GWERD QUALITY ASSURANCE PROJECT PLAN

Title: Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO: Analysis of Samples by the EPA Region VII Contract Laboratory for the November 2012 Sampling Event

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Principal Investigator Date

APPROVALS:

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Branch Chief Date

/S/ 2/25/2013

David Jewett, Technical Research Lead for Case Studies Date

/S/ 2/25/2013

Steve Vandegrift – GWERD QA Manager Date

Distribution List:

Distribution List:
Russell Neill, EPA/ORD/NRMRL/GWERD
Amy Wolfe, EPA/ORD/NRMRL/GWERD
Tony Lee, EPA/ORD/NRMRL/GWERD
Steve Acree, EPA/ORD/NRMRL/GWERD
Randall Ross, EPA/ORD/NRMRL/GWERD
Sujith Kumar, Shaw Environmental
Shauna Bennett, Shaw QC Coordinator*
Gregory Oberley, EPA Region 8
Mark Burkhardt, EPA Region 8
Zell Peterman, U.S. Geological Survey
Alex Kirkpatrick, Student Contractor
Cherri Adair, EPA/ORD/NRMRL/GWERD
Mark White, EPA/ORD/NRMRL/GWERD
Jorge Santo Domingo, EPA/ORD/NRMRL
Cynthia Caporale, EPA Region 3

*will distribute to Shaw staff

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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; or to 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.

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/hydraulic fracturing). The results of the research projects will provide the foundation for EPA's 2014 study report.

This QAPP provides information concerning the Well Injection stage of the HF water cycle as found in Figure 1 of the HF QMP and as described in the HF Study Plan. Appendix A of the HF QMP includes the links between the HF Study Plan questions and those QAPPs available at the time the HF QMP was published.

Analysis of Samples for Metals by ICP-MS and ICP-OES, Mercury by Cold Vapor Atomic Absorption Spectrometry (AAS), and Volatile Organic Compounds using GC/MS by Southwest Research Institute

Purpose

The purpose of this Addendum to the QAPP for the Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO, is to provide specifications and quality control (QC) acceptance criteria for the analysis of samples collected in November 2012 for metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). Samples were also analyzed for mercury by cold vapor AAS and volatile organic compounds (VOCs) by purge and trap-GC/MS.

The samples were analyzed through a Region 7 contract with ARDL, Inc. Southwest Research Institute (SwRI) is a subcontractor to ARDL, Inc. In previous sampling events, these samples were analyzed by Shaw for metals and VOCs, and by an EPA Superfund Analytical Services Contract Laboratory for metals.

Sample Handling and Custody

Samples were packed in coolers (on ice) and shipped overnight via UPS or FedEx to the laboratory, with appropriate chain of custody forms, and the cooler was sealed with custody seals.

Sample receipt and log-in was conducted as described in SwRI SOP #TAP-01-0103-016, "Sample Receipt Inspection."

Analytical Methods

The contract laboratory analyzed water samples for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V by ICP-MS. In addition, the contract laboratory analyzed water samples for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Na, P, S, Sb, Si, Sr, Ti, and Zn by ICP-OES. The contract laboratory performed the analysis in accordance with the EPA Methods 6020A for ICP-MS and 200.7 for ICP-OES. Both total and dissolved metals were analyzed. Sample digestion for total metals was done according to EPA Method 200.7. Samples for dissolved metals were not digested. Samples were also analyzed for mercury and volatile organic compounds in accordance with EPA Methods 7470A and EPA Method 8260B, respectively.

SOW and Project Plan Specifications:

A Statement of Work (SOW) was prepared and QA-approved prior to submitting the samples to the laboratory for analysis describing requirements for analytical methods and QA/QC.

The SOW Reporting Limits (RLs) are listed in the following tables.

Analyte	ICP-AES* RL (mg/L)	ICP-MS RL (µg/L)
Al	0.200	20
Sb		2
As		0.2
Ba	0.200	
Be	0.005	
Cd		0.2
Ca	0.5	
Cr		2
Co	0.050	
Cu		2
Fe	0.100	
Pb		0.10
Mg	0.5	
Mn	0.015	
Ni		1
K	0.5	
Se		1
Ag	0.010	
Na	1.75	
Tl		0.24
V	0.050	1
Zn	0.060	

Additional Analytes	ICP-AES RL (mg/L)	ICP-MS RL (µg/L)
B	0.35	-
Li		3
Mo		1
P	0.06	-
Si	0.5	-
Sr		5
Th		1
Ti	0.01	-
U		1

*AES: Atomic Emission Spectroscopy, equivalent to OES

(Note that Reporting Limits are equivalent to Quantitation Limits. SwRI uses RL in their reporting.) SOW requirement for the Reporting Limit for Hg by CV AAS is 0.2 µg/L.

The dissolved metals for ICP-MS or -OES analysis shall not be digested. If any ICP-MS analyte is detected by ICP-OES at levels equal to or greater than 100 times the ICP-MS RLs, that analyte will be reported from the ICP-OES and not ICP-MS.

TARGET COMPOUNDS	*TARGET LIMITS (µg/L)*	
	MDL	**QL or LOQ**
1,1,1-Trichloroethane	0.13	0.5
1,1,2-Trichloroethane	0.21	0.5
1,1-Dichloroethane	0.13	0.5
1,1-Dichloroethene	0.12	0.5
1,3,5-Trimethylbenzene	0.05	0.5
1,2,4-Trimethylbenzene	0.05	0.5
1,2-Dichlorobenzene	0.1	0.5
1,2-Dichloroethane	0.21	0.5
1,2,3-Trimethylbenzene*	0.07	0.5
1,3-Dichlorobenzene	0.16	0.5
1,4-Dichlorobenzene	0.17	0.5
Acetone	3.45	10
Benzene	0.06	0.5
c-1,2-Dichloroethene	0.14	0.5
Carbon disulfide	0.21	0.5
Carbon tetrachloride	0.12	0.5
Chlorobenzene	0.08	0.5
Chloroform	0.13	0.5
Diisopropyl ether*	0.11	1
Ethanol*	18	100
Ethyl benzene	0.06	0.5
Ethyl t-butyl ether*	0.08	1
Isopropyl alcohol*	2.37	10
Isopropyl benzene	0.05	0.5
m/p-Xylene	0.09	1
Methyl t-butyl ether	0.09	1
Methylene chloride	0.21	1
Naphthalene	0.31	1
o-Xylene	0.08	0.5
t-1,2-Dichloroethene	0.1	0.5

t-Amyl methyl ether*	0.09	1
t-Butyl alcohol*	2.41	10
Tetrachloroethene	0.13	0.5
Toluene	0.08	0.5
Trichloroethene	0.09	0.5
Vinyl chloride	0.18	0.5
Acrylonitrile		25

*These compounds were not routinely analyzed previously by the laboratory and required a new MDL study.

An MS/MSD (Matrix Spike/Matrix Spike Duplicate) and LCS (Laboratory Control Sample) shall be analyzed for every 20 samples received and/or for a given site as indicated on the shipping document.

Quality Control

The following Tables 1-4 summarizes the acceptance criteria and frequency for the QC checks conducted during the course of sample analysis.

Table 1. QC Checks for ICP-MS

QC Type or Operation	Acceptance Criterion	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is $r \geq 0.998$.	Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL for all analytes.
Initial Calibration Verification	90-110% Recovery	Following instrument calibration for each mass used.
Initial Calibration Blank	$\leq$RL	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	90-110% Recovery	For each mass used, at a frequency of at least after every 10 analytical runs, and at the end of each run.

QC Type or Operation	Acceptance Criterion	Frequency
Low Level Initial Calibration Verification (LLICV) and Low Level Continuing Calibration Verification (LLCCV) at the RL (identified by lab as CRDL)	70-130% Recovery	LLICV, following each instrument calibration., and LLCCV analyzed at the end of each run.
Continuing Calibration Blank	≤RL	At a frequency of at least after every 10 analytical runs, and at the end of each run. Performed immediately after the last CCV.
Interference Check Sample	For solution AB, ±20% of the analyte's true value; for solution A ±5 ppb or ±2 times the RL of the analyte's true value, whichever is greater.	At the beginning of the run after the ICB but before the CCV.
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the RL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution.	Every 20 samples.
Preparation or Method Blank	≤RL	Every 20 samples.
Laboratory Control Sample	80-120% Recovery	Every 20 samples.
Matrix Spike	75-125% Recovery (Recovery calculations are not required if sample concentration >4x spike added.)	Every 20 samples.
Post-Digestion Spike	80-120% Recovery per 6020A (Note that the lab SOP uses 75-125% Recovery)	Each time Matrix Spike Recovery is outside QC limits.

QC Type or Operation	Acceptance Criterion	Frequency
Duplicate Sample	RPD≤20% for sample values ≥5x RL	Every 20 samples.
ICP-MS Tune	Mass calibration must be within 0.1 amu of the true value in the mass regions of interest. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.	Prior to calibration.
Internal Standards	The absolute response of any one internal standard in a sample must not be <70% from the response in the calibration standard.	Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

Table 2. QC Checks for ICP-OES

QC Type	Acceptance Criteria	Frequency
Instrument Calibration	Criteria not given in 200.7.	Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification (QCS or Quality Control Standard)	95-105% Recovery	Immediately after calibration.
Initial Calibration Blank	≤RL	Analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument.
Continuing Calibration Verification (IPC or Instrument Performance Check)	90-110% Recovery	At beginning and end of run; every 10 samples during analytical run.

QC Type	Acceptance Criteria	Frequency
Continuing Calibration Blank	≤RL	Analyzed immediately after every Continuing Calibration Verification (CCV); at beginning and end of run and every 10 samples during an analytical run.
Interference Check Sample (SIC or Spectral Interference Check)	For solution AB, ±20% of the analyte's true value; for solution A ±20% of the interferent's true value, for all other analytes ±5 ppb or within ±2 times the RL of the analyte's true value, whichever is greater.	At the beginning of the run after the ICB but before the CCV and at the end of the run.
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution.	Every 20 samples.
Preparation Blank (LRB or Laboratory Reagent Blank)	≤RL	Every 20 samples.
Laboratory Control Sample (LFB or Laboratory Fortified Blank)	85-115% recovery	Every 20 samples.
Matrix Spike (LFM or Laboratory Fortified Matrix)	75-125% Recovery (Recovery calculations are not required if sample concentration >4x spike added.)	Every 20 samples.
Post-Digestion Spike	85-115% Recovery	Each time Matrix Spike Recovery is outside QC limits.
Duplicate Sample	RPD≤20% for sample values ≥5x RL; for sample values <5xRL, control limit = RL	Every 20 samples.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

Table 3. QC Checks for Mercury by Cold Vapor AAS

QC Type	Acceptance Criteria	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is r≥0.995.	Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL.
Initial Calibration Verification (ICV, second source)	90-110% Recovery	Immediately after calibration.
Initial Calibration Blank (ICB)	≤RL	Analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument.
Continuing Calibration Verification (CCV)	90-110% Recovery	Every 10 samples and at the end of the run.
Lower Limit of Quantitation Check (LLQC) (identified by lab as either CRI or CRA)	70-130% Recovery	Analyzed at beginning and the end of each run.
Continuing Calibration Blank (CCB)	≤RL	Analyzed immediately after every Continuing Calibration Verification (CCV); every 10 samples and at the end of the run.
Method Blank	≤RL	Every 20 samples.
Laboratory Control Sample	80-120% recovery	Every 20 samples.
Matrix Spike	75-125% Recovery (Recovery calculations are not required if the sample concentration is >4x the spike added.)	Every 20 samples.
Post-Digestion Spike	80-120% Recovery per Method 7000B as reference in 7470A (Note the lab sop uses 75-	If a MS and/or MSD are out of control.

QC Type	Acceptance Criteria	Frequency
	125% Recovery)	
Duplicate Sample	RPD≤20% for sample values ≥5x RL; for sample values <5xRL, control limit = RL	Every 20 samples.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

Table 4. QC Checks for VOCs by GC/MS

QC Type	Acceptance Criteria	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration requires RSD ≤15% or for alternate curve fits the correlation coefficient r≥0.990.	Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL.
System Performance Check	BFB Tune must meet tuning criteria in Table 4 of 8260B. Minimum average response factors for the SPC compounds* must meet criteria	Prior to sample analysis; beginning of each 12 hour shift.
Initial Calibration Verification (second source)	75-125% Recovery	Immediately after calibration.
Continuing Calibration Verification (CCV)	80-120% Recovery	Every 12 hours.
Surrogates	70-130% Recovery	All blanks, QC samples, and samples.
Internal Standards	EICP area must not vary by more than a factor of 2 (-50 to +100%) of the mid-point calibration standard. Retention time must not vary by more than 0.50 min of those in the mid-point calibration standard.	All blanks, QC samples, and samples.

QC Type	Acceptance Criteria	Frequency
Method Blank	≤RL ≤2xRL for methylene chloride, acetone, and 2-butanone	After calibration standards. Every 12 hours.
Laboratory Control Sample	70-130% Recovery 60-140% Recovery for t-butyl alcohol, isopropyl alcohol, and ethanol	Every 20 samples.
Matrix Spike	70-130% Recovery 60-140% Recovery for t-butyl alcohol, isopropyl alcohol, and ethanol	Every 20 samples.
Duplicate Sample (MS/MSD)	RPD≤30%	Every 20 samples.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

*SPC compounds minimum response factors (RF):

Chloromethane, min. RF = 0.10
1,1-Dichloroethane, min. RF = 0.10
Bromoform, min. RF = 0.10
1,1,2,2-Tetrachloroethane, min. RF = 0.30
Chlorobenzene, min. RF = 0.30

Data Review and Validation

The laboratory performed data review according to their SOP #TAP-01-0103-014, "Data Review and/or Data Validation."

A QA contractor or EPA staff, under the direction of the GWERD Quality Assurance Manager (QAM) will subsequently conduct an Audit of Data Quality on the data set according to NRMRL SOP LSAS-QA-02-0 "Performing Audits of Data Quality (ADQs)". The auditors will review the information presented in the data report, review the data, and ensure that appropriate project-specific data qualifiers are included in the data tables. Data transcription checks of 100% of the data will also be performed.

Reporting Requirements

Data deliverables were required in electronic format. The electronic data deliverable was to be provided to the RASP PO by 2:00pm CST on the 21st day after receipt of the last sample for a

given sampling event. (NOTE: If the due date falls on a Holiday, Saturday or Sunday, then the deliverables are due to EPA by 12:00pm on the first subsequent business day). Electronic deliverables included all analytical results (field and laboratory QC samples) and the associated narrative. In addition to the normal narrative and Excel spreadsheet required, the laboratory provided an electronic "CLP type" data package that included the written narrative, Forms 1's, QC data, & all supporting raw data. The package was organized and paginated. The entire data package was provided in a .pdf file format. The complete data package in .pdf format was provided within 48 hours of the electronic results and narrative.

NOTE: The associated narrative addressed each of the applicable areas listed below for every parameter group in the task order. This included a statement that the QA/QC criteria for every applicable area were in control or, conversely, that one or more QC outliers were present. For areas with outliers, the narrative specified each parameter which was out of control and the associated samples that were affected. In addition, the narrative indicated any and all corrective actions taken and the results of those actions as well as impact on the associated samples.

- Holding Times
- Initial Calibration
- Continuing Calibration
- Surrogates
- Internal Standards
- Laboratory Duplicate
- Matrix Spike/Matrix Spike Duplicate
- Laboratory Control Sample
- Method Blanks

Revision History

Revision Number	Date Approved	Revision
0	8/30/11	New document
1	4/30/12	Section 1: • Updated project organization (Jewett replaced Puls, added ALS Environmental contact, added Mravik with new duties) • Updated accreditation information in 1.5 to provide clarification Section 2: • Sampling timing has changed (also see Table 4) and been extended until spring of 2013 • Revised dissolved gas/methane isotope sample collection method to allow for more effective collection of samples and removed hydrogen and carbon dioxide as target analytes because of their limited value to the study • Changed preservative for low molecular weight acids from TSP to sodium hydroxide here and in Table 5 because TSP was identified as a source of acetate contamination • Replaced Standard Methods with EPA Methods for turbidity as it more appropriately reflects the method used as well as the preference for EPA Methods • Replaced Shaw lab sample contact with current personnel • CRDS will be used in the second and subsequent sampling events for H and O stable isotopes of water instead of IRMS, as CRDS is replacing the IRMS for analysis of water isotopes at RSKERC using RSKSOP-334, also added to Table 5 • Add sample collection for dissolved sulfate and dissolved sulfide for stable isotope analyses of sulfur; also added to Table 5. Needed to understand links between C and S cycling in groundwater • Added updated SOW for Isotech for the stable isotope analysis of sulfur • Updated information on Region VIII QA/QC regarding on-site QA audit and PEs • Added RSKSOP-334 for water isotopes (CRDS is replacing IRMS); also add to References and Table 5 • Added RPD/Blank sample data analysis • Provided clarification on sulfide and turbidity calibration checks • Duplicate acceptance criteria was changed from RPD<15 to

		RPD≤15, which was the original intent • Deleted 2.10.1 as information is redundant Section 3: Provided clarification on ADQ and PE requirements and to whom audit reports are provided Section4: • Added text on data report review and data usability to reflect actual practice Section 5: • Updated references, replaced alkalinity method with correct one and added CLP guidelines on data review Section 6: • Added this table on QAPP revision history • B and NO_3+NO_2 were removed from Table 3 as critical analytes due to the fact that they are not critical • Benzene, toluene, ethylbenzene, and xylenes were add to Table 3 as critical analytes • Table 5: Replaced EPA Method 220.7 with correct one, 200.7; deleted RSKSOP-259 as only RSKSOP-299 is used; replaced holding times of "No Information" with specific times for stable C and H isotopes based on info from lab • MDLs and QLs in Table 7 for RSKSOP-299v1 were changed to those listed in the SOP; footnote added to indicate that current MDLs and QLs are included in the laboratory reports • In Table 7 deleted gases that are not analyzed due to limited value to study (ethylene, acetylene, carbon dioxide, hydrogen) • Replaced Table 8 with update (removed compounds not analyzed and replaced limits with more recent ones determined by lab) • Provided corrections to QC requirements for DIC/DOC and added requirements for RSKSOP-334 for O, H stable isotopes of water in Table 9 • Replaced Table 10 with one the lab actually uses as discovered during the lab TSA July 2011 • Addition of tables 15; Isotech S/O isotope QA/QC • Added Table 18 of Data Qualifiers developed by PIs for data review/qualification
1, Addendum	11/28/12	• Title changed to reflect the focus of this addendum

		• Addition of specifications and quality control (QC) acceptance criteria for the reanalysis of samples for metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for the May 2012 sampling event. The EPA Superfund Analytical Services Contract Laboratory Program (EPA CLP) analyzed water samples for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Th, Tl and U by ICP-MS.
1, Addendum No. 2	1/10/13	• Title changed to reflect the focus of this addendum • Scope of addendum is limited to the SwRI analysis of samples for metals, mercury, and VOC analysis