GWERD QUALITY ASSURANCE PROJECT PLAN

Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO: Reanalysis of Samples for Metals by the EPA Superfund Analytical Services Contract Laboratory Program for the May 2012 Sampling Event

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Principal Investigator Date

APPROVALS:

/s/ 12/20/2012
Branch Chief Date

/s/ 12/20/2012
David Jewett, Technical Research Lead for Case Studies Date

/s/ 12/20/2012
Steve Vandegrift – GWERD QA Manager Date

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
*will distribute to Shaw staff

Mark Burkhardt, EPA Region 8
Zell Peterman, U.S. Geological Survey
Alex Kirkpatrick, Student Contractor
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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 Chemical Mixing; and Flowback and Produced Water stages 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.

Reanalysis of Samples for Metals by ICP-MS using the Contract Laboratory Program

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 re-analysis of samples collected May 2012 for trace metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Although the original ICP-MS analysis was completed using the appropriate QC checks, including use of the Interference Check Solution (ICS) for this case study, as an additional quality check the samples were analyzed using the EPA Superfund Analytical Services Contract Laboratory Program.

The samples were analyzed through the EPA Superfund Analytical Services Contract Laboratory Program (EPA CLP). Samples were sent for analysis under the EPA CLP Inorganic Statement of Work ISMO1.3, Exhibit D – Part B, "Analytical Methods for Inductively Coupled Plasma – Mass Spectrometry" (http://www.epa.gov/superfund/programs/clp/ism1.htm#pdf), with some minor requested modifications described in the Analytical Methods section below.

Sample Handling and Custody

Samples were packed in coolers (without ice) and shipped overnight via UPS or Fedex, to the contract laboratory awarded the work through the CLP, with appropriate chain of custody forms and the cooler was sealed with custody seals.

Sample receipt and log-in were conducted as described in EPA CLP Inorganic Statement of Work ISMO1.3, Exhibit F – "Chain-of-Custody, Document Control, and Written Standard Operating Procedures" (http://www.epa.gov/superfund/programs/clp/download/ism/ism12e-h.pdf).

Analytical Methods

The contract laboratory analyzed water/aqueous samples for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Th, Tl and U by ICP-MS. The reanalysis did not include Hg. Mercury was excluded because the sample holding time was exceeded. The contract laboratory performed the analysis in accordance with the EPA CLP Inorganic Statement of Work (SOW) ISM01.3, Exhibit D – Part B, "Analytical Methods for Inductively Coupled Plasma – Mass Spectrometry" (http://www.epa.gov/superfund/programs/clp/ism1.htm#pdf), with the following modifications:

[Note that for analysis conducted under the EPA CLP SOW, samples are grouped into batches of up to 20 called Sample Delivery Groups (SDGs).]

Modification to the SOW Specifications:

The contract Laboratory analyzed water/aqueous samples for the Target Analyte List (TAL) (Al, As, Cd, Cr, Cu, Ni, Pb, Sb, Se, and Tl) and the additional analytes Molybdenum (Mo, CASRN 7439-98-7), Thorium (Th, CASRN 7440-29-1) and Uranium (U, CASRN 7440-61-1) by ICP-MS as indicated on the Traffic Report/Chain of Custody Record and Laboratory Scheduling Notification form.

The Contract Required Quantitation Limits (CRQLs) for the following analytes and matrices were modified. All other CRQLs remained at the level specified in the SOW.

Analyte	**Aqueous CRQL (µg/L)**	**Aqueous Spike level (µg/L)**
Molybdenum	1.0	100
Thorium	1.0	100
Uranium	1.0	100

Some samples may be received at a reduced volume, less than 100 ml but greater than 50 ml. The samples were not be shipped at 4°C (±2°C). The Laboratory noted the temperature at the time of receipt in the SDG Narrative and proceeded with analysis.

Due to the reduced volume, the Laboratory used different samples to prepare the Duplicate sample and the Matrix Spike sample. The Laboratory prepared the original samples at an initial and final volume of 50 mL, and the Duplicate and Matrix Spike sample at initial and final volumes of 25 mL, reducing the reagents added appropriately.

The Laboratory:

- Performed the Initial Calibration as currently in the SOW except that the lowest non-blank standard was set at the CRQL for all analytes (SOW and additional).
- Added Mo, Th and U to the ICV and CCV at appropriate mid-range concentrations.
- Evaluated the ICB and CCB against the (modified) aqueous CRQLs.
- Performed the Matrix Spike at the levels specified above. Post-digestion spike requirements were per the SOW.
- Added Mo, Th and U to the LCS at 2 times the modified CRQLs.
- Added Mo, Th and U to Forms 1, 2A, 3, 4B, 5A (5B), 6, 7, 8, 9, 11, 13, and 16.

The acceptance criterion for the initial calibration correlation coefficient was modified to $r \geq 0.998$.

The Laboratory re-analyzed the low-level (at CRQL) calibration standard at the end of the run. The Percent Difference between the true value and the measured value was within ±30%.

The CCV and CCB was analyzed after every ten analytical samples.

The Laboratory was not required to add Th or U to the ICSA/ICSAB solutions. The Laboratory used a true value of zero (0) and acceptance windows of ±2x the modified aqueous CRQL unless a non-zero value was determined for the solutions.

The Laboratory was not required to bracket Th or U with an internal standard having a mass greater than 238. The analysis of the Bismuth internal standard at mass 209 was sufficient.

As part of the complete data package, the Laboratory provided:

- Method Detection Limits for Mo, Th and U.
- All masses monitored, and all masses used for quantitation.
- All corrections applied to the data to handle interferences and used to generate the final corrected instrument result.

Quality Control

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

Table 1. CLP 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≥0.998.	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 CRQL for all analytes.
Initial Calibration Verification	90-110% Recovery; % RSD≤5% for all replicate integrations	Following each instrument calibration for each mass used.
Initial Calibration Blank	≤CRQL	Following each instrument calibration, immediately after the ICV.

Continuing Calibration Verification	90-110% Recovery; % RSD≤5% for all replicate integrations;	For each mass used, at a frequency of at least after every 10 analytical runs, at the beginning of each day, and at the beginning and end of each run.
Low Level (at CRQL) Calibration Verification	70-130% Recovery	The Laboratory shall re-analyze the low-level (at CRQL) calibration standard at the end of each run.
Continuing Calibration Blank	≤CRQL	At a frequency of at least after every 10 analytical runs, at the beginning of each day, and at the beginning and end of each run. Performed immediately after the last CCV.
Interference Check Sample	±20% of the analyte's true value or ±2 times the CRQL of the analyte's true value, whichever is greater.	At the beginning of the run after the ICB but before the CCV.
Serial Dilution for ICP	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.	For each matrix type or for each SDG, whichever is more frequent.
Preparation Blank	≤CRQL	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Laboratory Control Sample	70-130% Recovery	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Spike Sample	75-125% Recovery	For each matrix type or for each SDG, whichever is more frequent.

Post-Digestion Spike	75-125% Recovery	Each time Spike Sample Recovery is outside QC limits.
Duplicate Sample Analysis	RPD<20 for sample values ≥5x CRQL; for sample values <5xCRQL, control limit = CRQL	For each matrix type or for each SDG, whichever is more frequent.
ICP-MS Tune	Mass calibration must be within 0.1 amu over the range of 6 to 210 amu, or the percent Relative Standard Deviation (%RSD) of all the integrations of the absolute signals of the analytes must be ≤5.0%.	Prior to calibration.
Internal Standards	The absolute response of any one internal standard must not deviate more than 60-125% from the original response in the calibration blank.	Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.
Determination of Method Detection Limits		Prior to contract award, annually thereafter, and after major instrument adjustment.

Data Review and Validation

Initial data validation wa conducted by the EPA CLP Sample Management Office (SMO) contractor. The EPA CLP SMO contractor performed a data assessment on the laboratory's hardcopy and electronic deliverable based on the requirements of the EPA CLP SOW ISMO1.3, the elements of the modified analysis as described above (and in the Request for Proposal),and the "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (http://www.epa.gov/superfund/programs/clp/download/ism/ism1nfg.pdf).

Neptune & Co., a QA contractor, under the direction of the GWERD Quality Assurance Manager (QAM) subsequently conducted 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 reviewed the information presented in the EPA CLP SMO data assessment, reviewed the data, and ensured that appropriate project-specific data qualifiers were added to the data tables. Data transcription checks occurred after the ADQ was completed.

Reporting Requirements

Hardcopy and electronic data reporting were required as specified per EPA CLP SOW ISM01.3. All hardcopy and electronic data were adjusted to incorporate modified specifications. This included attaching a copy of the requirements for modified analysis to the SDG Narrative. All samples analyzed for the same fraction within an SDG were analyzed under the same fractional requirements. The Laboratory did not include data for the same fraction with different requirements in the same SDG.

The Laboratory included the Modification Reference Number on each hardcopy data form under the "Mod. Ref. No:" header appearing on each form as well as the SamplePlusMethod/ClientMethodModificationID element of the electronic deliverable. The Laboratory also documented the Modification Reference Number and Solicitation Number on the SDG Coversheet and SDG Narrative.

Table 2. QAPP revision history.

Revision Number	Date Approved	Revision
0	8/30/2011	New document
1	4/30/2012	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$\leq$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	11/28/2012	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.