Quality Assurance Project Plan
For the Interlaboratory 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

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ESD Division Director:	/S/ Daniel Heggem, Acting Division Director, ESD	4/4/12 Date
ESD Quality Assurance Manager:	/S/ George Brilis, QAM, ESD	4/4/12 Date

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NOTICE

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LIST OF ABBREVIATIONS

BQR	Branch Quality Assurance Representative
CAS	Chemical Abstracts Service
CCV	Continuing Calibration Verification
COC	Chain-of-Custody
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
HPLC	High performance liquid chromatography
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
PI	Principal Investigator
QA	Quality assurance
QATS	Quality assurance tracking system
QC	Quality control
QAPP	Quality assurance project plan
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedure
TSA	Technical system audit

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SECTION A. PROJECT MANAGEMENT

A3 Distribution List

EPA, ORD, NERL, ESD	
Patrick DeArmond	(702) 798-2102
Lantis Osemwengie	(702) 798-2513
Brian Schumacher	(702) 798-2242
George Brilis	(702) 798-3128
Daniel Heggem	(702) 798-2278
Maliha Nash	(702) 798-2201
EPA, ORD, NERL, IO	
Michelle Henderson	(513) 569-7353
EPA, Region 5	
Lawrence Zintek	(312) 886-2925
Angela Ockrassa	(312) 353-3521
EPA, Region 3	
Jennifer Gundersen	(410) 305-2835
Cynthia Caporale	(410) 305-2732
Fred Foreman	(410) 305-2629
EPA, ORD, NRMRL, GWERD	
David Jewett	(580) 436-8560
EPA, ORD, OSP	
Stephen Watkins	(202) 564-3744
EPA, ORD, NERL, MCEARD	
Jody Shoemaker	(513) 569-7298
Margie Vazquez	(513) 569-7182

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A4 Project/Task Organization

The *Interlaboratory 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 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 three 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. National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division (GWERD), Ada, OK,

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

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

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.

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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	David Jewett, GWERD
Water sample preparation and spiking	Lantis Osemwengie, ESD
Method testing	Patrick DeArmond, ESD; Lawrence Zintek, Region 5; Jennifer Gundersen, Region 3; Jody Shoemaker, MCEARD
Data review 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
Data QA and QC review	Participating Laboratory's Quality Assurance Manager
QA oversight, problem resolution assistance, and tracking corrective action	Michelle Henderson, NERL

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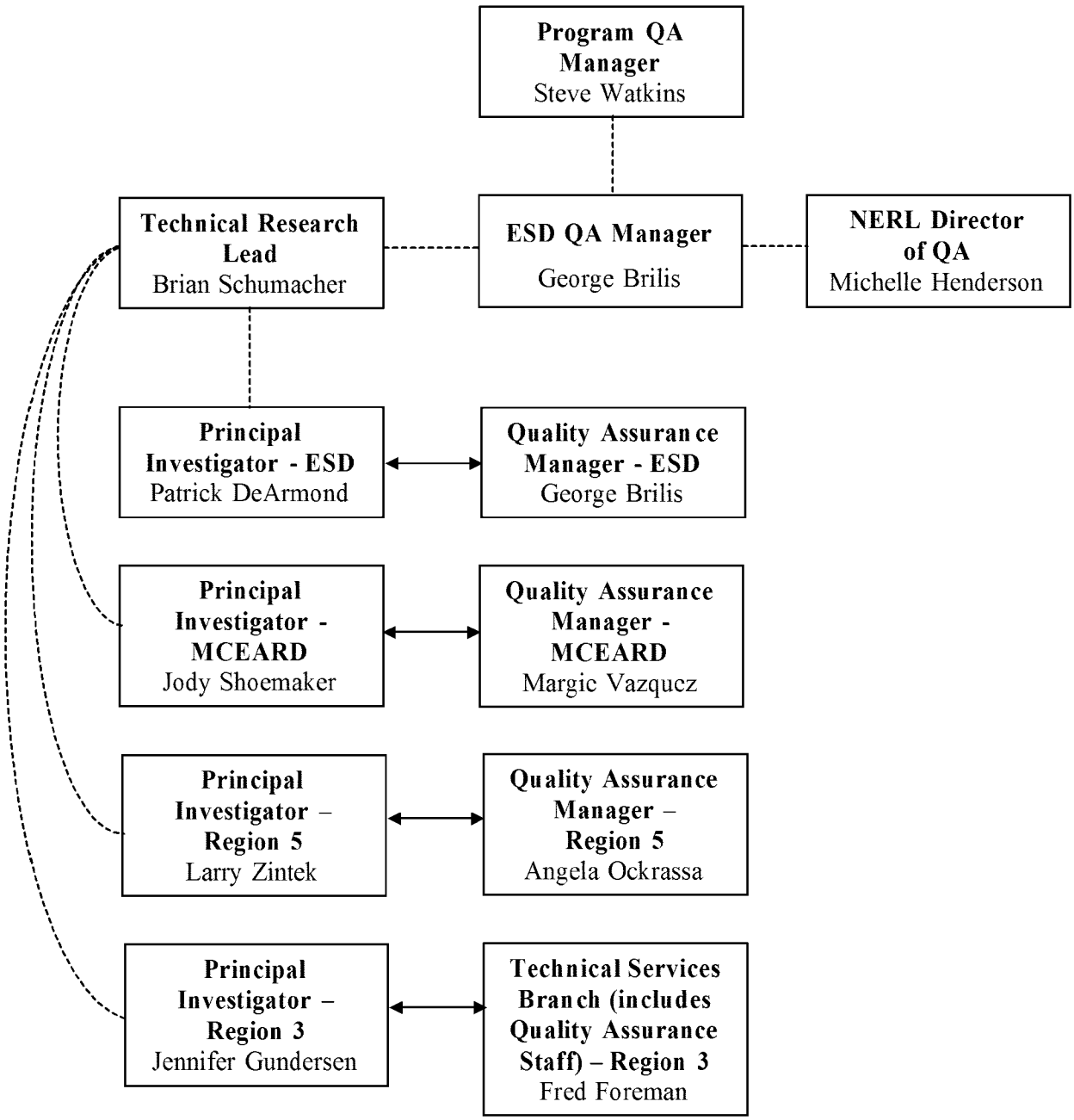

Figure 1. Organizational Flowchart for Glycol Method Study.

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A6 Project/Task Description

The primary objectives of this study are to: 1) verify the performance of Region 3 Standard Operating Procedure (SOP) in multiple laboratories [Phase 1], 2) validate the Region 3 SOP in multiple laboratories [Phase 2], and 3) evaluate and, if appropriate, revise the SOP and/or quality control (QC) acceptance criteria in the method. This may or may not include any unforeseen communications regarding instrument parameters, supplies, and/or equipment.

Verification for this study (Phase 1) will be performed in different laboratories to ensure that each laboratory can perform/follow the SOP provided by Region 3 with the goal of obtaining the same level of results as identified in the Region 3 laboratory. The quality assurance/quality control (QA/QC) procedures for this phase of the project will follow the QA/QC specified in the Region 3 SOP. Verification testing will be performed in laboratory grade water.

Validation for this study (Phase 2) will be performed through the submission of multiple blind samples (spiked and unspiked) in multiple matrices (laboratory grade water and drinking water from a well) to each participating laboratory for analysis. The QA/QC procedures for this phase of the project will follow the QA/QC specified in the Region 3 SOP and in this Quality Assurance Project Plan (QAPP).

To ensure that these study objectives are met, all participating laboratories shall strictly adhere to the above Phases 1 and 2 requiring that:

- Each laboratory verify and optimize the liquid chromatography/mass spectrometry /mass spectrometry (LC/MS/MS) conditions used by Region 3 on their instrumentation to meet Region 3 reporting limits or determine the reporting limits on their LC/MS/MS systems.
- Each laboratory follows all analytical and quality control procedures in the Region 3 SOP and this QAPP (depending on phase of the study).
- Any laboratory that wishes to deviate from the procedures in the Region 3 SOP or this QAPP shall obtain prior approval of the changes from the Research Technical 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 comprehensive quality assurance (QA) program 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.

A7 Quality Objectives and Criteria for Measurement Data

The Data Quality Objective for this study is that the results from three groups of samples must have their variance determined and the variance among the laboratories must agree to within 30% of the established average. If this criterion is met, then the method is considered to be robust, precise and acceptable for normal use. If the variance exceeds 40%, the method will need further evaluation for systematic errors.

Data quality indicators (DQIs) are typically assessed by evaluating the 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 spiked

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samples and duplicate un-spiked samples will be expressed as relative standard deviation (RSD) for replicates of three or more or as 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 validation phase of this study, representativeness will be ensured as only the ESD laboratory will prepare and send the samples 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 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

Special Training
To achieve the stated quality objectives, only analysts trained and experienced in the use of the 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; and on the EPA Hydraulic Fracturing website (http://epa.gov/hydraulicfracturing/) 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.

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.

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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%	RSD≤20%	$R^2 \geq 0.99$	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	< PQL [b]	Inspect the system and reanalyze the blank. Samples must be bracketed by acceptable QC or they will be invalidated.
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 invalidated.
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 invalidated.
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 invalidated.
Quality control check standard [e]	One per batch of samples [a]	100%	RSD≤25% [c]	± 20% of known value	Reanalyze, obtain new sample from Research Task Lead. Samples must be bracketed by acceptable QC or they will be invalidated.
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 invalidated.
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]PQL=practical quantitation limit, 5 times the MDL.

[c]Precision among replicates if more that 1 batch of samples are analyzed. RSD may be 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 the ESD laboratory independent of the ESD analyst and will be prepared from a different lot of the primary standards. One QCCS will be supplied to each participating laboratory.

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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.

Hardcopy Records - Hardcopy records will be maintained in accordance with each organizations 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 Branch QA Representative (BQR), or equivalent, shall perform a documented review of laboratory and electronic recordkeeping. For example, after reviewing a laboratory notebook, the BQR 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
Record-keeping will be permanent according to EPA Records Schedule 501.

Emails will be kept in ECMS, where available.

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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.

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SECTION B. MEASUREMENT

B1 Sampling Design

For the verification phase of this study, each participant laboratory will be sent a copy of the Region 3 SOP. 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 and Principal Investigators (PIs). 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 and surrogates will be sent to the Technical Research Lead in spreadsheet format (to be provided). 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 whatever water purification system is available at the laboratory.

For the validation phase of this study, three sets of seven "replicates" of water samples will be prepared by ESD-LV for a total of 21 blind samples. Samples for laboratory validation phase of the study will be prepared by an independent scientist (i.e., one not involved with the glycol method verification/validation study) at ESD-LV. ESD-LV shall not divulge the concentration to the participant laboratories. ESD-LV may discuss the appropriate spike concentrations with the Technical Research Lead and Project Quality Assurance Manager to ensure appropriate spike levels. Seven samples will be laboratory reagent water spiked at an unknown concentration. Seven samples will be drinking water from a drinking water wells at a selected field site. The seven samples from a drinking water well at a selected field site will be spiked at a known concentration of each compound.

B2 Sampling Methods

Bulk samples from drinking water wells will be acquired by NRMRL-Ada. Collection of 4 gallons 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.

Deionized (DI) water at ORD-ESD will be generated on site using a Barnstead NANOpure system. The cartridges for the system are changed when the resistivity is ≤ 14.0 MΩ·cm.

Information to be provided with the bulk sample shall include:

- a unique identification number as decided by NRMRL-Ada
- 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.

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B3 Sample Handling and Custody

All sample shipments will use the NRMRL Chain-of-Custody (COC) form shown in Appendix B.

As quickly as possible, NRMRL-Ada will ship the drinking well water samples to ESD-LV. Samples should be shipped on ice via overnight courier for arrival the following morning. Samples shall not be collected and shipped on a Thursday or Friday.

Samples prepared and submitted during the validation phase of the 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.

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 refrigerators shall be monitored with temperatures recorded.

Immediately after sample shipment (i.e., as soon as samples are in the custody of the carrier), the bulk water sampling team from GWERD will inform ESD of the shipment and provide information on the shipment, including sample numbers, numbers of coolers, and courier and bill number. ESD will confirm that samples have arrived in good condition and as scheduled. If necessary, the GWERD will implement tracking activities to locate any lost shipment(s) or resend samples due to loss in shipment. Once the samples are received, ESD will prepare the samples and send them to the participating laboratories within 2 days.

Similarly, immediately after sample shipment (i.e., as soon as samples are in the custody of the carrier) of the validation phase 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. If necessary, the 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 within a time frame to meet the 14 day holding time for the glycol samples.

Because glycol ethers are ubiquitous in the environment, including laboratories, the sample 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 an SOP from U.S. EPA Region 3.

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B5 Quality Control

Experiments to evaluate replicate analysis, fortified matrix analysis, blanks, continuing calibration standards, etc. are to be performed as part of on-going QA. Instrument performance must be assessed daily.

For the verification phase of this study, QC criteria presented in the Region 3 SOP shall be followed. The results of verification testing will be used to identify and quantify (1) the sources of significant variability in method performance, (2) probable systematic error, or method bias, (3) the usable dynamic range and limits of detection for method measurements, (4) method sensitivity, and (5) method ruggedness, the relative stability of method performance for small variations in critical method parameter values.

For the validation phase of this study, the QC criteria presented in the Region 3 SOP shall be followed as well as the QC criteria specified in Table 2 of this QAPP. Should there be a difference between the Region 3 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.

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

Method Detection Limits

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.

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.

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 SOP submitted by Region 3. Initial and continuing calibration shall follow the procedures specified in the SOP.

B9 Non-Direct Measurements

Not applicable.

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B10 Data Management

Data will be managed according to participating laboratories' data management policies and policies specified in the HF Quality Management Plan. For example, ESD-LV will follow the NERL IIQMP, 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).

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SECTION C. ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

This project will have a Technical Systems Audit (TSA) performed during the laboratory validation phase of the study. The findings of the TSA will be reported to the Research Technical Lead, NERL Director of Quality Assurance, and Program QA Manager (QAM).

After the laboratory verification and the laboratory validation phase of the project are 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 and/or delegate.

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

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

Table 3. Schedule of Audits.

Type of Audit	Frequency	Details
TSA	Conducted at each stage of method testing and development (e.g., during optimization of instrumental parameters, during optimization of method, etc.)	Performed by participating organization's QAM
Surveillance audit	Conducted once during laboratory validation phase	Performed by participating organization's QAM
ADQ	Conducted after method verification and validation once data has been collected.	Performed by participating organization's QAM

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 Research Technical Lead. Results of the verification of corrective actions and audit closure will be monitored by the organization's QAM and reported to Program QA Manager and NERL Director of Quality Assurance.

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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.

Data packages submitted by the participating laboratories shall include the following:

- Summary level data in spreadsheet format; (format to be provided);
- Individual results (in µg/L), including results for all target compounds found in all blanks.
- **Note**: Laboratories will not be allowed to average results or perform other data manipulations beyond those described in Region 3 SOP. 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;
- A list of the composition and concentrations of target compounds in the calibration, QA/QC, all samples analyzed, and a run chronology;
- Saved at participant lab - not reported unless asked by Technical Research Lead or Program QAM: Copies of all raw data, including chromatograms, quantitation reports, spectra, bench sheets, and laboratory notebooks showing weights, volumes, and other data that will allow verification of the calculations performed and will allow the final results reported to be traced to the raw data. Details and raw data from all runs may be requested and reviewed for determination as to whether further testing is required;
- A written report that details any problems associated with analysis of samples or standard solutions. The written report also must provide comments on the performance of any part of Region 3 SOP;
- A detailed description of any modifications to the procedures specified in Region 3 SOP;
- Laboratories also will be instructed to use the following rules in reporting results:
    - Quantitative results above or at the MDL - report value;
    - Quantitative results below the MDL - report value but "U" flag with footnote giving the MDL;
    - Nonquantitative results - report as less than the MDL value and state the MDL value;
    - ND (not detected) – use when no peaks associated with the compound are identified on the chromatogram;
    - The terms zero or trace are not to be used.

For the verification phase of the study, the participating laboratories shall have until March 22, 2012 (tentatively) to submit the data package to the Technical Research Lead. The Technical Research Lead and Principal Investigators will have 4 days from the receipt of the data to evaluate and report the findings. A conference call will be conducted after this phase with the participating laboratories to ensure the success of the multi-lab verification process.

For the validation phase of the study, the participating laboratories shall have until April 19, 2012 (tentatively) to submit the data package to the Technical Research Lead. The Technical Research Lead and Principal Investigators will have 5 days from the receipt of the data to evaluate and report the findings. A conference call will be conducted after this phase with the participating laboratories to ensure the success of the multi-lab validation process.

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D2 Verification and Validation Methods

Generated data will be reviewed by the PI 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.

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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:

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

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.

EPAPAV0111538

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.

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Appendix A

Region 3 SOP

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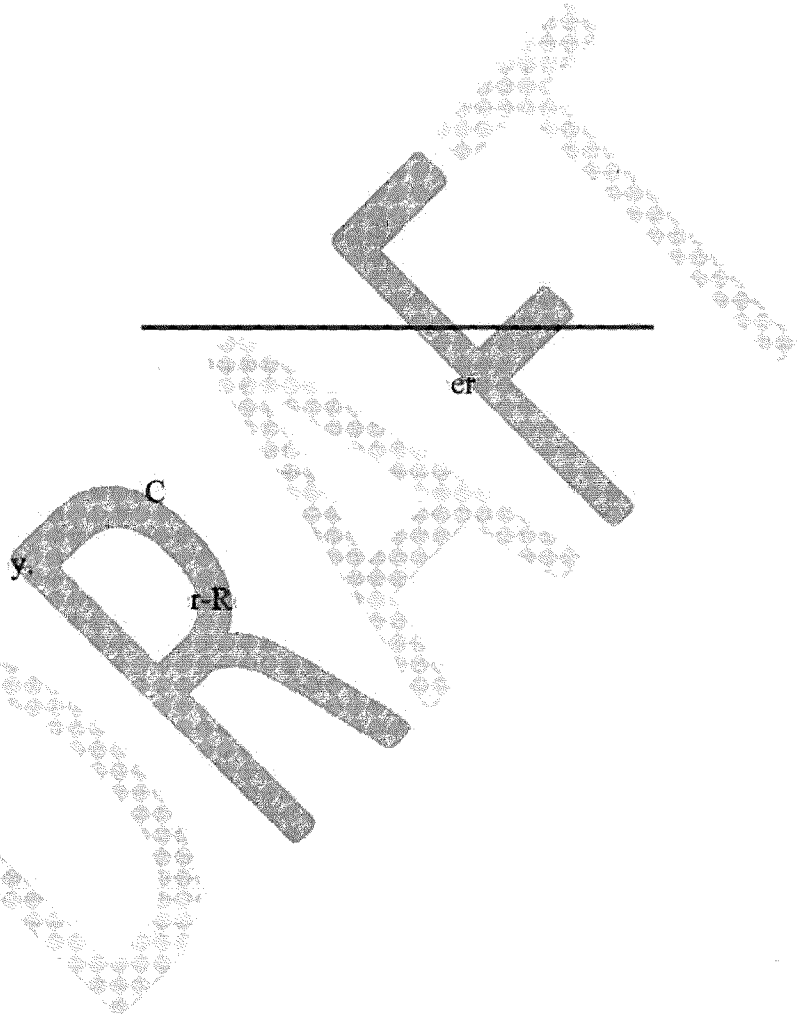

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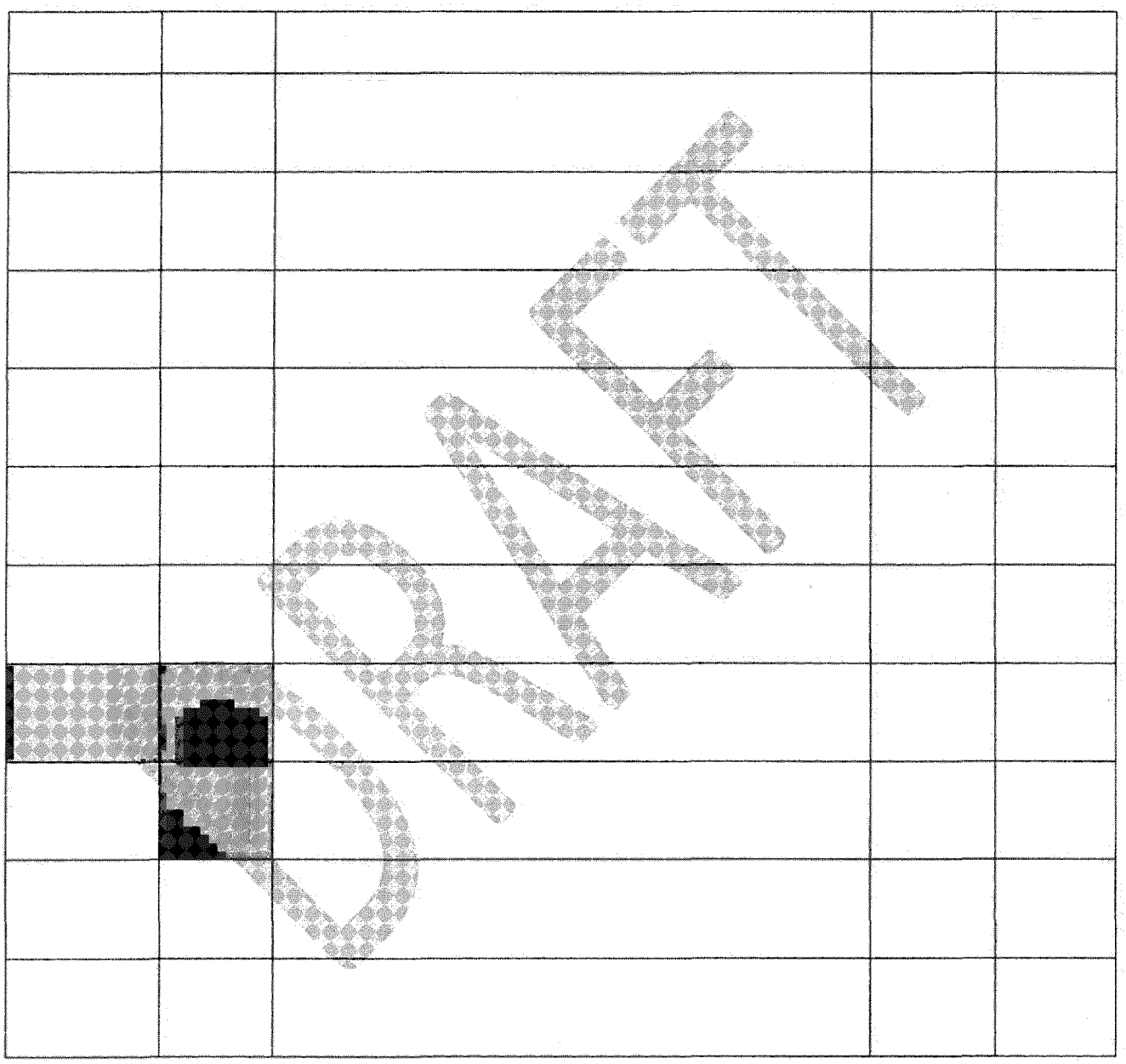
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Appendix B

NRMRL Chain of Custody Form

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USEPA, ORD, NRMRL

Sample Analysis Request and Chain of Custody (COC) Record

Project: Location: Project Manager/Phone:	Lab Name: Address: Contact Name/Phone:
Shipping Method: Shipping Tracking Number:	Shipping Date: Total Number of Shipping Containers:

Sample Number	Sample Matrix/Description	Date/Time Collected	Container Type	Preservation	Number of Containers	Requested Parameters						Special Instructions

Relinquished By: Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

Received By: Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

Comments:

Relinquished By: Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

Received By: Printed name: _____ Signature: _____ Affiliation: _____ Date:_____ Time:_____

Comments:

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

EPA-442 (CIN) (09/08)

Appendix C

NRMRL SOP for *Performing Audits of Data Quality (ADQs)*

EPAPAV0111560

STANDARD OPERATING PROCEDURE NRMRL	Category	QA
	Document No.	LSAS-QA-02-0
	Effective Date	5/4/11
	Revision Date	Not Applicable
	Revision No.	0
	Page No.	1 of 8
	Approval:	

TITLE: Performing Audits of Data Quality (ADQs)

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 project 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 NRMRL research activities.

2.0 Revision History

History of document changes

Date	Revision No.	Change	Ref. Section
01/03/11	0	New Procedure	Not Applicable

3.0 Persons Affected

This SOP applies to QA Managers (or designees) who perform ADQs and Technical Lead Persons (TLPs) who have data subjected to ADQs.

4.0 Policy

The NRMRL Quality Management Plan (QMP) requires that ADQs be performed by the QA Manager (or designee) for all QA Category 1 and 2 research projects. ADQs may also be performed for QA Category 3 and 4 research projects when specifically requested by management, when dictated by program requirements, or as determined to be necessary by the TLP or QA Manager. ADQs are performed by QA Managers or their designees.

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STANDARD OPERATING PROCEDURE *NRMRL*	Category	QA
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5.0 Definitions

5.1 Audit of Data Quality (ADQ) - a 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 Lead Person (TLP) – the NRMRL employee who is responsible for all technical aspects of a research project. For extramural projects, the Contracting Officer Representative (COR) or Project Officer (PO) is the TLP.

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 QA Category 1 and 2 projects. (The requirement for an ADQ and associated responsibilities must be included in the quality assurance project 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 TLP must coordinate audit activities with the QA Manager.

6.2 The TLP notifies the QA Manager 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

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projects may generate multiple data packages. The identification of specific data packages for review is made by the QA Manager to focus on the more critical parameters and to provide the best representation of the data generated. The QA Manager 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 as soon as possible after data generation begins (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 Manager.

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

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

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.

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

6.4 The QA Manager or designee prepares a checklist based on the type of data generated, such as the example checklist provided in Attachment 1 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 Manager 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 Manager. If problems are identified, additional verification is needed.

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

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

- **Introduction** to include audit information (e.g., TLP, 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

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deficiency and any effect on data quality and the recommended corrective action.

6.8 The QA Manager shall distribute the report to the TLP and the TLP's supervisor.

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

6.10 For ADQ findings, the QA Manager reviews the ADQ corrective actions and provides documentation to the TLP 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 Manager for verification prior to the use or reporting of the results.

6.12 The TLP must maintain the ADQ report and any responses in the project files. The QA Manager 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, EPA/600/R-99/080, January 2000

7.2 NRMRL Quality Management Plan, current edition

Prepared by: ETAVOS/MH
LSAS/LMD

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ATTACHMENT 1

EXAMPLE ADQ CHECKLIST

GENERAL INFORMATION

EPA Technical Lead Person (TLP):
Project Title:
Laboratory (Organization):
Report Identification/Date:
Sample Type(s)/Analyte(s):
QA Reviewer: ADQ Date:

ITEMS REVIEWED

	Yes	No	NA	Comments
Sample Information				
Are samples uniquely identified and correctly transcribed throughout the data package to the summary of results?				
Does sample collection documentation indicate that samples were collected as described in the QAPP?				
If calculations were used for sample collection information (e.g., air volumes), are these calculations correct?				
Does sample collection documentation indicate appropriate preservation?				
If applicable, is chain-of-custody documentation complete?				

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	Yes	No	NA	Comments
Sampling and Analysis Method Information				
Were methods specified in QAPP used?				
If method modifications were used, are these modifications appropriate and well documented?				
Were sample preparation and analytical method holding times met?				
Summary Of Results				
Are the correct units reported?				
Are reported results correct (verify any calculations performed[1])?				
Were QC samples (blanks, second source checks, surrogates, spikes, replicates) analyzed at the frequency specified in the QAPP?				
Did QC results meet the requirements specified in the QAPP?				
Raw Data				
Were instruments calibrated as described in the QAPP?				
Were calibration criteria met for initial and continuing checks?				
Were reported results analyzed within calibration range?				
Were instrument outputs correctly transcribed to data summary?				

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	Yes	No	NA	Comments
Data Qualifiers				
If QC requirements were not met, were corrective actions performed?				
If necessary, were data qualified appropriately?				

[1] A percentage of input values for software program-generated calculations and hand calculations must be verified, as determined to be appropriate by the QA Manager. If problems are identified, additional verification is needed.

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