared EPA O: drive as per the HF Quality Management Plan[1]; in the NERL Quality Assurance Tracking System (QATS) database once finally approved and cleared.

The Technical Research Lead will be responsible for distribution of the current version of the QAPP, timely communications with all involved participants and will retain copies of all management reports, memoranda, and correspondence between project personnel identified in A4.

Note: A *document* provides guidance and/or direction for performing work, making decisions, or rendering judgments which affect the quality of the products or services that customers receive.

Note: A *record* on the other hand proves that some type of required quality system action took place. Typically a form gets filled in and becomes a record. The form is a document and after it is filled-in, it becomes a record.

Table 2. Data Quality Indicators for Measurement Data.

QC Check	Frequency	Completeness	Precision	Accuracy	Corrective Action
5-point initial calibration	Prior to sample analysis	100%	N/A	$R^2 \geq 0.99$	No samples will be run until calibration passes criteria.
Instrument blank	One at beginning of each 8-hr analytical day, one at beginning of each batch of samples[a], and one at end of analytical day	100%	N/A	< RL[b]	Inspect the system and reanalyze the blank. Samples must be bracketed by acceptable QC or they should be flagged as 'LB'.
Laboratory control sample[d]	One per batch of samples[a]	100%	RPD≤30%[c]	± 30% of known value	Check the system and reanalyze the standard. Re-prepare the standard if necessary. Recalibrate the instrument if the criteria cannot be met. Samples must be bracketed by acceptable QC or they will be flagged with the appropriate 'K' flag.
Laboratory fortified matrix (e.g., matrix spike)	One per batch of samples[a]	100%	RPD≤30%[c]	Recovery between 70 and 130% of spike concentration	Review data to determine whether matrix interference is present. If so, narrate interference and flag recovery. If no interference is evident, verify the instrument is functioning properly by running a lab blank. Reanalyze recollected sample to verify recovery. Samples must be bracketed by acceptable QC or they will be flagged with the appropriate 'K' flag.
Laboratory replicate	One per batch of samples[a]	100%	RSD≤30%[c]	N/A	Inspect the system, narrate discrepancy. Samples must be bracketed by acceptable QC or they will be flagged as 'J6'.
Quality control check standard[e]	One per batch of samples[a]	100%	RSD≤25%[c]	± 20% of known value	Reanalyze the sample. Samples must be bracketed by acceptable QC or they will be flagged with the appropriate 'J' or 'K' flag.
Continuing calibration verification (CCV)	One at beginning of each 8-hr analytical day, one at beginning of each batch of samples[a], and one at end of analytical day	100%	RSD≤30%[c]	+/- 30% of known value	Inspect system and perform maintenance as needed. If system still fails CCV, perform a new 5-point calibration curve. Samples must be bracketed by acceptable QC or they will be flagged with the appropriate 'K' flag.
Method detection limit	Each chemical	100%	TBD for each HF chemical	TBD for each HF chemical	TBD for each HF chemical

[a]Batch of samples not to exceed 20 samples.
[b]RL=reporting limit, 5 ppb.
[c]Precision among replicates if more than 1 batch of samples are analyzed. RSD is applicable if more than 2 replicates are analyzed. Laboratory replicates shall be performed in at least triplicate.
[d]The laboratory control sample will be an approximate mid-calibration concentration sample prepared by the participating laboratory using their current primary standard lot.
[e]The quality control check standard (QCCS) will be prepared by each laboratory. For this verification study, the QCCS will be used to check the comparability of the purchased analytical standards among the laboratories. The laboratories shall provide information on the source of the QCCS and its nominal concentration.

Hardcopy Records - Hardcopy records will be maintained in accordance with each organization's record management policy. These records include, but are not limited to, recorded information such as the standard and sample preparation, blanks, calibration standards, and QC. Records will be retained in a laboratory notebook that is kept by the researchers. Separate, new hardbound laboratory notebooks specifically dedicated to this study are strongly encouraged. The laboratory notebook will contain a record of all sample analysis preparation activities and any other data that may be used to interpret results. All samples will be recorded in the laboratory notebook by a unique sample ID. The date of analysis will be recorded in a laboratory notebook. The location of electronic data generated from analysis of samples will also be recorded in the laboratory notebook, similar to an index, but expressed as a data management path. For example: EPA Computer Number; Hard Drive / Folder Name (Program name) / Subfolder Name (Project name) / Item Folder Name / File name with extension. Each participating laboratory QA Representative (QAR), or documented delegate, shall perform a documented review of laboratory and electronic recordkeeping. For example, after reviewing a laboratory notebook, the QAR shall initial and date that the review has been performed.

Electronic Records created or converted from hardcopies and/or generated by electronic devices, shall be maintained in a manner that maximizes the confidentiality, accessibility, and integrity of the data. All electronic data and notes shall be indexed and cross-referenced in a hardcopy notebook to record data and notation location and facilitate retrieval. The use of Project Titles shall be used to maintain an index of electronic data and those who contribute shall be "Data Stewards." Data may be transferred to electronic spreadsheets for analysis and presentation. It is strongly recommended that a new e-folder be created for this study.

Research Record Retention: The laboratory notebook and records will be retained in the laboratory (or office area) where these operations are performed until the conclusion of the study. At the end of the research study, the research records shall be archived according to EPA Records Schedule 501 *Applied and Directed Scientific Research*.

Records and documents that will be produced in conjunction with this project include:

- Raw data,
- Laboratory notebooks,
- Progress reports,
- Documentation of audits,
- Project interim report,
- Project final report,
- Standard operating procedures, and
- E-mails.

Disposition
For EPA laboratories, record-keeping will be permanent according to EPA Records Schedule 501.

Nonelectronic project files

- Includes documentation related to the formulation and approval of the research plan, the selection of the research methodology, quality assurance project plans, raw data, laboratory notebooks, project- or study-related correspondence, or other data collection media, copies of interim reports showing data tabulation results and interpretations, copies of the final reports, peer reviews, and quality assurance assessments.
    - **Permanent**
    - Close inactive records upon completion of project.
    - Transfer to the National Archives 20 years after file closure.

Electronic project files

- Includes documentation related to the formulation and approval of the research plan, the selection of the research methodology, quality assurance project plans, raw data, laboratory notebooks, project- or study-related correspondence, or other data collection media, copies of interim reports showing data tabulation results and interpretations, copies of the final reports, peer reviews, and quality assurance assessments.
    - **Permanent**
    - Close inactive records upon completion of project.
    - Transfer to the National Archives 5 years after file closure.

Project work papers and administrative correspondence

- Includes completed questionnaires or other documents used for data collection, drafts or copies of interim progress reports, and other work papers created in the course of the study.
    - **Disposable**
    - Close inactive records upon completion of the project.
    - Destroy 3 years after file closure.

Maintenance and calibration and inspection of equipment

- **Disposable**
- Close inactive records upon completion of the project.
- Destroy 5 years after file closure.

For non-EPA laboratories, record keeping will follow their laboratories record keeping policies which should mirror those policies described above. If different from the EPA recordkeeping policies and procedures, the non-EPA organization must communicate in writing, a copy of their hard and electronic recordkeeping policy(ies)

Regardless, each participating laboratory must keep a copy of their hard and electronic "Study-related" information, until otherwise instructed by EPA. If an participating laboratory does not have a hard and electronic recordkeeping policy(ies) – the EPA Technical Research Lead should be notified *immediately*.

SECTION B. MEASUREMENT

B1 Sampling Design

For the verification study, each participant laboratory will be sent a copy of the Region 3 draft SOP as Appendix A of this QAPP. The conditions in the SOP will be used as a starting point in order to optimize each instrument for the list of analytes on the participant laboratory's LC/MS/MS systems. If the reporting limits can be met in the participant laboratories, the laboratory will perform precision and accuracy tests in reagent water at the reporting limit, lowest level of calibration curve, and at the midpoint of the calibration curve. If the laboratory cannot meet the Region 3 reporting limits, then the reporting limit may be raised and calibration curve adjusted after consulting with the Technical Research Lead. This discrepancy may be caused by the different sensitivities of the LC/MS/MS systems used. All LC and MS conditions will be documented by the individual laboratories. All method parameters and recovery data for the target analytes will be sent to the Technical Research Lead in spreadsheet format.

At least seven replicates at each level shall be used in order to determine precision and accuracy and an MDL for each analyte in each laboratory (40CFR 136 Part B). The participating laboratory shall prepare the samples in deionized laboratory water using the water purification system is available at the laboratory and prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit.

For the verification study, four sets of seven to nine "replicates" of various water matrices will be prepared by ESD for a total of 28-36 blind samples. Samples will be prepared by an independent scientist (i.e., one not involved with the glycol method verification/validation study) at ESD. ESD shall not divulge the concentration to the participant laboratories.

B2 Sampling Methods

Bulk water samples from drinking water wells will be acquired from multiple sources around the country in areas where active shale oil and gas operations are occurring. Collection of 4 gallons at each site is anticipated to be sufficient for this project. The bulk samples will be collected in clean, capped amber glass containers and labeled with the source and date of sampling. Bulk samples will be stored at 4° C ± 2° C.

Deionized (DI) water at ESD will be generated on site using a Barnstead NANOpure system. The cartridges for the system are changed when the resistivity is ≤ 18.0 MΩ·cm.

Information to be provided with the bulk sample shall include:

- A unique identification number
- Sample location (longitude, latitude, altitude [where applicable])
- Brief description of sample source
- Date and time of acquisition
- Volume or weight of sample (approximations acceptable)
- Filtered or unfiltered sample with the micron unit of the filter provided
- Comments describing any unusual aspects of the sample or its acquisition.

B3 Sample Handling and Custody

All sample shipments will use the Chain-of-Custody (COC) form shown in Appendix B. Upon receipt of the samples, the participating analytical laboratory shall complete the COC form, scan, and send a copy of the completed form to the Technical Research Lead.

Bulk drinking well water samples should be shipped on ice via overnight courier for arrival the following morning to ESD.

Blind samples prepared and submitted during the verification study shall follow chain-of-custody procedures with documentation describing:

(1) The project name,
(2) Sample receipt date and time,
(3) Condition of samples received,
(4) Sample numbers received,
(5) Signatures of individual(s) receiving the samples, and
(6) If applicable, the air bill or other shipping number.

It is anticipated that the blind samples will be prepared and shipped on ice to the participating analytical laboratories on February 19, 2013. Samples should be received at the participating analytical laboratories on February 20, 2013. Immediately after sample shipment (i.e., as soon as samples are in the custody of the carrier) of the blind samples, ESD will inform the participating laboratories of the shipment and provide information on the shipment, including sample numbers, numbers of coolers, and courier and bill number. The participating laboratories will confirm that samples have arrived in good condition and as scheduled by returning the signed COC forms with notes indicating sample receipt and condition (preferably via email of the scanned COC forms). If necessary, ESD will implement tracking activities to locate any lost shipment(s) or resend samples due to loss in shipment. Once the samples are received, the participating laboratories shall analyze the samples as soon as possible and at a minimum, within a time frame to meet the 14 day holding time for the glycol samples. The number of days between blind sample receipt and analysis shall be recorded and provided to the Technical Research Lead (TRL).

Proper documentation will be maintained and analyst procedures documented. Samples will be properly labeled and stored in refrigerators maintained at 4° C ± 2° C. The temperatures of the refrigerators and/or freezers must be checked, and the temperatures recorded at a minimum of every working day until completion of this study. If a trend indicates that the cooling unit is unable to maintain desired temperature ranges, the problem should be rectified and if temperatures exceed 6° C, the EPA TRL must be notified.

Because glycol ethers are ubiquitous in the environment, including laboratories, the participating analytical laboratories must judiciously guard against sample contamination. Glycol and glycol ether free glassware and cleaning processes shall be used in all applications by all laboratories during this study.

B4 Analytical Methods

The analytical method to be used for this study will be provided as a draft SOP from U.S. EPA Region 3 (Appendix A).

B5 Quality Assurance/Quality Control

Quality assurance/quality control measures associated with this verification study will include the examination of blanks, various fortified matrix analysis, replicates, and method detection determinations. For this verification study, the QA/QC criteria presented in this QAPP shall be followed. Should there be a difference between the Region 3 draft SOP and the criteria in Table 2, the criteria in Table 2 shall be followed. Table 2 provides details of the QC samples to be performed, the minimum required frequency of analysis, the anticipated precision and accuracy numbers, and corrective actions to be taken should an acceptance criterion not be met. Copies of Certificates of Analysis for each standard used by the laboratory will be included as an attachment in the data package.

Should there be a difference between the Region 3 draft SOP and the criteria in Table 2, the criteria in Table 2 shall be followed. Table 2 provides details of the QC samples to be performed, the minimum required frequency of analysis, the anticipated precision and accuracy numbers, and corrective actions to be taken should an acceptance criterion not be met.

There are no proper surrogate standards available for this study.

There are no internal standards for this study.

Mass spectrometer tuning shall be performed before analysis of the blind samples and meet the acceptance criteria according to the instrument manufacturer's specifications. Information on the mass spectrometer tuning material shall be provided to the Technical Research Lead. Documentation of tuning will be included in each data package.

Instrument calibration requirements are specified in section B7.

Instrument blanks shall be prepared in laboratory DI water.

The use of secondary ions for multiple reaction monitoring for are not necessary for this study.

The laboratory control sample (LCS) is a mid-calibration level sample prepared by the participating analytical laboratory in laboratory DI water. The analytical laboratory shall use the stock standard provided by ESD to perform this spiking activity.

A laboratory fortified matrix (i.e., matrix spike) sample shall be prepared by the analytical laboratory by spiking 50 ppb into a separate aliquot of the blind sample and examining the recovery of the matrix spike. The analytical laboratory shall use the secondary source standard to perform this spiking activity.

A laboratory replicate shall be performed at each participating analytical laboratory by selecting a blind sample and analyzing it a minimum of three times (i.e., triplicate analysis).

A quality control check standard (QCCS) will be prepared by each laboratory. For this verification study, the QCCS will be used to check the comparability of the purchased analytical standards among the laboratories. The laboratories shall provide information on the source of the QCCS and its nominal concentration.

The continuing calibration verification (CCV) sample is one of the standards prepared for instrument calibration that is run to check that the initial calibration curve is stable.

An estimation of the method detection limit (MDL) for individual analytes identified from the glycol list will be made according to procedures as outlined in 40CFR 136 Part B.

The equations to be used for the calculation of the PARCC parameters and MDL are given in Section D3 of this QAPP.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

Preventative maintenance will be scheduled as needed and may be triggered by criteria in Table 2 (section A7). An instrument maintenance log book shall be maintained in the laboratory with each instrument.

Daily monitoring of instrument performance may include: source cleaning, chromatography troubleshooting, detector troubleshooting, or electronic troubleshooting. Daily monitoring of all critical instrumental parameters is required.

All appropriate pages relating to this study will be scanned and included with the data package.

B7 Instrument Calibration and Frequency

Various mass spectrometers will be used for obtaining mass spectra of the glycols. All of the mass spectrometers have distinctly different analyzers and operating conditions. Initial conditions will be based on the conditions specified in the draft SOP submitted by Region 3.

A 1000 ppb stock standard will be provided with the blind samples. The participating laboratories shall use this stock standard for the calibration standards.

Initial calibration shall be performed prior to any analysis of the blind samples. Initial calibration will be considered successful when a r^2 value is ≥ 0.99 for both linear and quadratic line fits. The calibration range should be between 5 and 300 ppb.

B9 Non-Direct Measurements

Not applicable.

B10 Data Management

Data will be managed according to participating laboratories' data management policies. For EPA laboratories, the data management policies are specified in the HF Quality Management Plan and laboratory quality management plans. For example, ESD will follow the NERL QMP, Section 8 and Appendix 6[1]. A daily laboratory notebook will be maintained to document all experiments carried out, principal results, data examples, sample identification, masses, standards concentrations, spikes, sample calculations, and volumes. Estimates of uncertainty should also be included. Because data is acquired under computer control, a hard copy and a disk copy will be maintained separate from the notebook due to the volume of data generated. Electronic data and information will be cross-indexed in the hardcopy notebook(s).

For non-EPA laboratories, record keeping will follow their laboratories record keeping policies, which should mirror those policies described in this QAPP. If different from the EPA record keeping policies, the technical lead and the lead QAM for this project should be notified in writing.

SECTION C. ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

EPA laboratories will undergo a Technical Systems Audit (TSA) during this verification study. The findings of the TSA will be reported to the Research Technical Lead, NERL Director of Quality Assurance, and Program QA Manager (QAM). For non-EPA laboratories, EPA recommends that each laboratory's QA manager perform a TSA and provide the results to the Technical Research Lead. An example TSA checklist is provided in Appendix C.

EPA laboratories will undergo a Technical Systems Audit (TSA) during this verification study. The findings of the TSA will be reported to the Research Technical Lead, NERL Director of Quality Assurance, and Program QA Manager (QAM). For non-EPA laboratories, each laboratory's QA Professional (QAP), or documented delegate, should perform an audits and/or and assessments as described in the Appendices of this document. The results of each audit and/or and assessment must be provided to the EPA TRL and the EPA QA Manager.

After the laboratory verification study is completed, the critical target analytes, selected by the participating organization's QA manager or delegate, will undergo an Audit of Data Quality (ADQ). NRMRL has an SOP for this activity that will be used by the participating organization's QA Manager (Appendix D).

A schedule of the applicable audits is listed in **Table 3**.

If corrective actions are identified in any of these audits, the participating EPA laboratory's QA Manager must inform the Program QAM, NERL Director of Quality Assurance, and Research Technical Lead. If corrective actions are identified in any of these audits at a non-EPA laboratory, that laboratory's QA Manager must inform the Research Technical Lead.

Table 3. Schedule of Audits.

Type of Audit	Frequency	Details
Readiness Review	Conducted prior to the receipt of samples.	Performed by participating organization's QAP or documented delegate (Appendix C)
Surveillance audit	Conducted once during laboratory validation phase	Performed by participating organization's QAP or documented delegate (Appendix D)
ADQ	Conducted after method verification and validation once data has been collected.	Performed by participating organization's QAP or documented delegate (Appendix E)

NOTE: All Appendices (checklists) shall be provided to all participants in Word format to facilitate completion. In addition, directions for the completion of checklists shall be emailed to all participants – prior to the receipt of samples by the laboratories.

C2 Reports to Management

Audit reports will have a 5 business day turnaround time in order to have effective corrective action due to the short duration of this project. Audit reports will be provided by the Organization's QAM to the Program QA Manager, NERL Director of Quality Assurance, and Technical Research Lead for EPA laboratories or just to the Technical Research Lead for non-EPA laboratories.

SECTION D. DATA VALIDATION AND USABILITY

D1 Data Review, Verification, and Validation

This QAPP shall govern the operation of the project at all times. Each responsible party listed in Section A4 shall adhere to the procedural requirements of the QAPP and ensure that subordinate personnel do likewise.

> **NOTICE:** Participating laboratories that are NELAC accredited, and operate on a commercial basis, may deviate from the data package structure described herein and instead use their routine, in-house structure which is provided to clients that request a "complete data package". In addition, the boldface items in the list below are requested.

Complete data package includes all documentation needed to be able to re-construct analysis. The package shall be provided electronically on disk or as an email attachment, including copies of:

- Summary level data in spreadsheet format.
- **Note 1:** summary level data should be calculated results from both linear and quadratic calibration curves.
- **Note 1a:** Individual results (in µg/L), including results for all target compounds found in all blanks.
- **Note 1b**: Laboratories will not be allowed to average results or perform other data manipulations beyond those described in Region 3 draft SOP, such as peak smoothing or weighting of the calibration curves. When results are below the minimum level of quantitation but are detected, laboratories will be required to report the actual calculated result, regardless of its value.

- **Chain-of-custody forms,**
- **Completed Readiness Review Questionnaire,**
- **Standards preparation logs/worksheets,**
- Calibration data,
- **Certificates of analysis for standards (calibration, spike, second source, etc.),**
- **Completed Surveillance Audit Checklist,**
- Raw data (including notebook pages),
- QC data, including reporting and detection limits,
- Data qualifiers,
- Quantitation (reporting) and detection limits,
- Deviations from method,
- Final calculated data in spreadsheet form verified by the laboratory,
- A detailed description of any modifications to the procedures specified in Region 3 draft SOP,
- Interpretation of impact on data from deviations from QC or method requirements, and
- **Completed Audit of Data Quality Checklist**.

Participating Laboratories should use the following data qualifiers in reporting results, if needed:

Qualifier	Definition
LB	The analyte was found in an associated laboratory blank above the Quantitation Limit (QL) and the concentration found in the sample was less than 10 times the concentration found in the laboratory blank.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample. No sample result will be reported.
K1	Samples may be biased high because of high percent recoveries in some Laboratory Control Standards and/or Matrix Spike samples.
K2	Samples may be biased low because of low percent recoveries in some Laboratory Control Standards and/or Matrix Spike samples.
K3	Potential spectral (mass or emission) interference.
J1	Estimated value. Laboratory calibration criteria not met.
J2	Estimated value. Laboratory Quality Assurance/Quality Control (QA/QC) acceptance criteria not met.
J3	Estimated value. Sample bottles were received from the field damaged.
J5	Estimated value. Holding time exceeded.
J6	Estimated value. Laboratory duplicate was not within control limits.
J8	Estimated value. Screening data.
ND	Not Detected

For this verification study, the participating laboratories shall have until March 22, 2013 (tentatively) to submit the data package to the Technical Research Lead. A conference call will be conducted after this phase with the participating laboratories to report the results of the multi-laboratory verification process.

D2 Verification and Validation Methods

Generated data will be reviewed by someone other than the analyst to verify how they were recorded, transformed, analyzed, and qualified. The data will be validated by a senior analyst who is external to the data generator but is fully knowledgeable about the analysis to determine whether the quality of the specific data set is relevant to the end use and to confirm that it was generated in accord with this QAPP.

The data are deemed acceptable and useable if no issues are identified that compromise the anticipated use of the data and if DQOs are met.

D3 Calculation of Data Quality Indicators

The calculation of data quality indicators will be based on the following equations[2]:

Accuracy

Accuracy will be assessed through the analysis of quality control samples. The analytical accuracy will be expressed as the percent recovery (%R) of an analyte that has been added to the environmental sample at a known concentration before analysis and is calculated according to the following equation:

$$\%R = 100\% \times \frac{(S - U)}{C_{sa}}$$

Where:
%R = percent recovery
S = measured concentration in spiked aliquot
U = measured concentration in unspiked aliquot
C_{sa} = actual concentration of spike added.

The following formula should be used for measurements where a standard reference material is used:

$$\%R = 100\% \times \frac{C_m}{C_{srm}}$$

Where:
%R = percent recovery
C_m= measured concentration of standard reference material
C_{srm} = actual concentration of standard reference material.

Precision

Precision will be determined through the use of field duplicates, matrix spike/matrix spike duplicates and duplicate quality control samples. The Relative Percent Difference (RPD) between the two results will be calculated and used as an indication of the precision of the analyses performed. The following formula should be used to calculate precision:

$$RPD = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2)/2}$$

Where:
RPD = relative percent difference
C_1 = larger of the two observed values
C_2 = smaller of the two observed values.

If calculated from three or more replicates, use %RSD rather than RPD:

$$\%\text{RSD} = (s / \bar{y}) \times 100\%$$

Where:
%RSD = relative standard deviation
s = standard deviation
y = mean of replicate analyses.

Completeness

Completeness is defined as the measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Data completeness will be expressed as the percentage of valid data obtained from the measurement system. For data to be considered valid, it must meet all the acceptable criteria, including accuracy and precision, as well as any other criteria required by the prescribed analytical method. The following formula should be used to calculate completeness:

$$\%\text{C} = 100\% \times \frac{V}{n}$$

Where:
%C = percent completeness
V = number of measurements judged valid
n = total number of measurements necessary to achieve a specified statistical level of confidence in decision making.

Method Detection Limits

Defined as follows for all measurements (40CFR 136 Part B):

$$\text{MDL} = t_{(n\text{-}1,\ 1\text{-}\alpha=0.99)} \times S$$

Where:
MDL = method detection limit
$t_{(n\text{-}1,\ 1\text{-}\alpha=0.99)}$ = Student's t-value approximate to a 99 percent confidence level and a standard deviation estimate with $(n - 1)$ degrees of freedom
S = standard deviation of the replicate analyses.

REFERENCES

1. Quality Management Plan – Plan to Study the Potential impacts of Hydraulic Fracturing on Drinking Water Resources. December 2011.

2. Simes, G.F. 1991. Preparation Aids for the Development of Category I Quality Assurance Project Plans. EPA/600/8-91/003.

Appendix A

Region 3 Draft SOP

Glycol Analysis of Aqueous Samples by Direct Injection HPLC/MS/MS

Effective Date: March 2012

EPA Region 3
Office of Analytical Services and Quality Assurance
701 Mapes Road
Fort Meade, Maryland 20755

Approved by:

Jill Bilyeu
Quality Assurance Officer

Date

Prepared by: Jennifer L. Gundersen, Ph.D.
Chemist, Laboratory Branch

Reviewed by:
Peer-Reviewer, Laboratory Branch

Updates Table

Peer reviewer's initials indicate that changes meet the NELAC and regulatory requirements described in Section 9.4 in SOP R3-QA060

Responsible Person	Date	Description of Change	Peer Reviewer	Date
		New SOP		

1 Scope and Application

1.1 This Standard Operating Procedure (SOP) documents and provides a descriptive method to perform glycol analysis by HPLC/MS/MS on liquid matrices.

1.2 This SOP is based on EPA SW-846 Method 8321B, 8000C and ASTM D7731-11^{E1} and applies to the measurement of glycols listed in Table 1.

Table 1: Analyte List

Analyte	CAS #	MDL (aqueous, ug/l)	NQL (aqueous, ug/l)
Diethylene glycol	111-46-6	In prep	25
Triethylene glycol	112-27-6	In prep	25
Tetraethylene glycol	112-60-7	In prep	25
2-Butoxyethanol	111-76-2	In prep	5
2-Methoxyethanol	109-86-4	In prep	10

2 Summary of the Method

2.1 The method employs high performance liquid chromatography (HPLC) coupled with positive electrospray ionization (ESI+) tandem mass spectrometry (MS/MS) for the determination of a suite of glycols in aqueous matrices.

2.2 A sample aliquot is directly injected into the HPLC/MS/MS system without extraction or derivitization. Concentration of each identified analyte is performed through linear, external standard calibration.

2.3 Target compounds are identified by retention time and one or more MRM (Multiple Reaction Monitoring) transition.

3 Definitions

3.1 Refer to the ESC Quality Manual for applicable definitions

3.1.1 MRM: Multiple Reaction Monitoring is the application of selected reaction monitoring to multiple product ions from one or more precursor ions.

4 Interferences

4.1 Suspended solids in the sample can clog frits in the sample management system and on the column. If site history suggests, samples may be filtered prior to introduction to the

HPLC/MS/MS system.

4.2 Matrix interferences may be caused by contaminants in the sample.

4.3 All reusable glassware must be cleaned according to procedures for cleaning glassware used in organic compound analyses per R3QA-054 Glassware Preparation for Organic Analyses.

5 Safety

5.1 Before beginning any procedures, refer to the Chemical Hygiene Plan (CHP) in the OASQA Quality Assurance Manual for general safety precautions and guidelines.

5.2 All sample prep work should be conducted in a fume hood.

5.3 The toxicity or carcinogenicity of each reagent used in this method may not have been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

5.4 Material Safety Data Sheets (MSDS) must be maintained in the facility for all reagents used in the laboratory. This information must be made available to all personnel prior to the performance of this SOP and upon staff request. The MSDS (hard copies) are currently located in the library as well as electronically on CD-ROM and online.

5.5 All applicable safety and compliance guidelines set forth by the EPA and by federal, state, and local regulations must be followed during the performance of this SOP. In addition, all procedures outlined in the OASQA Chemical Hygiene Plan must be adhered to. Stop all work in the event of a known or potential compromise to the health and safety of any person and immediately notify the Safety Officer, and other appropriate personnel as outlined in the CHP.

5.6 All laboratory waste must be handled in accordance with guidelines established in the CHP and the appropriate waste disposal procedures identified in Section 15.0 (Waste Management).

5.7 Analysts must be cognizant of all instrumental hazards (i.e. dangers from electrical shock, heat or explosion etc.).

5.8 All chemicals used in the performance of this SOP, as well as the samples, should be handled with caution. Adequate protective gear should be worn. At a minimum, this includes ANSI approved safety glasses and a lab coat to protect from chemical splashes, and powderless gloves made from acid resistant materials such as nitrile, latex, neoprene, butyl or PVC.

5.9 Spill procedures: Follow the procedures outlined in the ESC Occupant Emergency Plan (OEP), Hazardous Material Spills section. For minor spills (which can be handled by the analyst) wear safety glasses, lab coat, and gloves to clean up the material. For significant spills, immediately contact the SHEM Manager.

6 Equipment and Supplies

6.1 HPLC/MS/MS system: Analytical instrument and accessories suitable for automated injection of samples onto analytical HPLC columns and fragmentation and detection by a tandem mass spectrometer.

6.2 System used at R3-ESC: Waters (Milford, MA) TQD HPLC/MS/MS system: equipped with a 1 to 50 µL or 1 to 100 µL loop injector and electrospray (ESI) tandem mass spectrometer (MS/MS) capable of multiple reaction monitoring (MRM) and negative and positive ion mode.

6.3 HPLC column: Waters (Milford, MA) Atlantis dC18 3µm , 2.1 x 150mm. Other columns may be used if they provide sufficient retention and separation of the target analytes.

6.4 Data System: Computer system with software capable of accepting and processing raw detector data from the HPLC/MS/MS. The system must have the following capabilities:

Integrate peaks from raw data.
Provide peak height and peak area information.
Calculate and store calibration information.
Identify peaks of interest by retention time.
Quantitate peaks of interest using calibration obtained.
Produce chromatograms.
Allow overlay and comparison of chromatograms.
Produce reports with quantitation information.
Provide a vehicle for storing data.
Define manually integrated data on report.
The current system for operation and processing is Waters Empower2 (current revision)

6.5 Disposable 0.45um syringe tip filters, Teflon, if needed to remove suspended solids.

6.6 Disposable luer tip syringes, sized as appropriate, if needed to remove suspended solids.

6.7 Volumetric flasks - Class A glass: sized as appropriate

6.8 Micro syringes or Class A graduated (to deliver) pipets, sized as appropriate

6.9 Autosampler vials- Glass, 2 mL crimp top or screw top with Teflon-lined septum

6.10 Graduated cylinders, sized as appropriate

6.11 Disposable Pasteur pipets

7 Reagents and Standards

7.1 Reagents

7.1.1 Acetonitrile - HPLC grade or equivalent. Optima grade is preferred.

7.1.2 Organic-free, deionized water: ASTM Type III water provided and monitored in-house according to R3-QA065 (current revision) and further polished at a point of use Millipore unit to a resistivity of 18 MΩ-cm and a total organic carbon of less than 50 ppb.

7.1.3 Nitrogen gas, provided by liquid nitrogen dewars

7.1.4 Argon gas, provided by liquid argon dewars

7.1.5 Formic Acid, reagent grade.

7.1.6 Sodium Cesium Iodide, NaCsI. For instrument tuning. Provided annually by manufacturer with system preventive maintenance (PM) kit.

7.1.7 Mobile phase: Reservoir A1: H2O with 0.1% formic acid, Reservoir B1: Acetonitrile with 0.1% formic acid.

7.2 Standards

7.2.1 All standards are to be labeled with the Element standard number and the preparer's initials. This is a unique identifier and all standard information is referenced in Element. Other information may include: expiration date, concentration, and manufacturer.

7.2.2 Standards must be stored in glass containers at 4 +/-2°C.

7.2.3 Stock standard solution 100 mg/L (ppm) glycol mix – This solution can be purchased commercially as a certified standard. Stock standards should be stored at 4-6°C or according to manufacturer's suggestions until manufacturer's expiration. Expiration dates should be clearly specified on the label.

7.2.4 Intermediate standard solution (1.0 and 10 mg/L glycol mix) – Prepared by dilution of stock standard solution to 10 or 100 mL with reagent water. Intermediate standards may be stored at 4±2 °C for a period of up to 6 months. Expiration dates should be clearly specified on the label.

7.2.5 Calibration standards – Prepare dilutions of the intermediate standard solution to prepare five calibration standards Due to the varied responses of the analytes, recommended standard concentrations for establishing a calibration curve are: 5, 10, 25, 50, 100, 200, and 400µg/L (ppb). This range may be extended provided that the linear response can be adequately verified through satisfaction of all calibration criteria and quality control requirements. The low standard must be equivalent to or below the lowest result to be reported. All reported results must be within the calibration range.

8 Sample Collection, Preservation and Storage

8.1 This SOP does not describe sample collection procedures; however, the following guidelines are followed once samples are received at the laboratory.

8.2 Samples must be stored in tightly sealed glass at 4 +/- 2°C in a designated sample refrigerator. Recommended sample container is 40mL vial with Teflon septa without the use of acid preservation.

8.3 Analyze samples within 14 days of collection.

8.4 Samples extracted outside of holding time should be noted in the case narrative and qualified according to the lab QM.

9 Quality Control

9.1 Batch QC. The following are relevant QC criteria for this method taken from the OASQA Laboratory Quality Manual (current revision).

NELAC Requirement	Minimum Frequency	Acceptance Criteria	Corrective Action
Method Blank – BLK (clean matrix **processed**)	One per sample preparation batch[1]	Fails if the concentration of a targeted analyte in the blank is at or above the reporting limit, AND is greater than 1/10 of the amount measured in any sample. Criteria do not apply to sample results reported as less than values and mandated methods that require correction for blanks.	If outside acceptance criteria reprep affected samples or qualify sample results.
Laboratory Control Sample (LCS) – **BS** (clean matrix spiked with analytes of interest)	One per sample preparation batch [1]	±20% of expected value for aqueous samples. As per 8000C. LCS/BS is equivalent to CCV because there is no extraction. Sec 11.7.6	If outside acceptance criteria, first re-analyze the failed QC to verify difficulty. If still failing, perform corrective actions and reprep. affected

NELAC Requirement	Minimum Frequency	Acceptance Criteria	Corrective Action
			samples or qualify results.
Matrix Spike – MS (spiked or fortified sample)	One per 20 samples per matrix Selection of sample [3]	±30% of expected value for aqueous samples. This is a conservative /demanding limit based on acceptance criteria for spikes into clean matrix (LCS-BS) per 8000C Section 9.5.4..	If outside acceptance criteria, qualify the sample associated with failing QC results.
Matrix Spike Duplicate –MSD (analysis of second fortified aliquot, processed)	One per 20 samples per matrix and site Selection of sample [3]	Relative percent difference: 25, as per Method 8000C. ±30% of expected value for aqueous samples. As per Method 8000C, Sec 9.5.4. RPD≤25	If outside acceptance criteria, qualify the sample associated with failing QC results. Re-analyze the sample (holding time and sample volume permitting). If MS/MSD recoveries are high, first examine raw ion data for possible interference. If the problem is confirmed by re-analysis, include explanation in analytical report. If the MS/MSD recover problems are not confirmed and recoveries from the second analysis are within the QC limits, then report the second analysis and reject the first.
Initial Calibration –	At least five calibration standards with one at the Level of Quantitation (not to include the blank)	$r^2 \geq 0.99$ as per Method 8000C Sec 9.3.2. Minimum of 5 concentrations Method 8000C Sec 7.4.1.1	If the initial instrument calibration results are outside established acceptance criteria, corrective actions must be performed. Results associated with an unacceptable initial instrument calibration must be qualified. Results of samples not bracketed by initial instrument calibration standards (within calibration range) must be reported as having less certainty.
Second Source Quality Control Standard (QCS) – **SCV** (material is from a second source; **source independent** of calibration standards, not processed)	One per initial calibration	±20% of expected value as per Method 8000C. Sec 9.3.6.	If outside acceptance criteria, first re-analyze or reprep. the failed QC to verify difficulty. If still out, correct problem then recalibrate or qualify results.
Continuing Instrument	One at beginning, end and	±20% of expected value as per	If outside acceptance criteria,

NELAC Requirement	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration Verification – CCV	every 20 samples (analytical batch).	Method 8000C. Sec 1.1.7.6	first re-analyze or reprep the failed QC to verify difficulty. If reanalysis passes the first time, then continue run. If reanalysis fails but routine corrective actions correct the problem, then there must be two consecutive passing QCs before continuing the run. If it still fails, then recalibrate and reanalyze all samples since the last acceptable CCV or stop analysis (additional analyses shall not occur) and if any samples in the batch cannot be re-analyzed report data specifying the direction of the bias if clearly indicated.
Selectivity – Retention Time	All chromatography methods	All analytes in initial calibration standards, LCS/BS, SCV and CCV within windows established per method or in-house limits. The Empower software processing method currently sets the retention time window at ±5% of the analyte's retention time in the mid-point calibration curve.	If outside acceptance criteria, first re-analyze or reprep the failed QC to verify difficulty. If still out, correct problem then recalibrate or qualify results.
Surrogate – SUR	Organic only - All samples, standards, QC (Surrogate compounds as per SOP and mandated methods). Not currently used, may be added at a future date.	Not currently used, may be added at a later date.	If outside acceptance criteria, qualify results associated with failing QC.
Tuning	Mass spectrometry methods - before each analytical batch [1] ASTM D7731-11 states that tuning should be done according to manufacturer's directions. Because hardware tuning is done with NaCsI, tuning is recommended to be done yearly with the PM so that salts do not build up on the quadrupole.	According to manufacturer's directions.	Perform instrument maintenance and rerun tuning standard. Data associated with an unacceptable tune shall not be reported.

[1] ***Batch:*** *environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A* ***preparation batch*** *is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An* ***analytical batch*** *is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical*

batch can include prepared samples originating from various environmental matrices and can exceed 20 samples. (NELAC Quality Systems Committee)

[2] *The components to be spiked shall be as specified by the mandated test method. Any permit specified analytes, as specified by regulation or client requested shall also be included. If there are no specified components, the laboratory shall spike per the following:*
For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, the spike should be chosen that represents the chemistries and elution patterns of the components to be reported.
For those test methods that have extremely long lists of analytes, a representative number may be chosen using the following criteria for choosing the number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included over a two year period.
For methods that include 1-10 targets, spike all components.
For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater.
For methods that include 21 or more targets, spike at least 16 components.
(NELAC, Section D.1.1.3.1c)

[3] *The selected sample shall be rotated among client samples so various matrix problems may be noted and/or addressed.*

10 Calibration and Standardization

10.1 Refer to the Batch QC table for calibration criteria.

10.2 While many mass spectrometry methods require daily tuning to assure proper mass identification prior to each sample batch, ASTM Method D7731-11 states that tuning/mass calibration should be according to manufacturer's directions. According to the TQD Operator Manual, unless problems are noted, this system is only required to be tuned for proper mass identification annually with the system PM. Tuning is done with a NaCsI solution and repeated introduction of NaCsI can cause buildup of salt in the system and result in reduced sensitivity and will necessitate frequent cleaning.

10.3 Tuning to determine the correct system settings (cone voltage, desolvation temperature, source temperature etc) for a particular analyte is done as needed and according to manufacturer's directions. Representative settings for the analytes in this method are listed in Section 11.

10.4 Records of the annual system PM are maintained in the instrument maintenance log.

10.5 Suggested concentrations for the initial calibration levels are 5.0 to 400.0 ppb. If a wider calibration range is needed, more standard levels should be added provided the calibration curve remains linear. Suggested 5-point calibration levels is 5, 10, 25, 50, 100.

10.6 Linear calibration may be used if the $r^2 \geq 0.99$ and all continuing calibrations and calibration verifications pass. If linear calibration fails, calibration must be re-run.

10.7 The average of the retention times of the mid-level concentrations is to be used in the

processing method as the analyte retention time.

10.8 Certificates of analysis are stored in G201.

11 Procedure

11.1 Sample Preparation

11.1.1 Transfer sample to an autosampler vial using a glass Pasteur pipet. If necessary, filter the sample through a 0.45µm syringe tip filter and dispense into autosampler vial.

11.1.2 Prepare matrix spike samples in a 10.0 mL volumetric flask. Fill to about 50% with sample; add an appropriate volume of spike solution to achieve the needed concentration. The volume of spike added should not be more than 100-200ul (1-2% of the total sample volume) or it could affect the concentration in the source sample. Fill the volumetric flask to the mark with sample and mix by inverting several times. If necessary, filter the sample through a 0.45µm syringe tip filter and dispense into autosampler vial.

11.2 HPLC/MS analysis

11.2.1 Calibrate the HPLC/MS/MS with NaCsI, according to manufacturer's directions, during annual preventive maintenance. More frequent calibration with NaCsI can leave residue on the quadrupoles and should only be done following significant instrument repair.

11.2.2 Appropriate MRMs were determined during method development (see 11.2.6 below) but can be reevaluted as needed, by tuning with authentic, individual standards to determine the most abundant MRMs. Tuning may be done via the Waters Intellistart™ automated tuning program or manually through the tune page.

11.2.3 Mobile phases.

11.2.3.1 For 2-methoxyethanol, isocratic elution at 0.3ml/min at 98% A1 and 2% B1 is used.

11.2.3.2 For the other analytes a gradient is used.

Time (min)	Flow rate ml/min	% A1	% B1	Curve
Initial	0.4	98	2	Linear
3.0	0.4	98	2	Linear
10.5	0.4	85	15	Linear
12.5	0.4	85	15	Linear
13	0.4	98	2	Linear
13-19	0.4	98	2	Equilibration before next injection

11.2.4 The typical injection volume is 30 µL.

11.2.5 The gradient may be modified to achieve separation of target analytes in one run.

11.2.6 The following MRMs are monitored but may be adjusted depending on instrument response. The MRM marked * has a higher response and is used as the primary MRM for calibration and quantitation. The second MRM may be monitored and for supplementary confirmation but due to the lower response, cannot be used to confirm concentrations at the lower portions of the calibration curve. ASTM D7731-11 uses only one MRM per analyte.

Diethylene Glycol, Time: 0-5min, span: 0.2 Da, retention time (RT): 1.8min

Precursor (Da)	Product (Da)	Dwell (sec)	Cone voltage (V)	Collision energy V)
106.94	44.9*	0.2	18	48
106.94	88.4	0.2	18	22

Triethylene Glycol, Time:0-5min, span 0.2 Da, RT: 2.9min

Precursor (Da)	Product (Da)	Dwell (sec)	Cone voltage (V)	Collision energy V)
150.97	45.10*	0.2	24	26
150.97	89.00	0.2	24	24

Tetraethylene Glycol: Time 5-13min, span 0.2 Da, RT: 5.6 min

Precursor (Da)	Product (Da)	Dwell (sec)	Cone voltage (V)	Collision energy V)
195.05	45.10*	0.2	22	22
195.05	89.00	0.2	22	20

2-Butoxyethanol: Time, 5-13min, span 0.2 Da, RT: 10.6min

Precursor (Da)	Product (Da)	Dwell (sec)	Cone voltage (V)	Collision energy V)
118.93	57.10	0.2	16	20
118.93	63.00*	0.2	16	14

2-Methoxyethanol: Time 0-4min, span 0.2 Da, RT: 2.6min

Precursor (Da)	Product (Da)	Dwell (sec)	Cone voltage (V)	Collision energy V)
76.91	59.10*	0.2	12	8

11.2.7 MS/MS settings may be adjusted to meet quantitation limit requirements but are generally as follows:

	2-methoxyethanol	All other analytes
Desolvation temperature	350°C	400°C
Source temperature	150°C	150°C
Collision gas flow (Argon)	0.1ml/min	0.1ml/min
Cone gas	25 L/hr	25 L/hr
Desolvation gas	600 L/hr	800 L/hr
Ion Mode	Electrospray positive (ESI+)	Electrospray postive (ESI+)

Column temperature	30°C	30°C
Sample chamber	4°C	4°C
Inter-channel delay	0.005s	0.005s
Inter-scan delay	0.005s	0.005s

12 Data Analysis and Calculations

12.1 Refer to the current version of the Laboratory QM for Quality Control related equations and the policy on reporting significant figures.

12.2 Refer to R3QA-067 (current revision) for policies on manual integration.

12.3 Identify and confirm the presence of target analytes in the samples by matching the retention time of the MRM.

Compare the retention time of the MRM with the retention time determined during the initial calibration. The retention times should not be more than 5% different from the initial calibration average.

12.4 Linear (external) calibration may be used if the $r^2 \geq 0.99$.

12.5 Water samples

$$\text{Final result } (\mu g/L\ ClO_4^-) = (C)(D)$$

Where:
C = Concentration or calibration curve (µg/L analyte) D = Dilution factor (if needed)

13 Method Performance

13.1 Method performance is evaluated based on the criteria in Table 2.

13.2 DOC accuracy and precision data and MDL study data are maintained in the OASQA Central QS files.

13.3 NQLs are listed in Section 1. There are no problematic compounds associated with this method.

14 Pollution Prevention

14.1 This method has been developed to generate 10 mL or less of waste per aqueous sample. As this SOP is routinely performed, the analyst will consider other methods to reduce the use and generation of hazardous chemicals/waste.

14.2 Resource Management: Water Conservation. Laboratory personnel should be mindful

of water consumption, and whenever possible, employ practices that minimize water use.

15 Waste Management

15.1 *Waste type code*: Will vary with sample. Record the WO # on sample waste containers.

15.2 All laboratory waste must be handled in accordance with guidelines established in the ESC Chemical Hygiene Plan (current revision).

15.3 The waste flow chart is on file with the SHEM Office.

15.4 *Amount of waste per sample*: Approximately 10mL or less of waste will be generated per sample.

16 References

16.1 SW-846 Method 8321B,Solvent-extractable nonvolatile compounds by high-performance liquid chromatography/thermospray mass spectrometry or ultraviolet detection (rev 2, Feb 2007)

16.2 SW-846 Method 8000C, Determinative Chromatographic Procedures. (rev 3, March 2003)

16.3 ASTMD7731-11^{E1}, Standard Test Method for Determination of Dipropylene Glycol Monobutyl Ether in Sea Water by Liquid Chromatography/Tandem Mass Spectrometry. (August 2011)

16.4 Waters ACQUITY TQD Empower 2154 customer Familiarization Guide. Waters Corp. (2008) Milford MA.

16.5 EPA Region 3 OASQA Laboratory Quality Manual (QM), Current Revision.

16.6 EPA Region 3 OASQA Chemical Hygiene Plan, Current Revision.

16.7 EPA Region 3 OASQA Occupant Emergency Plan, Current Revision.

16.8 EPA Region 3 OASQA, Laboratory Notebook Policy, Current Revision.

16.9 TQD Maintenance logbook: SNB 357.

16.10 Waters TQD System Run Log: PNB 207

16.11 Certificates of analysis notebook: SNB 114

16.12 R3-QA067. Procedures for Manual Integration, Current revision.

16.13 R3-QA054. Glassware Preparation for Organic Analyses. Current revision.

16.14 R3-QA065. Calibration, Verification and Maintenance of Laboratory Support Equipemt. Current revision.

16.15 NELAC Standard. Current revision

17 Tables, Diagrams, Flowcharts and Validation Data

17.1 Waste handling flow chart is on file with the SHEM office.

17.2 QA/QC data is on file with the OASQA Quality Assurance Officer.

17.3 Attachment 1. EPA Internal Technical Review Checklist

Attachment 1: **Glycols by LC/MS (R3-QA239) Technical Review Checklist (TRC) Checklist**

For Internal Use Only

Site Name:_____ WO#_____
Analyst: _____ Date given to Reviewer:_____
Matrix (circle): Aqueous / Other _____
Program (circle): Superfund / RCRA / WPD (NPDES) / SDWA / Other: _____

The signature below indicates the following:
- This data meets the needs of the customer according to the request.
- The analysis was performed as per the SOP, or exceptions documented.
- All documentation needed to recreate the analyses has been reviewed.
- Data Review status set to Peer Reviewed in Element.

Peer Reviewer signature _____ Date accepted_____
If any data for this case is stored with another case file, give Site Name and WO#_____

Peer Reviewer Completes Section Below:

General:

	YES	NO	N/A	Comments
Raw data is identified with sample IDs, site name, WO#, analyst name, date of analysis.	____	____	____	

Quality Control:

	Yes	No	n/a	comments
NaCsI cal according to mfg recommendation within year				
Initial calibration: $r^2 \geq 0.99$				
Holding time: 14 days to analysis				
Method Blank < NQL				
SCV ~~(old term: LVM)~~ (±20%)				
CCV (old:CLC) (±20% mid-range)				
BS Blank spike (±20% mid range)				
Reported + results for samples met RT requirement for primary MRM fragment?				
Reported + results for samples met RT requirement for 2ndary MRM fragment or explained in narrative.				
Manual integration as per R3QA067				
Matrix spike/dup: ±30% aq, 25% mid range spike				

Calculations/Report:

Calculations and transcriptions checked. _____ ____ ____ _____
Element Draft Report reviewed. _____ ____ ____ _____
Deviations and problems documented. _____ ____ ____ _____

Additional Comments by Peer Reviewer:

_____
_____
_____
_____

Analyst ensures that the data case file is complete and accurate as per SOP R3QA-066:

____ Bench sheet or Work Order list
____ Sample Prep logs
____ Instrument run log
____ Standard/Reagent Prep log
____ Raw data
____ Data status set to analyzed
____ Appropriate TV sheets / Certificates of Analysis
____ Element Peer Review report

Additional Comments by Analyst on data issues:

_____
_____
_____
_____
_____
_____
_____

Appendix B

Chain of Custody Form

Chain of Custody Record (COC)
U.S. EPA

Shipping Method:_____ **Page:** ___ **of** ___
Airbill No.:_____ **Shipping Container:** ___ **of** ___

Project: Location: Site or Field Phone: Project Manager/Phone:	Lab Name: Address: Phone: Contact Name:

Sample ID	**Sampling Date/Time (24 hour)**	**Description (include matrix)**	**Volume/ Amount**	**Requested Parameters**						**Special Instructions, Preservation, Observations, Comments**

Total No. of Sample Containers:_____ Date:_____ Time:_____
Relinquished By:

Signature: _____

Printed Name: _____

Company/Affiliation: _____

Total No. of Sample Containers:_____ Date:_____ Time:_____
Received By:

Signature: _____

Printed Name:_____

Company/Affiliation: _____

Pink copy - Field Custodian, Yellow copy - Lab Custodian, White copy - Project Officer

EPA- 441 (CIN) (Rev. 7/07)

APPENDIX C

READINESS REVIEW QUESTIONNAIRE
(To be completed prior to sample receipt)

NOTE 1:

IT IS RECOGNIZED THAT EACH LABORATORY MAY OPERATE UNDER DIFFERENT "RULES". THEREFORE, NON-FEDERAL LABORATORY QUALITY ASSURANCE PROFESSIONALS MAY:

- **DELEGATE COMPLETION OF SOME OR ALL OF THE ITEMS IN THIS CHECKLIST;**
- **ADJUST VERBIAGE OF THE CHECKLIST ITEM, IF NECESSARY, PER DISCRETION OF THE QA PROFESSIONAL**

NOTE 2:

- **ALL ITEMS ARE CONSIDERED "GOOD LABORATORY PRACTICE";**
- **DOUBLE ASTERISKED ITEMS ARE "REQUIRED", AS A QUALITY RELATED NECESSITY FOR THIS STUDY.**

KEEP "ACCOUNTABILITY" IN THE FOREFRONT

READINESS REVIEW QUESTIONNAIRE
for the
Multi-Laboratory Verification of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry Study

Laboratory Name:

Address:

Building (if applicable):
Date of Evaluation: February XX, 2013
Prepared by: QA Professional (or Delegated Individual)

LABORATORY MANAGEMENT:	
****** What Month/Year was the Laboratory Quality Management Plan reviewed and/or approved?	
Has the Laboratory ever been evaluated by an external organization? If so, please provide the organization, month, and year.	

I LABORATORY BENCH ACTIVITIES AREA		
Attention is given to: (a) the overall organization and neatness, (b) the proper maintenance of facilities and instrumentation, (c) the general adequacy of the facilities to accomplish the required work.		
#	**ITEM**	**Y; N; or COMMENT**
	Activity Area	
A ******	Have laboratory bench areas been designated as the work space for sample handling such as for spiking, sample transfer to vials, and organization for instrument carousel (if using an auto-sampler)?	
B ******	Is a system in place for creating and storing records and documents?	
	Volumetric Equipment	
C	Will the laboratory use pipettes, syringes, or both for volumetric measurement of fluid transfer or spiking?	
D ******	Have the pipettes, and/or syringes been calibrated and checked within the last 12 months by a certified technician?	
	Standards	
E ******	What (or which company) will be the source of the Quality Control Check Standard (QCCS)?	
COMMENTS:		

II INSTRUMENTATION		
#	**ITEM**	**Y; N; or COMMENT**
A **	What is the Make/Model of the "LC/MS/MS" instrument?	
B **	What Month/Year was the LC/MS/MS last tuned/?	
C	What compound(s) will be used for Mass Calibration, if any?	
D	Are manufacturer's operating manuals and/or other relevant Standard Operating Procedures (SOP) readily available to the operator?	
E **	What Month/Year did the instrument operator last create a calibration curve and perform an analysis on the instrument that is intended for use in this study?	
F	Are sufficient in-house replacement parts available to ensure minimal downtime? (e.g., spare multipliers, filaments, chromatographic columns, traps)	
G	Does the laboratory perform regular preventive maintenance on the instruments?	
H **	Does a service record exist for the instrument that is intended for use in this study?	
I	Are raw electronic data, including quantitation output files and mass spectral libraries, archived on electronic-media?	
J **	Does a system exist to back-up electronic data and information?	
K	Is a log of the contents of the raw data available? (Example, instrument run log for the instrument intended for use in this study)	
COMMENTS:		

III DATA HANDLING AND REVIEW		
#	**ITEM**	**Y; N; or COMMENT**
A **	Is a system in place for creating and storing records and documents?	
B **	Has a person, other than the Instrument Operator, been designated to perform a Surveillance Audit [Appendix D] and/or "Audit of Data Quality" (Spot-check of data calculations) [Appendix E] of the Multi-Lab Study QAPP]?	
C	Have personnel been identified for the review of the overall data package structure prior to submission?	
COMMENTS:		

IV DATA MANAGEMENT		
#	**ITEM**	**Y; N; or COMMENT**
A	Are data and file access secured with password protection?	
B **	Has a person been assigned to assure that data generated by the system are checked for completeness and accuracy?	
C	When changes to data are required, is it a routine practice of the laboratory to document the changes?	
COMMENTS:		
V TASK QUALITY ASSURANCE PLAN		
#	**ITEM**	**Y; N; or COMMENT**
A	Who is assuring that the QAPP and related quality documents are distributed and readily available to appropriate scientists within your organization?	
COMMENTS:		

ATTESTED BY:

- Name:
- Position:
- Date:

APPENDIX D

SURVEILLANCE AUDIT CHECKLIST

(To be completed when samples are received and analysis has been initiated)

NOTE 1:

IT IS RECOGNIZED THAT EACH LABORATORY MAY OPERATE UNDER DIFFERENT "RULES". THEREFORE, NON-FEDERAL LABORATORY QUALITY ASSURANCE PROFESSIONALS MAY:

- **DELEGATE COMPLETION OF SOME OR ALL OF THE ITEMS IN THIS CHECKLIST;**
- **ADJUST VERBIAGE OF THE CHECKLIST ITEM, IF NECESSARY, PER DISCRETION OF THE QA PROFESSIONAL**

NOTE 2:

- **ALL ITEMS ARE CONSIDERED "GOOD LABORATORY PRACTICE";**
- **DOUBLE ASTERISKED ITEMS ARE "REQUIRED", AS A QUALITY RELATED NECESSITY FOR THIS STUDY.**

KEEP "ACCOUNTABILITY" IN THE FOREFRONT

SURVEILLANCE AUDIT CHECKLIST

for the
Multi-Laboratory Verification of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry Study

Laboratory Name:

Address:

Building (if applicable):
Date of Evaluation: February XX, 2013
Prepared by: QA Professional (or Delegated Individual)

SURVEILLANCE AUDIT FOR REGION 3 ANALYSIS SOP AND PROJECT QAPP	
SAMPLE RECEIPT	
ITEM	**Y, N, or COMMENT**
1. Were appropriate personnel notified when the samples arrived?	
2. Were two individuals present when the sample container(s) (coolers) were opened?	
**3. Was the Chain-of-Custody (CoC) document included in the ample container(s) (coolers)?	
4. Is the condition of the (CoC) document acceptable? (Example: If damaged by an accidental spill of sample, then it may not be readable)	
**5. Is the temperature of the sample container(s) available? (Does the container have a thermometer or other temperature monitoring device?)	
**6. If temperature is available, is the temperature within acceptable limits?	
7. Were the samples given "in-house" identification numbers?	
**8. Were the samples received in good condition and within holding time?	
SAMPLE ANALYSIS	
ITEM	**Y, N, or COMMENT**
9. Are the samples being analyzed within a reasonable holding time?	
**10. Is the Auto-run carousel set-up with the NELAC-related Quality control checks?	

**11. Are the samples (and standards) being stored as per Section 8 of the Region 3 SOP (4°C ± 2°C)?	
12. General good lab technique observed: pipette use, neatness & organization, labeling of vials, etc.?	
COMMENTS:	

ATTESTED BY:

- Name:
- Position:
- Date:

Appendix E1

STANDARD OPERATING PROCEDURE (SOP)

FOR PERFORMING AUDITS OF DATA QUALITY (ADQs)

and an

ADQ CHECKLIST

All Derived from EPA/ORD/NRMRL SOP "LSAS-QA-02-0"

(To be completed *after* analysis has been completed, and before data package is assembled and sent.)

NOTE 1:

IT IS RECOGNIZED THAT EACH LABORATORY MAY OPERATE UNDER DIFFERENT "RULES". THEREFORE, NON-FEDERAL LABORATORY QUALITY ASSURANCE PROFESSIONALS MAY:

- **DELEGATE COMPLETION OF SOME OR ALL OF THE ITEMS IN THIS CHECKLIST;**
- **ADJUST VERBIAGE OF THE CHECKLIST ITEM, IF NECESSARY, PER DISCRETION OF THE QA PROFESSIONAL.**

NOTE 2:

- **ALL ITEMS ARE CONSIDERED "GOOD LABORATORY PRACTICE";**
- **DOUBLE ASTERISKED ITEMS ARE "REQUIRED", AS A QUALITY RELATED NECESSITY FOR THIS STUDY.**

NOTE 3:

- **YELLOW HIGHLIGHT IS USED IN THE SOP TO IDENTIFY SOME AREAS OF QA PROFESSIONAL DISCRETION;**
- **SOME EDITS OF THE ORIGINAL SOP WERE MADE BY THE ESD QAM ("FORMAL" NAMING OF THIS SOP WAS NOT MADE BECAUSE IT MAY BE A "ONE-TIME" USE).**

KEEP "ACCOUNTABILITY" IN THE FOREFRONT

Performing Audits of Data Quality (ADQs)
As Required by the EPA Hydraulic Fracturing (HF) Quality Management Plan (QMP)

Derived from NRMRL "LSAS-QA-02-0

1.0 Purpose

ADQs are used to verify that reported data are of acceptable quality for their intended use. The ADQ is an examination of data after they have been collected and verified by project personnel. It is conducted to determine how well the measurement system performed with respect to the data quality indicator (DQI) goals specified in the QA program plan (QAPP) and whether the data were accumulated, transferred, reduced, calculated, summarized, and reported correctly. This procedure describes the process used to perform and document ADQs in support of Hydraulic Fracturing (HF) research activities.

NOTE: QA Professional discretion is yellow-highlighted throughout this SOP.

2.0 Revision History

History of document changes

Date	Revision No.	Change	Ref. Section
20130212	1	New Procedure	Not Applicable

3.0 Persons Affected

This SOP applies to QA Professionals (or delegate) who performs ADQs and Technical Lead Persons (TLPs) who have data subjected to ADQs.

4.0 Policy

The "Multi-Laboratory Verification of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry Study" QA Project Plan (QAPP) requires that ADQs be performed by the QA Professionals (or delegate). ADQs may also be performed when specifically requested by management, when dictated by program requirements, or as determined to be necessary by the Technical Research Lead or QA Professional. ADQs are performed by QA Professionals or their designees.

5.0 Definitions

5.1 Audit of Data Quality (ADQ) – is a "continual qualitative and quantitative evaluation" of the documentation and procedures associated with environmental measurements to verify that the reported data are of acceptable quality for their intended use.

5.2 Data Quality Indicators - quantitative statistics and qualitative descriptors that are used to interpret the degree of acceptability or utility of data to the user. The principal data quality indicators are precision, accuracy, comparability, completeness, and representativeness.

5.3 Technical Research Lead (TRL) – the EPA employee who is responsible for all technical aspects of a research project.

5.4 Deficiency – an identified deviation that impacts the quality of the reported results.

5.5 Finding - a deficiency that has a significant effect on the quality of the reported results.

5.6 Observation - a deficiency that does not have a significant effect on the quality of the reported results.

6.0 Procedures

6.1 The need for an ADQ is identified early in the project planning process based on the QA category; ADQs are required for HF projects. (The requirement for an ADQ and associated responsibilities must be included in the quality assurance program plan (QAPP) for these projects.) Other projects may be identified as needing an ADQ (see Section 4.0) early in the project planning process or at some other time during project implementation. When the need for an ADQ is identified, the TRL must coordinate audit activities with the QA Professional.

6.2 The TRL notifies the QA Professional when data packages that have already been verified by project personnel are available (if possible, advance notice should be given).

For some projects, minimal data packages may be generated, while other projects may generate multiple data packages. The identification of specific data packages for review is made by the QA Professional to focus on the more critical parameters and to provide the best representation of the data generated. The QA Professional may use discretion in the review process as to the amount of data that will be reviewed for a specific project.

Note: ADQs must begin when initial data packages and data summaries are available to ensure that any problems are identified and resolved in a timely manner. ADQs must then continue throughout a project as determined to be appropriate by the QA Professional.

6.3 The TRL provides summaries of results for reporting and complete project data packages to the QA Professional. In the case of extramural support, the need for this documentation must be identified in the procurement documentation. A complete data package may contain the following:

6.3.1 Chain of custody documentation; Sample information: a list of each sample by unique number; date of sampling; method of sampling; analysis required for each sample; matrix/preservation.

6.3.2 Method information: identification of reference method(s) or laboratory SOPs used, including sample preparation if applicable; any modifications to the stated methods.

6.3.3 Summary of results: sample results for reporting; reporting units; reporting basis (e.g. dry weight); reporting limits; QC results (e.g., blanks, surrogates, spikes, replicates).

6.3.4 Raw data: dates of sample preparation and analysis, sample preparation initial and final masses/volumes; raw data including sample analysis sheets, logs, copies of laboratory notebooks, or raw data from instrumentation; instrument checks; calibration documentation; and calculations and/or spreadsheets used to reduce data.

6.3.5 Data Qualifiers: any problems or issues with receipt, storage, handling, or analysis of samples including resolution; deviations from project/method requirements; QC requirements not met; impact to reported results.

Note: If any of the above is not provided for review, the QA Professional must evaluate the impact of the missing information on performing the ADQ. If necessary, the QA Professional will inform the TRL of the need for the missing information.

6.4 The QA Professional or designee prepares a checklist based on the type of data generated, such as the example checklist provided in this Appendix for measurement projects (additional items for review may be needed depending on the data being reviewed or a different checklist may be needed for non-measurement project types). The QAPP or other planning documents will be needed to identify data quality indicator requirements and goals. Multiple sections to the checklist may be needed if the data involves multiple sample matrices/analyte classes (e.g., air samples for metals, water samples for VOCs).

6.5 The QA Professional reviews the data packages(s) against the checklist. A representative set of the data is traced in detail from raw data and instrument readouts through data transcription or transference through data manipulation (either manually or electronically by commercial or customized software) through data reduction to summary data, data calculations, and final reported data. Particular attention is paid to the use of QC data in evaluating and reporting.

Note: For each data package reviewed, all calibration and QA/QC data must be reviewed. In addition, a percentage of input values for software program- generated calculations and hand calculations must be verified, as determined to be appropriate by the QA Professional. If problems are identified, additional verification is needed.

6.6 The QA Professional identifies deficiencies, if present, and designates them as findings or observations.

6.7 The QA Professional documents the results of the ADQ in a report. The draft report must be included the following at a minimum:

- Introduction to include audit information (e.g., TRL, project title, laboratory (organization), data package identifications, sample matrices/analyte classes, date, QA reviewer);
- Summary of findings and observations and a summary statement regarding the adequacy of the data for its intended use;
- Individual finding/observation discussions including a description of the deficiency and any effect on data quality and the recommended corrective action.

6.8 The QA Professional shall distribute the report to the TRL.

6.9 If the audit report contains findings, the TRL must respond in writing to the QA Professional (with a copy to the TRL's supervisor) with a plan for corrective actions. If the audit report contains observations only, the TRL is strongly encouraged to address the issues and provide a documented response to the QA Professional, but no additional QA review is needed.

6.10 For ADQ findings, the QA Professional reviews the ADQ corrective actions and provides documentation to the TRL and the appropriate supervisor regarding the acceptability of these corrective actions. The results cannot be used or reported until any needed corrective actions are determined to be acceptable.

6.11 Any required revisions to reported results must be made and submitted to the QA Professional for verification prior to the use or reporting of the results.

6.12 The TRL must maintain the ADQ report and any responses in the project files. The QA Professional must maintain the ADQ report and any responses in the QA files.

7.0 References

7.1 EPA *QA/G-7*, Guidance on Technical Audits and Related Assessments for Environmental Data Operations, EPN600/R-99/080, January 2000

7.2 NRMRL Quality Management Plan, current edition

Appendix E2

ADQ CHECKLIST

GENERAL INFORMATION

EPA Technical Research Lead Person (TLP): Brian Schumacher

Principal Investigator:

Project Title: *Multilaboratory Verification and Validation of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry* Study.

Laboratory (Organization):

Report Identification/Date:

Sample Type(s)/Analyte(s): Standards and Blind Samples

QA Professional:

ADQ Date:

ITEMS REVIEWED

	Y	N	N/A	Comments
Sample Information				
**1. Is the chain-of-custody documentation complete?				
**2. Are samples uniquely identified and correctly transcribed throughout the data package to the summary of results?				
3. Does sample collection documentation indicate that samples were collected as described in the QAPP?			X	
4. If calculations were used for sample collection information (e.g., air volumes), are these calculations correct?			X	
5. Were the samples and standards received stored in an appropriate manner (in a Cold Storage Unit)?				
COMMENTS:				

Sampling and Analysis Method Information				
6. Were methods specified in the R3 SOP used?				
7. If method modifications were made, are these modifications appropriate and well-documented?				
8. Were sample preparation and analytical method holding times met?				
COMMENTS:				
Summary of Results				
9. Are the correct units reported?				
10. Are reported results correct (verify any calculations performed)				
11. Were QC samples (blanks, second source checks, surrogates, spikes, replicates) analyzed at the frequency specified in the R3 SOP?				
12. Did the QC results meet the requirements specified in the QAPP?				
COMMENTS:				
Raw Data				
13. Were the instruments calibrated as described in the QAPP?				
14. Were the calibration criteria met for initial and continuing checks?				
15. Were reported results analyzed within calibration range?				
16. Were instrument outputs correctly transcribed to data summary?				
COMMENTS:				
Data Qualifiers				
17. If QC requirements were not met, were corrective actions performed?				
18. If necessary, were data qualified appropriately?				
COMMENTS:				

ATTESTED BY:

- Name:
- Position:
- Date: