

GWERD QUALITY ASSURANCE PROJECT PLAN

Title: Hydraulic Fracturing Retrospective Case Study, Bradford-Susquehanna Counties, PA:
Reanalysis of Samples for Metals by the EPA Superfund Analytical Services Contract
Laboratory Program for the April 2012 Sampling Event

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Disclaimer

EPA does not consider this internal planning document an official Agency dissemination of information under the Agency's Information Quality Guidelines, because it is not being used to formulate or support a regulation or guidance; 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](http://www.epa.gov/hydraulic%20fracturing)). The results of the research projects will provide the foundation for EPA's 2014 study report.

This QAPP provides information concerning the Chemical Mixing, Well Injection, and Flowback and Produced Water stage projects 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 (Revision 1) for the Hydraulic Fracturing Retrospective Case Study, Bradford-Susquehanna Counties, PA is to provide specifications and quality control (QC) acceptance criteria for the re-analysis of samples collected April 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 was 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, Cd, Cr, As, Cu, Pb, Ni, Se, Tl, U, Li, Th, and Sb 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) 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 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).]

The contract Laboratory analyzed water/aqueous samples for the Target Analyte List (TAL) (Al, Sb, As, Cd, Cr, Cu, Pb, Ni, Se, and Tl) and the additional analytes Lithium (Li, CASRN 7439-93-2), Thorium (Th, CASRN 7440-29-1) and Uranium (U, CASRN 7440-61-1) by ICP-MS as Section No. 1

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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)
Lithium	10.0	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 Li, 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 Li, Th and U to the LCS at 2 times the modified CRQLs.
- Added Li, 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 shall be within ±30%.

The CCV and CCB was analyzed after every 10 analytical samples.

The Laboratory was not required to add Li, 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

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CRQL unless a non-zero value was determined for the solutions.

The Laboratory did not use Lithium as an internal standard.

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 Li, 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 $r \geq 0.998$.	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 $\leq 5\%$ for all replicate integrations	Following each instrument calibration for each mass used.
Initial Calibration Blank	\leq CRQL	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	90-110% Recovery; % RSD $\leq 5\%$ 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.

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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	\leq 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	$\pm 20\%$ 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	\leq 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 $\geq 5 \times$ CRQL; for sample values $< 5 \times$ CRQL, 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 $\leq 5.0\%$.	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 was 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 ISM01.3, 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 auditor will 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.

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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.

Revision History

Table 1. QAPP revision history.

Revision Number	Date Approved	Revision
0	10/5/2011	New document
1	04/12/2012	<p>Section 1:</p> <ul style="list-style-type: none"> Updated project organization (Jewett replaced Puls, added ALS Environmental contact, added Mravik with new duties) Updated accreditation information in 1.5 to provide clarification <p>Section 2:</p> <ul style="list-style-type: none"> Added paragraph on sampling protocol with other stakeholders on site to minimize distractions and therefore minimize potential for errors during sampling. 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 Revised dissolved gas sample collection method to allow more effective collection of samples and changed preservative from TSP to sulfuric acid because TSP cannot be effectively used when collecting samples in inverted bottle position. Also removed hydrogen and carbon dioxide as target analytes because of their limited value in the study. Added Al, Li, and Th to ICP-MS analyses because Al detection limits were too high relative to the secondary MCL for Al and because Li and Th are present in Marcellus water. Removed Sb from ICP-OES analysis because of interference problems. Added radiometric (Ra-226, Ra-228, gross alpha and beta) analyses/with information on bottle types and preservation methods. Marcellus water is known to contain these and their analyses may aid in evaluating potential impacts. Replaced Standard Methods with EPA Methods for turbidity and alkalinity as they more appropriately reflect the method used and preference is for EPA Methods Added clarification for which samples require filtration 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 Added ALS Environmental for analysis of ^{226}Ra, ^{228}Ra, gross alpha/beta Added statement of work for ALS radiometric analysis and updated SOW for Isotech with clarification of requirements

		<ul style="list-style-type: none"> • Updated information on Region VIII QA/QC regarding on-site QA audit and PEs • Added RSKSOP-334 for water isotopes (CRDS is replacing IRMS) • Added ALS QA/QC requirements • 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 • Provided clarification on ADQ and PE requirements and to whom audit reports are provided <p>Section 4:</p> <ul style="list-style-type: none"> • Added additional information on data report review and data usability to reflect actual practice <p>Section 5:</p> <ul style="list-style-type: none"> • Added references, ALS Environmental SOPs, RSKSOP for analysis of stable isotopes of H and O in water by CRDS, and CLP guidelines on data review <p>Section 6:</p> <ul style="list-style-type: none"> • Added this table on QAPP revision history • Added dissolved gases as critical analytes; this was an oversight in the original QAPP and should have been included • Added radiochemicals to Table 5, holding times for stable isotopes C, H, Sr and SOP for CRDS • Added DIC/DOC to Table 7 (it was missing) • Replaced Table 8 with update (removed compounds not analyzed and replaced limits with more recent ones determined by lab) • Corrected QC requirements for DIC/DOC and added additional ones for O,H stable isotopes of water by CRDS in Table 9 • Replaced Table 10 with one the lab actually uses as discovered during the lab TSA July 2011 • Added Tables 16 and 17 for ALS QA/QC requirements • Added Table 18 of Data Qualifiers developed by PIs for data review/qualification
1, Addendum	December 10, 2012	<ul style="list-style-type: none"> • Title changed to reflect the focus of the Addendum • Scope of Addendum is limited to the CLP metals reanalysis