QUALITY ASSURANCE PROJECT PLAN
Category I Research Project

Assessment of the fate of contaminants in hydraulic fracturing wastewater treatment process and characterization of wastewater residuals

EPA QA Log Number: W-17020

U.S. Environmental Protection Agency
Contract No. EP-C-09-041
Work Assignment No. 4-02 (3-02)

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Revision 1
January 15, 2014

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

This QAPP provides information concerning the Wastewater Treatment and Waste Disposal 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.

SECTION A - PROJECT MANAGEMENT

A1 TITLE AND APPROVAL SHEET

Shaw Environmental & Infrastructure, Inc. Concurrences:

1. E. Radha Krishnan, P.E., Program Manager

/s/	1/16/14
Signature	Date

2. Gune Silva, Ph.D., Project Leader

/s/	1/16/14
Signature	Date

3. Steven Jones, ASQ CQA/CQE, Quality Assurance Manager

/s/	1/16/14
Signature	Date

U.S. Environmental Protection Agency Endorsement for Implementation:

1. Samuel Hayes, Ph.D., Water Supply and Water Resources Division, Associate Division Director

/s/	1/27/14
Signature	Date

2. Christopher A. Impellitteri, Ph.D., Principal Investigator

/s/	1/18/14
Signature	Date

3. Craig L. Patterson, P.E., Work Assignment Manager

/s/	1/16/14
Signature	Date

4. John Olszewski, Ph.D. Water Supply and Water Resources Division, Quality Assurance Manager

/s/	1/27/14
Signature	Date

5. Holly Ferguson, Environmental Technology Assessment, Verification and Outcomes Staff, Quality Assurance Manager

/s/	1/27/14
Signature	Date

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A2.1 ACRONYMS/DEFINITIONS

ADQ	Audit of Data Quality
ASQ	American Society for Quality
AWBERC	Andrew W. Breidenbach Environmental Research Center
CQA	Certified Quality Auditor
CQE	Certified Quality Engineer
DER	Duplicate Error Rate
DRO	Diesel Range Organics
EPA	U.S. Environmental Protection Agency
GRO	Gasoline Range Organics
HASP	Health and Safety Plan
HAZWOPER	Hazardous Waste Operations and Emergency Response
HF	Hydraulic Fracturing
HFWW	Hydraulic Fracturing Wastewater
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
MDC	Minimum Detectable Concentration
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NRMRL	National Risk Management Research Laboratory
ORD	Office of Research and Development
ORISE	Oak Ridge Institute for Science and Education
OSHA	Occupational Safety and Health Administration
P.E.	Professional Engineer
PI	Principal Investigator
POTW	Publicly Owned Treatment Works
PRDL	Project-Required Detection Limits
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QL	Quantitation Limit
QMP	Quality Management Plan
RCRA	Resource Conservation and Recovery Act
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SEM	Scanning Electron Microscopy
SHAW	Shaw Environmental & Infrastructure, Inc.
SHEM	Safety, Health, and Environmental Management
SOP	Standard Operating Procedure
SVOC	Semi-volatile organic compound
SWRI	Southwest Research Institute
TDS	Total Dissolved Solids
T&E	Test and Evaluation
TOC	Total Organic Carbon
TSA	Technical System Assessment
TSS	Total Suspended Solids

VOC	Volatile Organic Compound
WA	Work Assignment
WW	Wastewater
WSWRD	Water Supply and Water Resources Division
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

A3 DISTRIBUTION LIST

U.S. Environmental Protection Agency

Samuel Hayes, Ph.D.	Water Supply and Water Resources Division, Associate Division Director
Christopher A. Impellitteri, Ph.D.	Water Supply and Water Resources Division, Principal Investigator
Craig L. Patterson, P.E.	Water Supply and Water Resources Division, Work Assignment Manager
John Olszewski, Ph.D.	Water Supply and Water Resources Division Quality Assurance Manager
Holly Ferguson	National Risk Management Research Laboratory Environmental Technology Assessment, Verification and Outcomes Quality Assurance Manager
Kit Daniels	Project Scientist
Dana Macke	Project Scientist
Barry Evans	Region 7, Kansas City, KS
Jesse Kiernan	Region 8, Golden, CO
Cindy White	Region 4, Montgomery, AL
Steve Harmon	Project Scientist

Oak Ridge Institute for Science and Education

Xuan Li	Post Doctoral Fellow/Scientist

Shaw Environmental & Infrastructure, Inc.

E. Radha Krishnan, P.E.	Program Manager
Gune Silva, Ph.D.	Project Leader
Steven Jones, ASQ CQA/CQE	Quality Assurance Manager
Jill Webster	Project Scientist
Nancy Shaw	Project Scientist
Mark Domino (Shaw subcontractor)	Project Chemist
Nicole Sojda	Project Scientist
Tim Kling	Project Scientist

Sharon Kidney	Central Files Coordinator (all correspondence and original documents)

ALS Environmental Radiochemistry Laboratory

Amy Wolf	ALS, Fort Collins, CO

A4 PROJECT/TASK ORGANIZATION

The overall project management and distribution of responsibilities among the project personnel are described in this section. Figure A4.1 shows the project organization chart and Table A4.1 presents the project roles and responsibilities of the various project staff.

Dr. John C. Ireland, U.S. Environmental Protection Agency (EPA), at the EPA Test and Evaluation (T&E) Facility in Cincinnati, Ohio serves as the Project Officer for EPA Contract No: EP-C-09-041.

Dr. Samuel Hayes, EPA Office of Research and Development (ORD)/National Risk Management Research Laboratory (NRMRL)/Water Supply and Water Resources Division (WSWRD) at the EPA Andrew W. Breidenbach Environmental Research Center (AWBERC) in Cincinnati, Ohio serves at the WSWRD Associate Division Director.

Dr. Christopher A. Impellitteri, EPA ORD/NRMRL/WSWRD at EPA AWBERC is the principal investigator (PI) of the project. Dr. Impellitteri is responsible for planning and coordination of field sample collection, transportation, processing and preservation, storage, distribution, preparation, analyses, data analyses and final report/manuscript preparation. Dr. Impellitteri will also serve as Technical Research Lead and liaise with other parties including the Office of Water, utilities in EPA Region 3, ALS Environmental Radiochemistry Laboratory, EPA Region 7, and EPA Region 8.

Mr. Craig L. Patterson, **P.E.,** EPA ORD/NRMRL/WSWRD at the EPA T&E Facility is the EPA Work Assignment (WA) Manager of the project. Mr. Patterson is responsible for overall technical direction of Work Assignment (WA) 3-02 and ensuring that the data deliverables received from Shaw Environmental & Infrastructure, Inc. (Shaw) under the EPA T&E Facility Contract satisfies the project objectives.

Dr. John Olszewski, EPA ORD/NRMRL/WSWRD at EPA AWBERC serves as the EPA WSWRD Quality Assurance (QA) Manager is responsible for QA review of the Quality Assurance Project Plan (QAPP), conducting QA assessments, and QA review of all deliverables.

Ms. Holly Ferguson, EPA ORD/NRMRL at EPA AWBERC serves as the NRMRL Environmental Technology Assessment, Verification and Outcomes QA Manager and is responsible for QA review of the QAPP, conducting QA assessments, and QA review of the final report.

Mr. Kit Daniels, Ms. Dana Macke and Dr. Stephen Harmon, EPA ORD/NRMRL/WSWRD at EPA AWBERC serve as the EPA Project Scientists. Mr. Daniels and Ms. Macke are responsible for collection, preservation, transportation, and distribution of field samples. They are also responsible for maintaining a chain of custody form for the samples. Mr. Daniels and

Ms. Macke will deliver samples to the EPA T&E Facility at the direction of the EPA WA Manager. Mr. Stephen Harmon will perform x-ray diffraction (XRD), x-ray fluorescence (XRF), scanning electron microscopy (SEM) -energy dispersive x-ray spectroscopy, and x-ray absorption spectroscopy (XAS) analyses.

Dr. Xuan Li with the Oak Ridge Institute for Science and Education (ORISE) stationed at EPA AWBERC will provide as needed support for XRD, XRF, SEM and XAS analyses.

Mr. Barry Evans with EPA Region 7 serves as the primary point of contact for volatile organic compound (VOC) analysis that will be performed by Southwest Research Institute (SWRI), and will ensure that QAPP training is provided to responsible SWRI staff.

Mr. Jesse Kiernan with EPA Region 8 serves as the primary point of contact for semi-volatile organic compound (SVOC), gasoline range organics (GRO), and diesel range organics (DRO) analyses, , and will ensure that QAPP training is provided to responsible Region 8 staff.

Ms. Cindy White with EPA Region 4 serves as the primary point of contact for gross alpha/beta, radium 226, radium 228 and uranium analyses of sludge samples, and will ensure that QAPP training is provided to responsible Region 4 staff.

Ms. Amy Wolf with ALS Environmental Radiochemistry Laboratory (ALS Environmental) in Fort Collins, CO, serves as the primary point of contact for gross alpha/beta, radium 226 and radium 228 analyses, and will ensure that QAPP training is provided to responsible ALS Environmental staff.

Mr. Radha Krishnan, **P.E.,** with Shaw serves as the Shaw Program Manager for the Shaw T&E Facility Contract and is responsible for overall project management, program coordination, and management review of Shaw deliverables to EPA.

Mr. Steven Jones, ASQ CQA/CQE, with Shaw serves as the Shaw QA Manager for the Shaw T&E Facility Contract and is responsible for oversight of the Shaw Quality Management Plan (QMP) quality program implementation, QA review of documents and deliverables, providing guidance for and verifying implementation of quality program requirements as described in this QAPP, and conducting project assessments. Mr. Jones is also responsible for reviewing data received from ALS Environmental Radiochemistry Laboratory, SWRI (through EPA Region 7), and EPA Region 8. Mr. Jones reports to the Shaw Corporate Quality Manager and is organizationally independent of the project.

Mr. Paul C. Kefauver with Shaw serves at the Shaw Compliance and Permits Specialist for the Shaw T&E Facility Contract and is responsible for coordinating and maintaining facility-specific training records for the Shaw Team staff.

Dr. Gune Silva with Shaw serves as the Shaw Project Leader for the Shaw T&E Facility Contract and is responsible for project planning and coordination of day-to-day activities that are conducted by the Shaw Team staff, and overseeing the activities conducted by the Shaw Team staff to ensure implementation of the requirements as stated in this QAPP. Dr. Silva serves as the primary point of contact for all samples that are received at the EPA T&E Facility for sample processing/analysis. The Shaw Project Leader is also responsible for coordinating the submittal of deliverables to the Shaw Program Manager and Shaw QA Manager for review, providing Shaw Team staff training on the requirements of this QAPP, maintaining project records, including chain of custody forms for received samples, preparation of samples for analysis, maintaining documentation for standard preparation and sample analysis, sample analysis, verifying that analytical data generated by the Shaw Team staff meet the requirements of this QAPP, data entry/reporting, and ensuring that deliverables are peer reviewed prior to submittal to EPA.

Ms. Jill Webster, Ms. Nancy Shaw, Ms. Nicole Sojda, and Mr. Tim Kling with Shaw serve as Shaw Project Scientists. Ms. Webster will perform total organic carbon (using TOC analyzer), anion analysis using Ion Chromatography (IC), ammonia, total dissolved solids (TDS) and total suspended solids (TSS) analyses. Ms. Webster is responsible for preparation of samples for analysis, maintaining documentation for standard preparation and sample analysis, implementing the quality assurance/quality control (QA/QC) requirements for sample analyses as specified in this QAPP, and data transferring/entering to Microsoft Excel. Ms. Nancy Shaw, Ms. Nicole Sojda, and Mr. Tim Kling will provide as needed support for TDS and TSS analyses.

Mr. John Brannon with Shaw serves as a Shaw Project Scientist. Mr. Brannon is responsible for collection, preservation, transportation, and distribution of field samples. He is also responsible for maintaining a chain of custody form for the samples. Mr. Brannon will deliver samples to the EPA T&E Facility at the direction of the EPA WA Manager or the PI.

Mr. Mark Domino with Industrial & Environmental Services, LLC, an on-site subcontractor to Shaw, serves as the Project Chemist. Mr. Domino will perform metal analysis using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Mr. Domino is responsible for preparation of samples for analysis, maintaining documentation for standard preparation and sample analysis, implementing the QA/QC requirements for sample analyses as specified in this QAPP, and data transferring to Microsoft Excel.

Figure A4.1 Project Organization

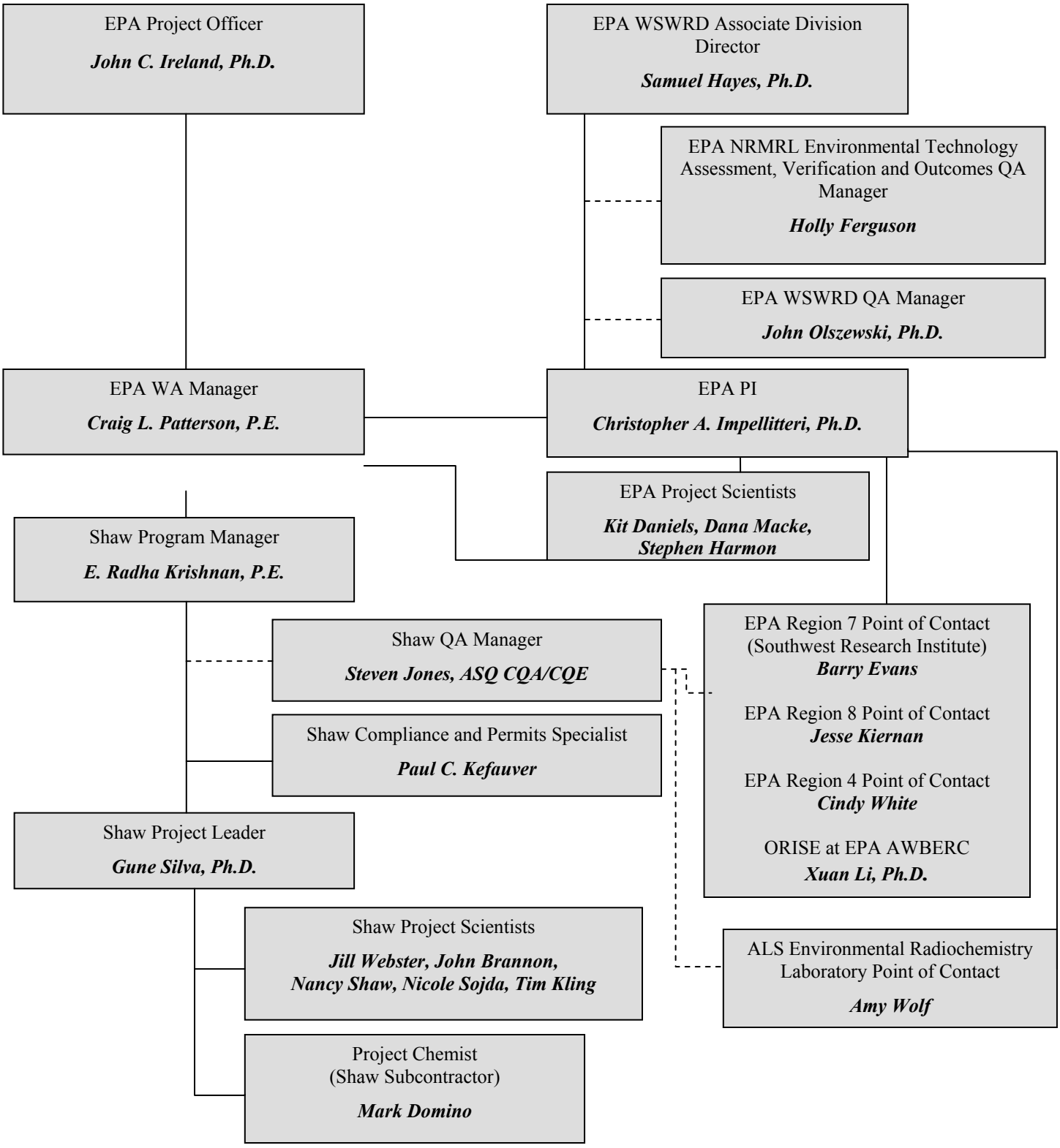

Table A4.1 Project Roles and Contact Information

Name of Person/Affiliation	Project Role	Phone Number, email
John C. Ireland, Ph.D./EPA	T&E Facility Contract Project Officer	513-569-7413, Ireland.John@epa.gov
Samuel Hayes, Ph.D. /EPA	WSWRD Associate Division Director	513-569-7514, Hayes.Samuel@epa.gov
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Craig L. Patterson, P.E./EPA	WA Manager	513-487-2805, Patterson.Craig@epa.gov
John Olszewski, Ph.D./EPA	WSWRD QA Manager	513-569-7481, Olszewski.John@epa.gov
Kit Daniels/EPA	Project Scientist	513-569-7018, Daniels.Kit@epa.gov
Dana Macke/EPA	Project Scientist	513-569-7570, Macke.Dana@epa.gov
Stephen Harmon/EPA	Project Scientist	513-569-7184 Harmon.Steve@epa.gov
Xuan Li, Ph.D./ORISE	Post Doctoral Fellow/Scientist	513-569-7954 Li.xuan@epa.gov
Amy Wolf/ALS Environmental Radiochemistry Laboratory, Fort Collins,	ALS Point of Contact for gross alpha/ beta, Radium 226 and Radium 228	970-490-1511, Amy.Wolf@ALSGlobal.com
Barry Evans/EPA, Region 7	Region 7 Point of Contact for SWRI VOC analysis	913-581-5144, Evans.Barry@epa.gov
Jesse Kiernan/EPA, Region 8	Region 8 Point of Contact for SVOC, GRO, and DRO analyses	303-312-7767, Kiernan.Jesse@epa.gov
Cindy White/ EPA, Region 4	Region 4 Point of Contact for gross alpha/ beta, Radium 226 /228 and Uranium analyses of sludge samples	334-270-7052 White.Cindy@epa.gov
E. Radha Krishnan, P.E. /Shaw	Program Manager/Project leadership/ peer review	513-782-4730, Radha.Krishnan@cbifederalservices.com
Steven Jones, ASQ CQA/CQE/ Shaw	QA Manager	513-782-4655, Steven.Jones@cbifederalservices.com
Paul C. Kefauver/Shaw	Compliance and Permits Specialist	513-569-7057 Kefauver.Paul@epa.gov
Gune Silva, Ph.D./Shaw	Project Leader	513-569-7853, Silva.Gune@epa.gov
Jill Webster/Shaw	Project Scientist	513-487-2822, Webster.Jill@epa.gov
Nicole Sojda/Shaw	Project Scientist	513-569-7996 Nicole.Sojda@cbifederalservices.com
Nancy Shaw/Shaw	Project Scientist	513-569-7996 Shaw.Nancy@epa.gov
Tim Kling/Shaw	Project Scientist	513-487-2819 Timothy.Kling@cbifederalservices.com

Name of Person/Affiliation	Project Role	Phone Number, email
John Brannon/Shaw	Project Scientist	513-569-7112 Brannon.John@epa.gov
Mark Domino/Shaw Subcontractor (Industrial & Environmental Services, LLC)	Project Chemist	513-569-7687 Domino.Mark@epa.gov

A5 PROBLEM DEFINITION/BACKGROUND

Hydraulic fracturing (HF) is widely used to extract oil, shale gas and coal bed methane. This practice for oil and gas exploration causes major challenges for water consumption and management because it consumes a large volume of fresh water and generates the largest single stream of contaminated flow-back wastewater (WW). Hence, the success of the HF technique is dependent on an efficient and cost-effective HF flow-back WW (or simply named HFWW) treatment technology.

The HFWW generated at HF sites typically contains high levels of dissolved solids (including chloride and bromide salts) and heavy metals from natural sources as well as chemical additives from various stages of the HF process. To remove aforementioned contaminants and total dissolved solids (TDS), HFWW is treated to varying degrees by both non-commercial and commercial facilities. In the treatment process, HFWW is fed into the system as influent and contaminants removed or reduced water is discharged as effluent to the environment or re-use. However, many states and municipalities are still grappling with issues surrounding HFWW treatment because there are concerns about the treatability of HFWW.

Commercial treatment facilities employ several chemical and non-chemical methods including chemical precipitation, evaporation/distillation, adsorption, ion-exchange, advanced oxidation, coagulation/flocculation, thermal, and filtration to treat HFWW. The level of contaminants removal in HFWW, thus, can vary depending on the treatment processes. The heterogeneity of constituents in groundwater, a part of the HFWW, makes the treatment process more challenging and difficult. In addition, there will be a concentrated sludge, brine, or salt-cake which cannot be treated and must be disposed with known and unknown contaminants regardless of the treatment type. Therefore, it is vital to evaluate the treatment process in terms of liquid (influent and effluent) and produced residuals for sustainable industry and cleaner environment.

A6 PROJECT/TASK DESCRIPTION

Primary Objective – Assessment of the fate of various contaminants listed in Table A6.1 within the HFWW treatment process for a total of three to five commercial treatment/ reuse plants.

Secondary Objective – Comparison of different EPA solid digestion techniques for metal recoveries at commercial treatment/ reuse plants.

A6.1 Primary Objective (Task 1) – Assessment of the fate of various contaminants listed in Table A6.1 within the HFWW treatment process for a total of three to five commercial treatment/ reuse plants.

The set objective will be achieved by collecting and analyzing HFWW influent, effluent, and sludge/residuals samples from 1) a total of three to five commercial HFWW treatment/ reuse plants. At each HFWW treatment/ reuse plant, influent samples will be collected from the first tank within the HFWW process (tap on side of tank) and effluent samples will be collected from the last tank within the HFWW process (tap on side of tank). Sludge samples will also be collected at each treatment/ reuse plant within the HFWW process.

HFWW influent and effluent samples from each site will be collected to determine the concentrations of the various analytes shown in Table A6.1. The contaminants in HFWW influent may have one or more of the following effects within the treatment process: degradation, reaction with other contaminants, transformation and/or settling in sludge. Additionally, the aforementioned processes could influence the formation of by-products. However, no attempt will be made to quantify the by-products, as the overall objective will be to determine the ability of the treatment process to remove contaminants from the influent. The fate of contaminants at the commercial treatment plants and reuse plants will be assessed by comparing the concentration/amounts of contaminants in HFWW influent and effluent.

As outlined in Section A6.2, metal concentrations in sludge will be determined after digesting the sludge samples using three EPA methods for qualitative purposes. There will be no attempt to quantify the total metal content in the sludge/solids by averaging the measured metal concentrations across the digestion methods. In addition, sludge/residual samples (wet and dried/homogenized) will be analyzed for qualitative purposes for a selected set of metal analytes (barium, strontium, chromium, copper, and zinc) by XRD, XRF SEM-energy dispersive x-ray spectroscopy, and XAS. Sludge samples will also be analyzed for Radium 226, Radium 228, Alpha, Beta as well as Uranium (Table B4.1). Radioactive and metal speciation qualitative data will be used to characterize the sludge mineralogy and radioactivity. This is important for assessing risk due to the potential mobility of the metals. Sample analyses will be carried out according to ASTM or established SOPs (Table B4.1).

EPA-approved methods will be used for digestion of metals in influent and effluent samples prior to metals analysis. Microwave assisted nitric acid digestion (EPA Method 3015A, Appendix A) will be used to determine total metal contaminants in HFWW influent and effluent samples. HFWW samples from each site will also be analyzed for dissolved metals using EPA Method 3005A (Appendix B). Due to differences of the digestion methods for recovering

certain analytes (further discussed in Section A6.2), it may not be possible to quantify all of the metal analytes listed in Table A6.1. For the primary objective, metal analyte concentrations of HFWW liquid samples will not be reported if Performance Evaluation (PE) sample results fail for both digestion methods (EPA Methods 3005A and 3015A). Thus, a minimum of one liquid digestion method with passing PE (when there is a commercially available PE sample within the analytical range) is required to report metal analyte concentrations for both liquid digestion methods. The reporting of metal concentrations data will also be dependent on the QC acceptance criteria for each analyte in each analytical batch. In other words, the results for metal analytes reported for the primary objective will not only be dependent on passing PE samples for at least one digestion method, but also on associated QC acceptance criteria for each analyte in each analytical batch. Metal analyte concentration results will be qualified if any QC failure occurs.

Table A6.1 List of contaminants that will be evaluated for this study

Contaminants	CAS Number	Measurement Importance
Metals		
Aluminum	7429-90-5	Non-critical
Antimony	7440-36-0	Non-critical
Arsenic	**7440-38-2**	**Critical**
Barium	**7440-39-3**	**Critical**
Beryllium	7440-41-7	Non-critical
Boron [1]	**7440-42-8**	**Critical**
Cadmium	7440-43-9	Non-critical
Calcium	7440-70-2	Non-critical
Cerium	7440-45-1	Non-critical
Chromium	**7440-47-3**	**Critical**
Cobalt	7440-48-4	Non-critical
Copper	7440-50-8	Non-critical
Iron	**7460-89-6**	**Critical**
Lead	7430-92-1	Non-critical
Lithium	7439-93-2	Non-critical
Magnesium	**7439-95-4**	**Critical**
Manganese	**7439-96-5**	**Critical**
Mercury	7439-97-6	Non-critical
Molybdenum	7439-98-7	Non-critical
Nickel	7440-02-0	Non-critical
Potassium	7440-09-7	Non-critical
Selenium	7782-49-2	Non-critical
Silver	7440-22-4	Non-critical
Sodium	**7440-23-5**	**Critical**
Strontium	**7440-24-6**	**Critical**
Thallium	7440-28-0	Non-critical
Tin	7440-31-5	Non-critical
Titanium	7440-32-6	Non-critical
Vanadium	7440-62-2	Non-critical

Contaminants	CAS Number	Measurement Importance
Zinc	7440-66-6	Non-critical
Anions		
Bromide	**7726-95-6**	**Critical**
Chloride	**16887-00-6**	**Critical**
Fluoride	7782-41-4	Non-critical
Nitrate	84145-82-4	Non-critical
Nitrite	14797-65-0	Non-critical
Phosphate	98059-61-1	Non-critical
Sulfate	7664-93-9	Non-critical
General Chemistry Water Parameters		
Ammonia		Non-critical
Total Organic Carbon (TOC)		Non-critical
pH		Non-critical
Conductivity		Non-critical
TDS		Non-critical
TSS		Non-critical
Other Group of Chemicals/Parameters		
Radium 226/228 (aqueous)		**Critical**
Radium 226/228 (solid)		Non-critical
Gross alpha/ Gross beta		Non-critical
Diesel Range Organics (DRO)		Non-critical
Gasoline Range Organics (GRO)		Non-critical
Semi-volatile organic compounds (SVOCs)		Non-critical
Volatile Organic Compounds (VOCs)		Non-critical
X-ray Diffraction (XRD)		Non-critical
X-ray Fluorescence (XRF)		Non-critical
Scanning Electron Microscopy (SEM)		Non-critical
X-ray Absorption Spectroscopy (XAS)		Non-critical
Uranium		Non-critical

1. **Boron will not be determined for EPA Digestion Method 3052.**

A6.2 Secondary Objective (Task 2) - Comparison of different EPA solid digestion techniques for metal recoveries at commercial treatment/ reuse plants.

There are several established digestion methods to quantify metal content in solids. Some methods are less time-consuming than others but pose human health risks. In addition, studies on the methods for the determination of metals in different matrices have reported varying recoveries. Hence, identification of quick and accurate methods to quantify metal contaminants in HFWW residuals is important to help the fast growing industry while protecting the environment. Thus, metal contaminants in HFWW residuals will be assessed and compared using several existing EPA sample digestion methods.

In order to determine metal contaminants in the HFWW residuals, solid samples will be digested following EPA Method 3050B (hot plate assisted nitric/hydrochloric acid digestion) (Appendix C), EPA Method 3051A (microwave assisted nitric acid digestion) (Appendix D), and EPA Method 3052 (microwave assisted nitric/hydrofluoric acid digestion) (Appendix E). Note that

boron will not be determined for EPA Digestion Method 3052 due to potential dissolution of any borosilicate glass present using that method. The metals shown in Table A6.1 can be analyzed within the quantification limits using ICP-OES, however, when samples contain refractory compounds, such as silicon dioxide, alumina, titanium dioxide and other oxides, they will not be dissolved and in some cases may sequester target metals (EPA Method 3051A). Additionally, the type and volume of acids used in each digestion method may impact the ability to quantify certain metals by ICP-OES. For example, hydrochloric acid can improve the recovery of antimony, iron, aluminum and silver, but, the addition of HCl may limit the quantitation or increase the difficulties of quantitation of other analytes (EPA Method 3050). For aforementioned reasons and knowing the complex composition of the samples and interactions during each digestion, quantification of each analyte listed in Table A6.1 may not be possible for each digestion method due to the sample matrix interferences (type and concentrations of analytes present in the matrix) and digestion method-specific limitations mentioned in this section. Performance Evaluation samples will be analyzed prior to field sample analysis when analytes are commercially available within the analytical range of the laboratory used for this project and will provide additional insight on the ability to quantify each analyte by ICP-OES per solid digestion method. In cases where the PE sample for a given analyte did not pass for any of the solid digestion methods being compared in this study, that analyte will not be reported. In cases where the PE sample for a given analyte passes for at least one solid digestion method, or for which no commercially available PE sample was available, all three analytical results will be reported and compared. For analytes without a commercially available PE sample, data usability for each analytical batch will be determined based on the associated QC acceptance criteria, which include the use of second source standards. In all cases, data qualifiers will be applied to the results of HFWW sludge samples if any QC failure occurs. The limitation of the digestion methods will provide additional information for the secondary objective on the comparison of different EPA solid digestion techniques for metal recoveries at commercial treatment/reuse plants, and for assessing the efficacy of the digestion methods used at the EPA T&E Facility laboratory for this study. The limitation of the digestion methods will provide additional information for the secondary objective on comparison of different EPA solid digestion techniques for metal recoveries at commercial treatment/reuse plants, and for assessing the efficacy of the digestion methods used at the EPA T&E Facility laboratory for this study. The PE sample results that will be completed prior to field sample analysis will provide additional insight on the ability to quantify each analyte per digestion method.

Each field collected wet HFWW sludge/residual sample received from the field sites (Site 1, 2, 3 and 5) collected in the double-wrapped plastic bags per Table B1.1 will be thoroughly mixed in each respective plastic bag by inverting the sludge/residual sample in the bag multiple times by hand without opening the bag. One half of the each field collected sludge/residual samples will be processed by oven drying at 60 ºC for 48 hours, then crushed using a clean mortar and pestle

prior to pass-through a 2 mm µm sieve and thoroughly mixed to obtain sample uniformity. The mortar and pestle will be acid-washed (5% nitric acid) prior to and after each use. The dried processed sample (dried/crushed/sieved) will then be stored in clean HDPE bottles. Both the processed dry and unprocessed wet samples will be stored at 4˚C for analysis. Aliquot of each wet samples will be analyzed for percent moisture in triplicate. For each digestion method, the processed dry sludge/residual samples will be digested in triplicate in accordance with the respective methods. An aliquot of both the processed dry and wet sludge/residual samples will be placed into clean HDPE bottles and delivered to EPA AWBERC in a cooler at 4±2 °C for qualitative XRD, XRF, SEM and XAS analyses. Sub-samples for XAS analysis at the Argonne National Laboratory, Chicago, IL will be transported at 4±2 °C in a cooler/ice chest by the EPA AWBERC Project Scientists/PI. An aliquot of wet sludge sample in clean HDPE bottles from each site will also be shipped to the EPA National Air Radiation Environmental Laboratory (NAREL) in Montgomery, Alabama by Shaw Project Leader for Radium 226, Radium 228, Alpha, Beta, and Uranium analyses.

The impact of the three digestion techniques on recovery of metal contaminants for each treatment technique will be tested using ANOVA. Significant differences between/among means will be determined using protected Fisher's least significant difference test, only when results are significantly different. The SYSTAT (Systat for Windows, version 11) will be used to perform statistical analysis. Data from three digestion methods will be tabulated to present the measured concentrations of the various metal contaminants.

A6.3 Project Schedule

Activities for this WA will be performed from October 2012 to December 2013. The project schedule and main activities to be conducted are shown in Table A6.2.

Table A6.2 Project Schedule

	Oct 2012	Dec 2012	Feb 2013	Apr 2013	Jun 2013	Aug 2013	Oct 2013	Dec 2013	Feb 2014
QAPP Preparation									
Field Sampling									
Sample Analysis									
Data Verification/Validation									
Monthly Reports									
Report Writing									
Report Submission									

A7 QUALITY OBJECTIVES AND CRITERIA

This is an EPA NRMRL Category I research project. In order to address the project objectives, generation of reliable data is vital. It is widely known that environmental samples are heterogeneous and variable even at micro-scale. Thus, the chances of controlling the variability in environmental samples will be difficult. Sample collection utilizing homogenization with equal proportion, maintaining at the same oxidation/reduction status, preservation (acidification, oxygen-free condition) and storage at cold conditions (at ≤6°C) can help minimize further variability. Additionally, the use of calibrated measuring and weight equipment, appropriate laboratory ware (e.g. not to use glassware for Si and B determination), unadulterated chemicals from the same vendor as well as maintaining quality control measures during sample analysis further strengthens the generation of reliable data. The QA/QC and verification criteria for the analytical methods used during this project are discussed in Section B.

A8 SPECIAL TRAINING/CERTIFICATION

All personnel working at the EPA T&E Facility must have completed the Occupational Safety and Health Administration (OSHA) 40/24-hour Hazardous Waste Operations and Emergency Response (HAZWOPER) and Resource Conservation and Recovery Act (RCRA) 8-hour training. In addition, personnel performing laboratory and field sampling activities will complete training required by the EPA Cincinnati Chemical Hygiene Plan. The Health and Safety Plan (HASP) on file includes information on the project-specific safety training and requirements.

As required by the EPA ORD Policies and Procedures Manual, Section 13.4, *Quality Assurance/ Quality Control Practices for ORD Laboratories Conducting Research*, analyst proficiency to perform sample analysis in accordance with an approved analytical method will be demonstrated and documented for the Shaw Team analysts to perform sample analysis in support of this WA. The following must be completed by the analyst to demonstrate proficiency with the analytical method: 1) performing valid initial calibrations, 2) performing MDL determinations, 3) demonstrating that their results meet all minimum QA/QC acceptance criteria as presented in the method document or the SOP including satisfactorily analyzing performance evaluation samples. The performance evaluation samples will be analyzed for all analytical methods prior to performing sample analysis under this QAPP.

The EPA Region 8 laboratory is accredited by the National Environmental Laboratory Accreditation Program (NELAP) through the state of Texas, Southwest Research Institute. The SWRI laboratory is NELAP accredited and ISO certified. The ALS Environmental laboratory in Fort Collins, CO holds a current Radioactive Materials Handling License from the state of Colorado, and is NELAC accredited in Utah, with over 18 total state accreditations, and is USDA licensed to accept samples from outside the United States (OCONUS). For the off-site

laboratories (ALS Environmental, SWRI and Region 8), training documentation and PE sample analyses are performed during accreditation.

EPA T&E Facility-specific training documentation is maintained by the Shaw Compliance and Permits Specialist at the EPA T&E Facility for Shaw Team staff. Safety training records for EPA and EPA contractor staff are maintained by the EPA Safety, Health, and Environmental Management (SHEM) Office at EPA AWBERC. ALS Environmental, SWRI and Region 8 analysts should have current Health and Safety training records.

Staff training of QAPP responsibilities and requirements will be provided within one week of QAPP endorsement by the EPA QA Team. The Shaw Project Leader will provide the training for the Shaw Team staff. The points of contact for the respective off-site laboratories (ALS Environmental, Region 7 and Region 8) will ensure that QAPP requirements are communicated to responsible staff.

A9 DOCUMENTS AND RECORDS

Data collection efforts will not be initiated under this WA until this QAPP has been approved by EPA. Upon approval, an electronic copy of this QAPP will be prepared and identified as a controlled document by approval signatures on Section A1, Title Approval Sheet. The Shaw Project Leader will provide and/or make available the most current versions of this QAPP to all persons identified in Section A3, Distribution List. The Shaw Project Leader is responsible for ensuring that designated project personnel have the current version of the approved QAPP. Revisions and amendments to controlled WA documents (i.e., this QAPP and associated SOPs) will be reviewed and approved by the same process as the original. Persons identified in Section A3, Distribution List, will be advised by the Shaw Project Leader of the updates by E-mail memorandum, during staff meetings, or other appropriate method as determined by the needs of the project. Project staff will be responsible for destroying superseded versions of controlled documents upon notice.

Field and laboratory paper records will be maintained in accordance with Section 13.2, *Paper Laboratory Records*, of the EPA ORD Policies and Procedures Manual. The Shaw Project Leader will submit the raw data, including calculations and QA/QC requirements, electronically in Microsoft Excel format to the EPA WA Manager on monthly basis. Monthly progress reports will be generated by the Shaw Project Leader, reviewed by the Shaw Program Manager, and submitted to EPA every month. Distribution of the monthly report to other agencies will be at the discretion of the EPA WA Manager. The expected product of this research will be in a final report describing the analytical results of the samples analyzed.

Raw data for sub-contracted and regional laboratories shall be included with the data reports. Calibration and QC data and results shall be included. Field notebooks will be kept as well as

customized data entry forms if needed. All information needed to confirm final reported data will be included.

Records will be generated in both paper (hard copy) and electronic formats, and submitted in the format requested by the EPA WA Manager. The following original documents generated in support of WA activities constitute records which will be managed by the Shaw Team:

- Contract-required documents and deliverables;
- WA-specific planning documents (i.e., Work Plan and this QAPP);
- Documentation that supports fulfillment of WA-specific planning document requirements, including QA assessment reports;
- Incoming WA-related correspondence from EPA;
- Outgoing WA-related correspondence to EPA.

Controlled access facilities that provide a suitable environment to minimize deterioration, tampering, damage, and loss will be used for the storage of records. Whenever possible, electronic records will be maintained on a secure network server that is backed up on a routine basis. Electronic records that are not maintained on a secure network server will be periodically backed up to a secure second source storage media, transferred to an archive media (e.g., compact discs, optical discs, magnetic tape, or equivalent), or printed. Electronic records that are to be transferred for retention will be transferred to an archive media or printed, as directed by EPA. Original records generated under this WA will be retained permanently. Records for archive will be stored at EPA T&E Facility Central Files, unless otherwise directed by the EPA WA Manager.

Off-site laboratories will provide to the Shaw QA Manager complete data packages for samples analyzed (see QAPP Section D.2) in printed form, electronically, and/or on disk, including applicable Standard Operating Procedures used, relevant laboratory notebook pages, quantitation limits (reporting) and detection limits, and deviations from method.

SECTION B DATA GENERATION AND ACQUISITION

Removal of contaminants in the HFWW treatment process will vary as a function of contaminant properties and treatment at commercial WW treatment/reuse facilities. Contaminants may be sequestered or degraded at various junctures within the treatment/reuse process. To improve management of hazardous contaminants, determination of particular priority contaminants that are removed within the treatment process is imperative. During the treatment process, some metal contaminants may not be removed/degraded and these will be assessed by measuring contaminant concentrations in HFWW influent, effluent and residuals.

B1 SAMPLING PROCESS AND DESIGN

HFWW samples collection, preservation and transportation from a total of three to five treatment/ reuse plant field sites to the EPA T&E Facility, ALS Environmental, SWRI and Region 8 will be performed by the EPA Project Scientist under the supervision and guidance of the EPA WA Manager and PI. Contract staff may be tasked with accompanying the field sampling team of EPA for collecting the field samples. Water used for field blanks, equipment blanks, and trip blanks will be taken from the EPA T&E Facility (Nanopure). Water will be filled into a 5 L carboy and taken to the field.

At each field site, pH and conductivity of both influent and effluent HFWW will be measured using portable HANNA or YSI pH/Conductivity meters prior to sample collection. These parameters will be measured according to Standard Method 4500B (pH) and Standard Method 2510B (conductivity).

For the commercial HFWW treatment/reuse plants, influent samples will be collected from the first tank (tap on side of tank) and effluent samples will be collected from the last tank (tap on side of tank). Sludge samples will be collected within the HFWW process (sampled with disposable gloves and placed into double-wrapped Ziploc plastic bags).

The influent and effluent samples at the field sites will be collected directly into the sample containers after discarding the initial flow from the sampling port for 30 seconds. Liquid samples collected for dissolved metals analysis will be filtered using a 0.45 micron filter attached to disposable syringes in the field, and then the filtrate preserved as shown in Table B1.1. Based on the HFWW treatment process and sample matrix variability, one field blank will be included per matrix (influent, effluent, and sludge/residuals) per day. Sample containers, preservation, and holding times are shown in Table B1.1. The collected samples will be shipped using cold preservation (ice or ice packs) in coolers/ice chest via courier (e.g., FedEx), overnight, to the appropriate laboratories with chain of custody forms and custody seals (Appendix F). Samples collected for analysis at the EPA T&E Facility may also be field-preserved and transported on

the same day in a cooler/ice chest by the field sampling team to the EPA T&E Facility. All samples will be packaged in accordance with the requirements stated in Section B.3.

Samples will be shipped to ALS Environmental for Radium 226, Radium 228 and gross alpha and gross beta analysis. These samples will be field-preserved by adding HNO_3.

ALS Environmental
Radiochemistry Laboratory
c/o Amy Wolf
225 Commerce Drive
Fort Collins, CO 80524
Ph: 970-490-1511

Samples will be shipped to SWRI for VOC analysis. Samples will be field-preserved using HCl to obtain a pH < 2. Four trip blanks per cooler/ice chest are required for VOC samples.

Southwest Research Institute (SWRI)
ATTN: Herb Schattenberg, Division 01
6220 Culebra Road
San Antonio, TX 78238
Ph: 210-522-3051

No one should contact the SWRI lab directly but should contact Barry Evans (with EPA Region 7) via work phone (913) 551-5144, cell phone (913) 709-7822, or email (Evans.Barry@epa.gov) and he will forward the information to Dean Dickerson at ARDL (prime contractor for this project) who will inform SWRI. If it is urgent and Barry Evans is not available, then contact Dean Dickerson @ ARDL directly. Dean's phone number is (618) 244-3235, ext. 227 and his email is ddickerson@ardlinc.com.

Samples will be shipped to EPA Region 8 for semi-volatile organic compounds, diesel range organic (DRO) and gasoline range organic (GRO) analyses. DRO and GRO samples will be field-preserved using HCl.

EPA Region 8 Lab
c/o Jesse Kiernan
16194 West 45th Drive
Golden, CO 80403
Ph: 303-312-7767

All other samples (dissolved/total metals, ammonia nitrogen, TOC, anions, TDS, and TSS) will be shipped or transported to:

EPA T&E Facility
c/o Gune Silva
1600 Gest Street,
Cincinnati, Ohio 45204
Ph: 513-569-7853

A portion of the dry and wet sludge samples from each site (Site 1, 2, 3, and 5) prepared at the EPA T&E Facility will be transferred to EPA AWBERC for XRD, XRF, SEM and XAS analyses (see Sections A6.1and 2).

EPA AWBERC
Stephen Harmon
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
Ph: 513-569-7184

Approximately 10 g of wet sludge samples from each site will also be shipped to EPA NAREL, Region 4 for Radium 226, Radium 228 and gross alpha, gross beta and Uranium analyses (see Section A6. 1 and 2).

EPA NAREL
Cindy White
540S Morris Avenue
Montgomery, AL, 36115
Ph: 334 270 7052

B2 SAMPLING METHODS

Two sampling events covering the treatment/ reuse plant field sites are planned for this study, one event in June 2013 and one event in August 2013. The quantities of sample to be collected for each matrix/analysis (including field/equipment blanks and trip blanks) are shown in Table B1.1, and reflect the number of samples needed per field site to complete all analyses for this study. Samples will not be accepted by the laboratories on weekends or holidays, so sample collection will need to be planned so that samples are collected, shipped, and analyzed within holding times. Each sample container must have a sample label affixed to the container. Each sample label must be legibly written with indelible (i.e., waterproof) ink. The information that is written on the sample label must match the information on the Chain of Custody (COC) form in Appendix F.

Field QC samples will include field/equipment blanks, trip blanks, and temperature blanks.

A field blank is a sample of Nanopure water poured into the container in the field, preserved and shipped to the laboratory with field samples. For the dissolved metal samples that involve field filtration through a 0.45 µm filter, the field blank will be processed as a sample through the disposable filter setup, then preserved, to also serve as an equipment blank.

A field duplicate is a duplicate environmental sample taken at the same time under identical circumstances to assess field sampling precision and homogeneity. Each sample is treated identically throughout field and laboratory analytical procedures. Field duplicates will be

collected at a frequency of one per sampling site (either influent or effluent sample), and at least one influent and one effluent field duplicate sample will be collected during each field sampling event.

A trip blank is an aliquot of reagent water that is taken from the laboratory to the sampling site and transported back to the laboratory without having been exposed to sampling procedures, typically analyzed only for volatile compounds.

A temperature blank is a VOA vial or other small sample bottle filled with Nanopure water that is placed in each cooler. Upon arrival at the laboratory, the temperature of this vial is measured. The temperature blank is not analyzed and does not measure introduced contamination.

Field personnel will notify each laboratory point of contact when samples are shipped to each of the laboratories and will notify the point of contact as soon as possible if a scheduled shipment has been cancelled.

Table B1.1 Sample Containers, Preservation and Holding Times

Parameter	Sample Containers	Quantity of Influent and Effluent Samples (For analysis at EPA T&E Facility)	Quantity of Samples (For analysis at ALS, SWRI, and Region 8)	Preservation (All preservations will be carried out at each field site)	Max. Holding Time
Treatment/Reuse Facility Influent and Effluent					
Dissolved Metals[1]	Two 1L Amber HDPE	1 x 1 L Influent 1 x 1 L Effluent	--	Filtered 0.45 µm, acidified using HNO_3 to pH< 2, Cool ≤6°C	180 days (Hg only 28 days)
	Two 1 L Amber HDPE for equipment blanks	1 x 1 L Influent 1 x 1 L Effluent	--		
	One 1 L Amber HDPE for field duplicate[2]	1 x 1 L (Influent or Effluent[2])	--		
Total Metals	Two 1 L HDPE Amber	1 x 1 L Influent 1 x 1 L Effluent	--	Unfiltered, acidified using HNO_3 to pH< 2, Cool ≤6°C	180 days (Hg only 28 days)
	Two 1 L Amber HDPE field blanks	1 x 1 L Influent 1 x 1 L Effluent	--		
	One 1 L Amber HDPE for field duplicate[2]	1 x 1 L (Influent or Effluent[2])	--		
Ammonia Nitrogen (NH_3-N)	Two 100 mL Amber Glass	1 x 100 mL Influent 1 x 100 mL Effluent	--	HCl, pH<2; Cool ≤6°C	28 days
	Two 100 mL Amber Glass Field blanks	1 x 100 mL Influent 1 x 100 mL Effluent	--		
	One 100 mL Amber Glass for field duplicate[2]	1 x 100 mL (Influent or Effluent[2])			
Total Organic Carbon (TOC)	Two 100 mL Amber Glass	1 x 100 mL Influent 1 x 100 mL Effluent	--	No headspace H_3PO_4, pH<2; Cool ≤6°C	28 days
	Two 100 mL Amber Glass Field blanks	1 x 100 mL Influent 1 x 100 mL Effluent	--		
	One 100 mL Amber HDPE for field duplicate[2]	1 x 100 mL (Influent or Effluent[2])			
Anions	Two 100 mL HDPE Amber	1 x 100 mL Influent 1 x 100 mL Effluent	--	Cool ≤6°C	28 days (NO_3^-, NO_2^- PO_4 48 hrs)
	Two 100 mL HDPE Field blanks	1 x 100 mL Influent 1 x 100 mL Effluent	--		
	One 100 mL HDPE for field duplicate[2]	1 x 100 mL (Influent or Effluent[2])	--		

Parameter	Sample Containers	Quantity of Influent and Effluent Samples (For analysis at EPA T&E Facility)	Quantity of Samples (For analysis at ALS, SWRI, and Region 8)	Preservation (All preservations will be carried out at each field site)	Max. Holding Time
Total Dissolved Solids[3] (TDS)	Three 1 L HDPE Amber	1 x 1 L Influent 2 x 1 L Effluent	--	Cool ≤6°C	7 days
	One 1 L Amber HDPE for field duplicate[2]	1 x 1 L (Influent[2])			
Total Suspended Solids[3] (TSS)	Three 1 L HDPE Amber	1 x 1 L Influent 2 x 1 L Effluent	--	Cool ≤6°C	7 days
	One 1 L Amber HDPE for field duplicate[2]	1 x 1 L (Influent[2])			
Temperature blank (EPA T&E Facility)	One 40 mL Vial	1 x 40 mL Vial per cooler	--	Cool ≤6°C	Measure temperature upon receipt
Radium 226 (aqueous)	Two 1 L HDPE	--	1 x 1 L Influent 1 x 1 L Effluent	Acidified using HNO_3 to pH< 2	180 days
	Two 1L HDPE for field blanks		1 x 1 L Influent 1 x 1 L Effluent		
	One 1 L HDPE for field duplicate[2]		1 x 1 L HDPE (Influent or Effluent[2])		
Radium 228 (aqueous)	Two 1L HDPE		1 x 1 L Influent 1 x 1 L Effluent	Acidified using HNO_3 to pH< 2	180 days
	Two 1L HDPE for field blanks		1 x 1 L Influent 1 x 1 L Effluent		
	One 1 L HDPE for field duplicate[2]		1 x 1 L HDPE (Influent or Effluent[2])		
Gross Alpha/Beta (aqueous)	Two 1L HDPE		1 x 1 L Influent 1 x 1 L Effluent	Acidified using HNO_3 to pH< 2	180 days
	Two 1L HDPE for field blanks		1 x 1 L Influent 1 x 1 L Effluent		
	One 1 L HDPE for field duplicate[2]		1 x 1 L HDPE (Influent or Effluent[2])		
Volatile Organic Compounds (VOCs)	Eight 40 mL amber glass vials with PTFE-faced septa		4 x 40 mL Influent 4 x 40 mL Effluent	HCl to pH <2 No headspace, Cool ≤6°C	14 days
	Four 40mL amber glass vials for trip blanks		4 x 40 mL per cooler	No headspace, Cool ≤6°C	
	Eight 40mL amber glass vials for field blanks		4 x 40 mL Influent 4 x 40 mL Effluent	HCl to pH <2 No headspace, Cool ≤6°C	
	Four 40mL amber glass vials for field duplicate[2]		4 x 40 mL (Influent or Effluent)	HCl to pH <2 No headspace, Cool <6°C	

Parameter	Sample Containers	Quantity of Influent and Effluent Samples (For analysis at EPA T&E Facility)	Quantity of Samples (For analysis at ALS, SWRI, and Region 8)	Preservation (All preservations will be carried out at each field site)	Max. Holding Time
Temperature blank (SWRI)	One 40 mL Vial	--	1 x 40 mL per cooler	Cool ≤6°C	Measure temperature upon receipt
Semi-volatile organic compounds (SVOCs)	Two 1L amber glass bottles		1 x 1 L Influent 1 x 1 L Effluent	Cool ≤6°C	7 days until extraction, 30 days after extraction
	Two 1 L amber glass bottles for field blanks		1 x 1 L Influent 1 x 1 L Effluent		
	One 1 L amber glass bottle for field duplicate[2]		1 x 1 L amber bottle (Influent or Effluent[2])		
Diesel Range Organics (DRO)	Four 1L amber glass bottles		2 x 1 L Influent 2 x 1 L Effluent	HCl, pH<2; Cool ≤6°C	7 days until extraction, 40 days after extraction
	Two 1 L amber glass bottles for field blanks		1 x 1 L Influent 1 x 1 L Effluent		
	One 1 L amber glass bottle for field duplicate[2]		1 x 1 L amber bottle (Influent or Effluent[2])		
Gasoline Range Organics (GRO)	Four 40 mL amber glass vials		2 x 40 mL Influent 2 x 40 mL Effluent	No headspace; HCl, pH<2; refrigerate ≤6°C	14 days
	Two 40 mL amber glass vials for field blanks		1 x 40 mL Influent 1 x 40 mL Effluent		
	One 40mL amber glass vials for field duplicate[2]		1 x 40 mL (Influent or Effluent)		
Temperature blank (EPA Region 8)	One 40 mL Vial	--	1 x 40 mL per cooler	Cool ≤6°C	Measure temperature upon receipt
Treatment/Reuse Facility Solid Residues					
Metals (See Table A6.1), XRD[4], XRF[4], SEM[4] and XAS[4] Ra 226[4], Ra228[4], Alpha[4], Beta[4], U234[4], U235[4] and U 238[4] (solid)	Double-wrapped plastic bags	500 g		Cool ≤6°C	No holding time requirement, but digest within 28 days

1 For dissolved metals, samples will be filtered in the field using a 0.45 micron filter prior to preservation.
2 Field duplicates will be collected at a frequency of one per sampling site (either influent or effluent sample), and at least one influent and one effluent field duplicate sample will be collected during each field sampling event.
3 Additional effluent sample volumes are required for TSS and TDS analyses due to the anticipated lower solid content in the effluent samples.
4 Aliquots from the 500 g sludge/residues samples will be collected in the laboratory for XRD, XRF, SEM, XAS analyses and EPA NAREL Ra 226, Ra 228, alpha, beta, U234, U235 and U238 analyses, separately (see Section A6.2).

B3 SAMPLE HANDLING AND CUSTODY

Preservation of samples is required to retain integrity. The most common preservation techniques include pH adjustment and temperature control. Field personnel collecting HFWW treatment process samples will use EPA-recommended containers and adhere to EPA-recommended preservation techniques for the parameters of concern. Table B1.1 provides the sample containers, preservation requirements, and holding times for the parameters. Sample containers with appropriate preservation will be prepared at the EPA T&E Facility, and then taken to the field.

A chain-of-custody (Appendix F) will be used to maintain a record of sample collection, transfer between personnel, shipment, analytical requests, and receipt by the laboratory. The following chain-of-custody procedures will be followed to guarantee sample custody documentation. A sample will be considered under proper custody if (1) it is in actual physical possession of the responsible person; (2) it is in view of the responsible person; (3) is locked in a container controlled by the person; or (4) has been placed into a designated secure area by the responsible person. The COC will be sealed in a Ziploc bag and taped to the inside of the ice chest lid with the samples. Indelible ink will be used for all markings on the COC. The original record will accompany the shipment. Each distinct sample will appear on a separate line. Any writing errors made on the COC will be crossed out with a single line, initialed, dated and rewritten.

Chain of Custody documentation must include:

- site name (project name)
- sampler's name/signature
- sample ID (station number)
- date and time of collection (recorded in 24 hour clock time)
- type of sample (grab or composite)
- sample description (station location) (indicate if sample has been filtered for dissolved components or if it is a field duplicate)
- number of containers
- parameters requested (i.e., tests, methods)
- sample tag numbers (in remarks)
- date, time and signatures for sample receipt and transfer

Containers will be double bagged via Ziploc bags. Bagged containers will be placed in coolers with ice, and packed with appropriate packing material. Bagged ice or gel packs will be packed on top and around the samples to ensure samples remain at or below 6°C while in transit. Samples are not to be frozen. The lid will be sealed with shipping tape and custody seals will be affixed to the cooler.

Coolers will be labeled with the origin and destination locations on a FedEx, or other common courier, airbill. Department of Transportation and/or courier approved shipping containers must be used, and loaded coolers shall not be heavier than 50 pounds. Samples shall be identified in shipping paperwork as "environmental laboratory samples." Samples are to be shipped/ transported on the same day that they are collected.

Field personnel who collect the samples are responsible for the care and custody of the samples until they are transferred or delivered to the delivery agent. A laboratory notebook will be used by the field sampling team to record the details of the field sampling event, including all information required for the samples. A chain-of-custody form will accompany all samples. When transferring the samples, the individuals relinquishing and receiving the samples will sign, date, and note the time on the chain-of-custody form.

All containers used to collect the samples will be labeled. This label will contain the site name, sample matrix, QC type (as applicable), type of analysis, date and time of sampling. A laboratory notebook will be used to record the details that will be signed, dated, and witnessed. The collected samples will be analyzed as soon as possible for best results. At any rate, samples will be stored for a period not exceeding the maximum holding time (Table B1.1).

B4 ANALYTICAL METHODS

The analysis methods for the analytes in Table A6.1 are summarized in Table B4.1. If analytical instrumentation software/hardware allows for data export, data from analytical equipment will be transferred to Microsoft Excel spreadsheets from each sample analysis sequence to minimize errors associated with data transcription.

All analysis methods listed in Table B4.1 below will be implemented as specified by the appropriate method, with the exception of a modification to Section 7.6 of EPA SW-846 Method 6010C (Appendix G). For the HFWW project, 31 metal contaminants (Table A6.1) will be analyzed in three separate groups employing different plasma viewing options to minimize spectral interferences. Group 1 (radial view) consists of 9 metals including Barium, Beryllium, Calcium, Iron, Lithium, Magnesium, Potassium, Sodium and Strontium. Group 2 (axial view) consists of 15 metals including Aluminum, Arsenic, Cadmium, Cerium, Chromium, Cobalt, Copper, Lead, Manganese, Nickel, Selenium, Silver, Thallium, Vanadium, and Zinc. Group 3 (either radial or axial view) consists of 5 metals including Antimony, Boron, Molybdenum, Tin and Titanium. Mercury will be analyzed as a single analyte to maintain appropriate matrix match and to avoid generation of high volume of ICP-OES effluent containing mercury. A solution of 2% (v/v) trace metal HNO_3 containing 1 mg/L $AuCl_3$ will be used for preparation of samples and standards. The Au ion acts as a strong oxidizing agent that converts or maintains mercury ion in solution.

Table B4.1 Outline of Analysis Methods

Parameter	Measurement	Laboratory	Instrument	Analytical Method
HFWW and Residues				
Dissolved Metals	Critical	T&E Facility	Hot plate or equivalent liquid digestion, as specified in Section 7.2 of Method 3005A	EPA Method 3005A (Appendix B)
Total Metals	Critical	T&E Facility	Microwave assisted liquid digestion	EPA Method 3015A (Appendix A)
			Hot plate assisted solid digestion	EPA Method 3050B (Appendix C)
			Microwave assisted solid digestion	EPA Method 3051A (Appendix D)
			Microwave assisted solid digestion	EPA Method 3052 (Appendix E)
Dissolved and Total Metals	Critical	T&E Facility	Perkin Elmer Trace analyzer ICP-OES	EPA Method 6010C (Appendix G)
Anions	Critical	T&E Facility	Ion Chromatograph (IC), using AS-9 Dionex chromatography column.	EPA Method 300.1 (Appendix H)
Radium 226 (aqueous)	Critical	ALS Environmental	Scintillation cell system	EPA Method 903.1 (Appendix I)
Radium 228 (aqueous)	Critical	ALS Environmental	Gas-flow proportional counting system	EPA Method 904.0 (Appendix J)
Gross Alpha/Beta (aqueous)	Non-critical	ALS Environmental	Gas-flow proportional counting system	EPA Method 900.0 (Appendix K)
Volatile Organic Compounds (VOCs)	Non-critical	SWRI	Gas Chromatography/Mass spectrometry (GC/MS)	EPA SW-846 8260B (Appendix L)
Semi-volatile Organic Compounds (SVOCs)	Non-critical	Region 8	Gas Chromatography/Mass spectrometry (GC/MS)	EPA SW-846 8270D (Appendix M)
Diesel Range Organics/ Gasoline Range Organics	Non-critical	Region 8	Gas Chromatography/Flame Ionization Detector (GC/FID)	EPA SW-846 8015C (Appendix N)
Total Organic Carbon	Non-critical	T&E Facility	Total Organic Carbon Analyzer (TOC) Persulfate-UV Oxidation	EPA Method 415.3 (Appendix O)
Ammonia Nitrogen (NH_3-N)	Non-critical	T&E Facility	HACH DR2700 Colorimeter	HACH Method 10200 (Appendix P)
pH	Non-critical	Field Sampling Sites	HANNA or YSI Meters, temperature compensated	(Standard Method 4500B (Appendix Q)
Conductivity	Non-critical	Field Sampling Sites	HANNA or YSI Meters, temperature compensated	(Standard Method 2510B (Appendix R)
Total Dissolved Solids (TDS)	Non-critical	T&E Facility	Wet Chemistry	Shaw T&E SOP 510 (Appendix S)
Total Suspended Solids (TSS)	Non-critical	T&E Facility	Wet Chemistry	Shaw T&E SOP 509 (Appendix T)
Constituents of Ba, Cr, Cu, Sr, Zn	Non-critical	AWBERC	X-ray diffraction	ASTM D 934-80 (Appendix U)
Percent concentration of Ba, Cr, Cu, Sr, Zn	Non-critical	AWBERC	X-ray fluorescence	ASTM D2332 (Appendix V)
Particle size of elements between Ba and S	Non-critical	AWBERC	Scanning Electron Microscopy	ASTM E 1508 (Appendix W)
Chemical speciation Ba, Cr, Cu, Sr, Zn	Non-critical	Argonne National Laboratory	X-ray absorption spectroscopy	SOP-Dr Scheckel (Appendix X)
Radium 226/228, Gross Alpha/Beta, U234, U235 and U238 (solid)	Non-critical	Region 4	Alpha spectrometric system consisting of multichannel analyzer	NAREL AM/SOP 1 (Appendix Y)

B5 QUALITY CONTROL

Instruments/equipment will be maintained in accordance with the EPA ORD Policies and Procedures Manual, Section 13.4, *Minimum Quality Assurance (QA)/Quality Control (QC) Practices for ORD Laboratories Conducting Research*, and in accordance with the Standard Operating Procedures (SOPs) and analytical methods shown in Table B4.1, including the temperature monitoring requirements as specified in Section 13.4 (environmental conditions and sample storage) for laboratory support equipment. All analytical data will be collected in accordance with the QA/QC procedures specified in this QAPP. Tables B5.1 (a-f) summarize the QA/QC checks, acceptance criteria, and corrective actions for the analysis to be conducted at each of the laboratories as well as the field sites. The data quality indicators for the analyses are defined in Sections B5.1 through B5.4.

If problems occur during analysis that cannot be resolved by the analyst, the laboratory point of contact will be notified immediately. The laboratory point of contact will determine corrective action and the issue will be documented, at a minimum, in the laboratory notebook.

B5.1 Precision

Precision is how repeated measurements closely agree with each other. Laboratory duplicates and triplicates will be used to ensure precision.

The relative percent difference (RPD) between duplicates will be calculated as follows:

$$\%\,RPD = \frac{|C1 - C2|}{0.5(C1 + C2)} \times 100$$

Where: C_1 = Concentration of the analyte in the sample
C_2 = Concentration of the analyte in the matrix duplicate

The relative standard deviation between replicates will be calculated as follows:

$$\%\,RSD = (\frac{S}{y'}) \times 100$$

Where: S = Standard deviation
y' = Mean of the replicates

B5.2 Accuracy

Accuracy is the nearness of a test result to the true value (recovery). Both standard addition (spiking) and standard checks are common techniques for checking the accuracy. For matrix spikes, the percent recovery is calculated as follows:

$$\%R = \frac{(Cs - Cu)}{Ca} \times 100$$

Where: C_s = Concentration in spiked aliquot
C_u = Concentration in unspiked aliquot
C_a = Actual concentration of spike added

For standard checks, the percent recovery will be calculated as follows:

$$\%R = \frac{Cm}{Ca} \times 100$$

Where: C_m = measured concentration of the check standard
C_a = actual concentration of the check standard

B5.3 Comparability

Data comparability will be maintained through the use of defined and consistent sampling and analytical procedures.

B5.4 Sensitivity

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest. The minimum concentration will be determined by the method, thus the MDL is implemented (EPA, 1986). MDLs for all analytes are calculated as outlined in CFR Title 40: Protection of the Environment Part 136-Guidelines establishing test procedures for the analysis of pollutants, Appendix B to Part 136-Definition and procedure for the determination of the Method Detection Limit-Revision 1.11. Positive results for analytes/compounds which are below the Quantitation Limit (QL) will be qualified and will not be included in statistical analyses.

MDL is the lowest concentration that is different from zero with a 99% level of confidence. To determine the MDL, the lowest standard concentration or below used for the calibration will be injected seven times and the MDL will be calculated using the following equation:

$$MDL = t(n-1, 1-\alpha = 0.99) \times S$$

Where: n = the number of replicates
S = Standard deviation of the replicates

The MDLs will be accepted only when MDL < spike concentration and MDL > 0.1 spike concentration except where there are not specified in the analytical method. The estimated Project-Required Detection Limits (PRDLs) are calculated as ten times the appropriate MDL for each analyte (Table B5.2). The MDLs and PRDLs will be used as guidance for determining the QLs for each group of analytes/compounds. The lowest calibration standard concentration will serve as the quantitation limit (QL), below which, all results will be reported as estimated value with a "J" qualifier. The QC acceptance criteria for the low-level calibration standard will be based on the criteria stated in each method. It should be noted that data will not be reported less than the lowest calibration standard without qualification.

Table B5.1a Summary of EPA T&E Facility QA/QC Checks for metals, anions, TOC, ammonia, TSS, and TDS

Parameter	QC Type	Purpose QC	Method	Frequency	Acceptance Criteria
Total and Dissolved Metals (EPA Method 6010C)	Initial calibration	Standardization of instrument	Mixed calibration Standards and calibration blank	Prior to each batch of analysis or after ICV failure	Second order curve $r^2 \geq 0.998$ (Section 10.4)
	Initial calibration verification (ICV)	Assess the validity of the calibration curve	Second (2^{nd}) source	After initial calibration	±10 % of the analytes true value (Sections 10.3.2&10.3.3)
	Low-level initial calibration verification (LLICV)	Assess instrument calibration	Same source low-level check.	After initial calibration	±30 % of the analytes true value (Section 10.3.3)
	Calibration Blanks (ICB & CCB)	Assess whether there are any traces of analytes of interest in reagent water	Acidified reagent water (2-5%)	Following ICV (ICB) and following each continuing calibration verification (CCB)	< low-level calibration standard (QL) (Sections 10.3.1.2 & 10.3.4)
	Continuing calibration verification (LLCCV and CCV)	Assess whether the instrument is within acceptable calibration throughout period in which samples were analyzed	Low-level and mid-point calibration point	LLCCV at the end of the sample batch CCV after every 10 samples and at the end of the sample batch	±30 % of the analytes true value for LLCCV ±10 % of the analytes true value for CCV (Sections 10.3.1.2 & 10.3.4)
	Lower limit quantitation check (LLQC)	Verify lower quantitation limits	Same source prepared at the lowest calibration standard concentration	For each preparation method as part of each analyst's initial demonstration of capability and after any significant changes in instrumentation	±30 % of the analytes true value
	Interference check solution (ICS)	Assess the level of other interferents	Elements of interest at 0.5-1.0 mg/L	One per batch after initial calibration	±20 % of the analytes true value (Sections 4.2.9 & 4.6)
	Method Blank (MB)	Assess contamination introduced from containers and reagents, carried throughout the entire sample	A volume of reagent water specific in the method (e.g. Method 3015A 45 mL)	One per batch of sample preparation	< low-level standard concentration (QL), or < 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater (Section 9.6).

Parameter	QC Type	Purpose QC	Method	Frequency	Acceptance Criteria
		preparation and analysis process			
	Laboratory control sample (LCS)	Assess overall method used to extract analytes of interest, carried throughout the entire sample preparation and analysis process	For liquid, Spike with mid-point concentration For solid, use standard reference material (SRMs)	One per batch of sample preparation	For liquid, ±20 % of the analytes true value; For solid (commercially prepared), manufacturer's established acceptance criteria (Section 9.6)
	Matrix Spike (MS)/ Matrix Spike Duplicate (MSD)	Assess the accuracy in a given matrix	A separate aliquot of the sample spiked with known concentrations of analytes	One per sample matrix	±25 % of the analytes true value for MS and 20% RPD for MSD (Section 9.8)
	Post digestion spike addition	Assess MS/MSD failures	Spike aliquot of post-digested sample	Analyzed only if there is an MS or MSD failure	±20 % of the analytes true value (Section 9.9.1)
	Laboratory duplicate	A precision measurement in a given matrix	A separate aliquot of the sample carried through the complete preparation and analytical procedure	One per batch	≤20% RPD for sample values (Section 9.8)
	Dilution test	Assess accuracy of dilution technique	Dilute the sample using reagent matrix	One per batch	±10 % of the original value for 1:5 dilution (Section 9.9.2)
	Field duplicate	Assess field sampling precision and homogeneity	Duplicate sample collected in the field at the same time under identical circumstances	One per field sampling site	±30% RPD for sample results > 5x QL
	Equipment blank (only for dissolved metals)	Assess whether there are any contamination during sample filtration	Nanopure water filtered through 0.45 µm filter with preservatives	One blank per matrix	Concentrations that are greater than the low-level standard concentration should be investigated.
	Field blank	Assess contamination introduced from containers, environment and reagents	Nanopure water with preservatives	One blank per matrix	Concentrations that are greater than the low-level standard concentration should be investigated.

Parameter	QC Type	Purpose QC	Method	Frequency	Acceptance Criteria
Total Organic Carbon (EPA Method 415.3)	Initial calibration	Standardization of instrument	Calibration	A new calibration curve is generated when fresh standards are made and/or when CCCs fail	Calibration curve must have $R^2 \geq$ 0.993 before proceeding with analysis (Section 10.2)
	Laboratory Blank (LB)	Assess whether there are any traces of analytes of interest in reagent water		One LB with each analysis batch	TOC must be ≤0.35 mg/L (Section 9.9)
	Continuing calibration checks (CCC)	Assess whether the instrument is within acceptable calibration throughout period in which samples were analyzed	A same source calibration standard	Analysis of Low-CCC at the beginning of each batch. Subsequent CCCs analyzed after every 10 samples and after the last sample	Low-CCC ±50% of the true value (Sections 9.5 & 10.3.1) Mid-CCC ±20% of the true value (Sections 9.5 & 10.3.2) High-CCC ±15% of the true value (Sections 9.5 & 10.3.3)
	Field duplicate	Assess field sampling precision and homogeneity	Two separate samples collected at the same time	One per field sampling site	≤20% RPD for samples > 5x QL (Section 9.6)
	Laboratory fortified sample matrix (LFM)	Assess matrix interference	Add known concentrations of analytes to a sample	One LFM with each sample matrix	Recovery 70-130% (Section 9.8)
	Quality control sample (QCS)	Assess the quality of the calibration standards and laboratory instrument performance	A second source different from the source of calibration standards	The QCS should be analyzed immediately after calibration	Analyzed value of 1-5 mg/L QCS must be within ±20% of the true value (Section 9.11)
	Field blank	Assess contamination introduced from containers, environment and reagents	Nanopure water with preservatives	One blank per WW sample matrix	Concentrations that are greater than the low-level standard concentration should be investigated.

Parameter	QC Type	Purpose QC	Method	Frequency	Acceptance Criteria
Anions (EPA Method 300.1)	Initial calibration	Standardization of instrument	Calibration	Once per sequence, after initial calibration check or continuing calibration check failure, or whenever fresh eluent is prepared	Initial calibration needs to be verified with an initial calibration check and the QCS (Section 10.5)
	Initial calibration check	Assess calibration curve	An individual calibration standard	Analyzed immediately after the calibration curve	±25 % of true value (QL to 10x QL) ±15% of true value (>10x QL) (Section 10.5.1)
	Quality control sample (QCS)	Assess calibration standards and laboratory instrument performance	A source of external to the lab and different from the source of calibration	After initial calibration	±15 % of true value (Section 9.2.2)
	Instrument Performance Check (IPC)	Assess instrument performance	Peak Gaussian Factor (PGF) will be calculated using initial calibration check peak	One per batch	0.8-1.15 (Section 9.3.3.1)
	Continuing and end calibration check	Assess whether the instrument is within acceptable calibration throughout period in which samples were analyzed	An individual calibration standard	After every 10 samples	±25 % of true value (QL to 10x QL) ±15 % of true value (Greater than 10x QL) (Section 10.5.1)
	Laboratory reagent blank (LRB)	Assess interferences in the laboratory environment, reagents and the apparatus	An aliquot of reagent water	After every 10 samples and at the end	<MDL (Section 9.3.1)
	Field duplicates	Assess field sampling precision and homogeneity	Two separate samples collected at the same time	One per field sampling site	<20% RPD for samples > 5x QL (Section 9.4.3.3)
	Surrogate	Assess the performance of instrument	Add same concentration of surrogate	With each calibration and sample	Recovery of 90-115%

Parameter	QC Type	Purpose QC	Method	Frequency	Acceptance Criteria
					(Sections 7.5.1, 9.4.2.1 & 9.4.2.2)
	Laboratory duplicate	Assess specifically laboratory procedures	Two sample aliquots taken in the laboratory from a single sample	One per batch	<20% RPD (Section 9.4.3.3)
	Laboratory fortified blank (LFB)	Assess whether the laboratory is capable of recovering analyte in blank matrix	An aliquot of reagent water spiked with a known amount of analytes	One per batch	±25% of true value (QL to 10x QL) ±15% of true value (>10x QL) (Section 9.3.2.2)
	Laboratory fortified sample matrix (LFM)	Assess whether sample matrix contributes bias to the analytical results	Add known concentrations of analytes to sample	One with each WW sample matrix	±25% of the original value (Section 9.4.1.4)
	Field blank	Assess contamination introduced from containers, environment and reagents	Nanopure water	One blank per WW sample matrix	Concentrations that are greater than the low-level standard concentration should be investigated.
Ammonia (HACH Method 10200)	Initial calibration adjustment	Standardization of instrument	The factory prepared calibration curve is adjusted using a mid range calibration standard (0.2 mg/L)	Initially, and if accuracy check fails	Calibration is verified with a secondary standard set (0.1 ± 0.04 and 0.4 ±0.06 mg/L)
	Accuracy check	Assess calibration	0.20 mg/L NH_3-N solution	Immediately after calibration	0.18-0.22 mg/L
	Laboratory blank	Assess contamination in laboratory reagent water	Disinfectant residual free nanopure water	One per sample batch	<0.1 mg/L
	Field blank	Assess contamination introduced from containers, environment and reagents	Nanopure water with preservatives	One blank per WW sample matrix	<0.1 mg/L
	Laboratory Duplicate	Assess method precision	Analyze 2 aliquots of the same sample	One per batch	±20% RPD
	Field Duplicates	Assess field sampling precision and homogeneity	Duplicate sample collected in the field at the same time under identical circumstances	One per field sampling site	±30% RPD for sample results > 5x QL
Total Dissolved Solids	Method blank	Assess contamination	Glass fiber filtered 250 mL of reagent	One blank sample per analysis	<2 mg/L

Parameter	QC Type	Purpose QC	Method	Frequency	Acceptance Criteria
(T&E SOP 510)			water	batch	(Section 11.1)
	Check standard	Assess method accuracy	Add 500 mg of dried NaCl and dilute to 1 L.	One per batch	±25% of known value (Section 11.3)
	Laboratory Duplicate	Assess method precision	Analyze 2 aliquots of the same sample	One per batch	±20% RPD (Section 11.3)
	Field Duplicates	Assess both field and laboratory precision	Duplicate sample collected in the field at the same time under identical circumstances	One per field sampling site	±30% RPD for sample results > 5x QL
Total Suspended Solids (T&E SOP 509)	Laboratory blank	Assess contamination	Glass fiber filtered 250 mL of reagent water	One blank per batch	<2 mg/L (Section 11.1)
	Check standard	Assess method accuracy	Add 400 mg of dried activated charcoal and dilute to 1 L with reagent water	One per batch	±25% of known value (Section 11.3)
	Laboratory duplicate	Assess method precision	Analyze 2 aliquots of the same sample	One per batch	±20% RPD (Section 11.3)
	Field Duplicates	Assess field sampling precision and homogeneity	Duplicate sample collected in the field at the same time under identical circumstances	One per field sampling site	±30% RPD for sample results > 5x QL
Temperature	Temperature Blanks	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler	Record temperature; condition noted on COC form

Table B5.1b Summary of Field QA/QC Checks for pH and conductivity

Parameter	QC Sample	Purpose	Method	Frequency	Acceptance Criteria/ Corrective Action
pH (Standard Method 4500-H^+ B)	Calibration		Initial using 2 pH buffer calibration solutions	Prior to each batch of analysis per WW sample matrix	Verify calibration with third pH buffer. Recalibrate if verification is outside of ± 0.1 pH unit acceptance criteria and re-check with third pH buffer. Sample analysis cannot proceed without a passing third pH buffer calibration verification check.
	Third pH buffer	Assess the calibration	3 pH units different from the second pH buffer	Immediately after calibration and at the end of analytical batch	± 0.1 pH unit of true pH buffer solution value (Section 4)
	Field duplicate	Assess field sampling precision and homogeneity	Duplicate sample collected in the field at the same time under identical circumstances	One per field sampling site	± 0.2 pH units between duplicate sample results
Conductivity (Standard Method 2510B)	Calibration		Read standard KCL solution	Prior to each batch of analysis	1000 µS/cm @ 25oC calibration solution, 20 mL sachet (Section 4)
	Field duplicate	Assess field sampling precision and homogeneity	Duplicate sample collected in the field at the same time under identical circumstances	One per field sampling site	±30% RPD for sample results > 5x QL

Table B5.1c Summary of ALS Environmental QA/QC requirements for Ra226 Ra228 Gross Alpha/Beta (from Case Study QAPP-PA) and Uranium (from National Air Radiation Environmental Laboratory (NAREL) SOP)

QC Type	Uranium (frequency; performance criteria)	Radium-226 (frequency; performance criteria)	Radium-228 (frequency, performance criteria)	Gross Alpha/Beta (frequency, performance criteria)
Method Blanks	1 per batch of 20 (or 5% frequency); <MDC	1 per batch of 20 (or 5% frequency); <MDC	1 per batch of 20 (or 5% frequency); <MDC	5% with minimum of 1 per batch of samples; <MDC
Blank Spikes (LCS)	1 per batch of 20 (or 5% frequency); Relative Standard Counting < 5%	1 per batch of 20 (or 5% frequency); 67-120% Recovery	1 per batch of 20 (or 5% frequency); 70-130% Recovery	5% with minimum of 1 per batch; 70-130% Recovery
Laboratory Duplicates	1 per batch of 20 ±30% RPD for sample results > 5x QL	Minimum frequency of 10%; DER<2.13	Minimum frequency of 10%. (Duplicate samples with activity levels <5X RL will not be assessed with RPD); DER<2.13	10% with minimum of 1 per batch; DER<2.13
Field Duplicates	NA	1 per field sampling site; ±30% RPD for sample results > 5x QL	1 per field sampling site; ±30% RPD for sample results > 5x QL	1 per field sampling site; ±30% RPD for sample results > 5x QL
Matrix Spikes	NA	NA	NA	5% with minimum of 1 per batch; 70-130% Recovery
Calibration	NIST-traceable radionuclides solution; calibration performed at least annually	NIST-traceable ^{226}Ra solution; calibration performed at least annually	Calibration with NIST-traceable ^{89}Sr, i.e., comparable to the beta activity of ^{228}Ac.	Calibration NIST-traceable ^{241}Am for gross alpha and ^{90}Sr for beta
Tracer/Carrier Limits	NA	40-110% Recovery	40-110% Recovery	NA

Table B5.1d Summary of SWRI QA/QC requirements for VOC (from Case Study QAPP-PA)

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 (SPC)	BFB Tune must meet tuning criteria in Table 4 of EPA Method 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)	%D≤20% for analytes using RF; 80-120% Recovery for analytes using curve fitting	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.
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.
Laboratory Duplicates (MS/MSD)	RPD<30%	Every 20 samples.
Field Duplicates	±30% RPD for sample results > 5x QL	One per field site.
Trip Blanks (VOCs)	<RL; if >RL, PI will determine if significant relative to sample data.	Two in each cooler with VOA samples.
Temperature Blanks	Record temperature; condition noted on COC form	One per cooler.
Field Blanks	Concentrations that are greater than the low-level standard concentration should be investigated.	One blank per WW sample matrix.

*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

Table B5.1e Summary of Region 8 QA/QC requirements for Semi-volatiles, DRO and GRO (from Case Study QAPP-PA)

QC Type	Semi-volatiles	DRO	GRO	Frequency
Method Blanks	<RL Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed	<RL Preparation or Method Blank	<RL Preparation or Method Blank and IBL	At least one per sample set
Surrogate Spikes	Limits based upon statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
Internal Standards Verification.	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
Initial multilevel calibration	ICAL: minimum of 6 levels (.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD≤20%, r^2≥0.990	ICAL: 10-500 ug/L RSD≤20% or r^2≥0.990	ICAL: .25-12.5 ug/L for gasoline (different range for other compounds) RSD≤20% or r^2≥0.990	As required (not daily if pass ICV)
Initial and Continuing Calibration Checks	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set, every tenth sample, and end of sample set
Second Source Standards	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
Laboratory Control Samples	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater
Matrix Spikes	Same as LCS	Same as LCS	70-130% of expected value	One per WW sample matrix
Matrix Spike/ Matrix Spike Duplicate	% Recovery same as MS RPD ≤ 30	% Recovery same as MS, RPD ≤ 25	% Recovery same as MS, RPD ≤ 25	One per WW sample matrix
Field Duplicates	±30% RPD for sample results > 5x QL	±30% RPD for sample results > 5x QL	±30% RPD for sample results > 5x QL	One per field site
Temperature Blanks	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler.	Record temperature; condition noted on COC form

Table B5.1f Summary of QA/QC requirements for XRD, XRF, SEM and XAS qualitative analyses

QC Type	XRD	XRF	SEM	XAS	Frequency
Initial Calibration Standard Check	Standard Crystalline material whose "d" spacings are accurately known such as Quartz (Si), Errors of about ± 0.1° 2 θ angle are accepted	NIST 2780 for Sr, NIST 2782 for Ba Cr and both NIST 2780/2782 for Cu and Zn as calibration standards ± 30 % of certified value	1) A spectrum from pure Al standards shall be calibrated on two X-ray peaks followed by pure Cu in the same spectrum 2) Perform background subtraction method in the manufacturer's software prior to calibration . 3) Use different analytical line when the interested element is only 10% to improve precision .	1) Calibration with fluorescence requires at least one million counts. . 2) A typical goal is between 60,000 to 120,000 counts per second (cps). 3) Calibration with energy requires a metal foil of interest. For example, Pb the energy is 13,035 eV. If the measured value is off, the monochromator can be realigned via software to the correct energy. (Au) (11919 eV l-edge)" to "(Au) (11919 eV L3 edge) 4) When foil of exact metal is not possible, a reference foil that is close to interested metal energy should be used. For example, when As (11867 eV) foil is not possible, usually gold (Au) (11919 eV l-edge) is used. 5) Use Athena software Autobk algorithm for background and normalization corrections.	At the beginning of analysis for XRD, XRF and XAS At the beginning and after every 10 sample for SEM
Second Source Standards/ Reference Material	Comparison of "d" spacings and intensities of the three strongest lines of Quartz ± 30 % of expected intensities	Internal standards may be used to provide direct comparison ± 30 % of certified value	Inter-laboratory metallurgical specimens to determine the precision N/A	SRM (e.g. $BaSO_4$, $SrSO_4$, $Cr_2K_2O_7$ and CrK_2O_4) will be analyzed for quantitative assessment N/A	Each time after calibration
Laboratory duplicates	±30% RPD for sample results	±30% RPD for sample results	±30% RPD for sample results	±30% RPD for sample results	One per batch of 20 samples

Table B5.2 Established MDL and Estimated QL for Critical Parameters

Contaminants	MDL mg L^{-1}	QL mg L^{-1}
Metals		
Arsenic	0.0063	0.1000
Barium	0.0019	0.0125
Boron	0.0471	0.5000
Chromium	0.0027	0.1000
Iron	0.0173	0.1250
Magnesium	0.0018	0.0625
Manganese	0.0023	0.1000
Sodium	0.0107	0.5000
Strontium	0.0024	0.0625
Anions		
Bromide	0.0217	0.1000
Chloride	0.0162	0.1000
Other Group of Chemicals (pCi/L)		
Radium 226 (aqueous)	1	10.00
Radium 228 (aqueous)	1	10.00

Note: For each analyte, the lowest calibration standard concentration will serve as the quantitation limit (QL), below which, all results will be reported as estimated value with a "J" qualifier. Actual MDLs and QLs will be included with the analytical reports for Metals, TOC, Anions, VOCs, SVOCs, DRO, and GRO analyses.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION AND MAINTENANCE

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. Generally, variability in known concentration of analytes will be used to test and inspect the instruments. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by the manufacturer's representative as needed.

B7 INSTRUMENT/EQUIPMENT CALIBRATION FREQUENCY

Instrument calibration frequency for the various analyses is discussed in Table B5.1 (a-f).

B8 INSPECTION/ ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Supplies and consumables are listed in the attached method, and will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined. Catalog number and batch number and expiry dates of supplies will be recorded in the general supplies/chemicals register. Catalog number and batch number and expiry dates of standards used for each calibration will be recorded.

B9 NON-DIRECT MEASUREMENTS

Non-direct data such as computer databases and programs will not be used in this study. Interim summary reports will be prepared presenting the analytical results from the HFWW treatment/reuse plants.

B10 DATA MANAGEMENT

As stated in Section A.9, laboratory paper and electronic records will be maintained in accordance with Section A.9. Data from each wet chemistry analysis will be recorded in a laboratory notebook or datasheet and each page will be dated and signed by the Shaw analyst(s) who performs the analysis. Printed data from equipment runs will be filed separately in a three-ring binder(s) and labeled "HFWW WA-3-02" with the name of the analyte, year and the month. Raw data will be kept as hard copies and computer files. Raw data from chemical instrumentation will be retained as required by EPA Record Schedules 501 and 507 and will be backed up onto a separate external hard drive.

If analytical instrumentation software/hardware allows for data export, raw instrument data will be automatically entered to Microsoft Excel spreadsheets. Microsoft Excel spreadsheets used for calculations and statistical analyses will be initially verified for accuracy by the analyst and then sent to a second reviewer. For manually entered data, transcription will also be checked initially for errors by the analyst and then sent to a second analyst for review. Final data will be expressed in units shown in Table B10.1.

Table B10.1 Reporting Units

Parameter	Units
Metals	mg/L, mg/kg
Anions	mg/L
Radium 226/228	pCi/L
Gross Alpha/Beta	pCi/L
Uranium	pCi/L
Volatile Organic Compounds (VOCs)	µg/L
Semi-Volatile Organic Compounds (SVOCs)	µg/L
Diesel Range Organics (DRO)	µg/L
Gasoline Range Organics (GRO)	µg/L
Total Organic Carbon (TOC)	mg/L
Ammonia Nitrogen (NH_3-N)	mg/L
pH	pH Units
Conductivity	µS/cm
Total Dissolved Solids (TDS)	mg/L
Total Suspended Solids (TSS)	mg/L

SECTION C ASSESSMENT AND OVERSIGHT

C1 EPA ASSESSMENTS AND RESPONSE ACTIONS

EPA will conduct readiness reviews, Technical Systems Audits (TSAs), Audits of Data Quality (ADQs), and Performance Evaluations (PEs) of Shaw activities. The other labs were previously evaluated during other parts of overall research study. Readiness reviews will be conducted prior to the collection of any field samples to ensure that all personnel, training, equipment, supplies, and procedures are available and acceptable for environmental data to be collected in accordance with the governing QAPP. Acceptability or issues that were identified during readiness reviews will be communicated to the PI and EPA WA Manager via email. TSAs and PEs will be conducted early in the project to allow for identification and correction of any issues that may affect data quality. TSAs will be conducted on both field and laboratory activities. Laboratory TSAs will focus on the critical target analytes. Detailed checklists, based on the procedures and requirements specified in this QAPP, related SOPs, and EPA Methods will be prepared and used during these TSAs. These audits will be conducted by the EPA/NRMRL HF QA HF Team or by QA support contractors with oversight by the EPA/NRMRL QA HF Team.

ADQs will be conducted on a representative sample of data for the critical target analytes. These audits will be conducted by the EPA/NRMRL HF QA HF Team or by QA support contractors with oversight by the EPA/NRMRL QA HF Team. See Section D1 for additional discussion on ADQs.

PEs will be conducted on target analytes (shown in Table A6.1) for those that are available commercially such as those from ERA, A Waters Company (Golden, CO). As part of the readiness review, PE samples must pass acceptably (as applicable) before any analysis can be done on project samples.

Assessors do not have stop work authority; however, they can advise the PI if a stop work order is needed in situations where data quality may be significantly impacted, or for safety reasons. The PI makes the final determination as to whether or not to issue a stop work order.

For TSA and ADQ reports that identify deficiencies requiring corrective action, the audited party must provide a written response to each Finding and Observation to the PI, which shall include a plan for corrective action and a schedule. (If the audited party is a contractor, then the response shall be delivered to the EPA WA Manager who will ensure delivery to the PI.) The PI is responsible for ensuring that audit findings are resolved. The QA HF Team will review the written responses to determine their appropriateness. If the audited party is other than the PI, then the PI shall also review and concur with the corrective actions. The QA Management Team will track implementation and completion of corrective actions. After all corrective actions have been implemented and confirmed to be completed; the QA HF Team shall send documentation to

the EPA WA Manager and his supervisor that the audit is closed. Audit reports and responses shall be maintained by the EPA WA Manager in the project file and the QA HF Team in the QA files, including QLOG.

C1.1 Assessments

TSAs will be conducted on both field and laboratory activities. Detailed checklists will based on the procedures and requirements specified in this QAPP, SOPs, and EPA Methods will be prepared and used during these TSAs. One field TSA will be conducted. It is anticipated this will take place during the first sampling event. The laboratory audit will take place when samples are in the laboratory's possession and in the process of being analyzed.

Laboratory TSAs will focus on the critical target analytes and will be conducted on-site at the EPA T&E Facility laboratories run by Shaw contractors. It is anticipated this will take place immediately following the first sampling event.

ADQs will be conducted on a representative sample of data for the critical target analytes for several initial data packages and then for subsequent data packages as determined to be necessary by project personnel based on issues identified. Additional ADQs will be performed as determined to be necessary by project participants.

C1.2 Assessment Results and Reports

At the conclusion of a TSA, a debriefing shall be held between the auditor and the PI or audited party to discuss the assessment results. TSA and ADQ results will be documented in reports to the PI, the PIs first-line manager, and the WSWRD HF QA Manager and the ETAV QA Manager. If any serious problems are identified that require immediate action, the QA Manager will verbally convey these problems at the time of the audit to the PI or audited party.

The PI is responsible for responding to the reports as well ensuring that corrective actions are implemented in a timely manner to ensure that quality impacts to project results are minimal.

C2 SHAW ASSESSMENTS AND RESPONSE ACTIONS

The Shaw QA Manager will conduct assessments to verify compliance with the requirements of this QAPP. Assessment activities include technical system assessments (TSAs), readiness reviews, and surveillances. TSAs, readiness reviews, and surveillances are further discussed in Section 9.0 of the Shaw T&E Facility Contract QMP. Corrective actions that are implemented in response to assessment findings are documented and tracked in accordance with Section 11 of the Shaw QMP.

EPA, at their discretion, may also conduct assessments to verify compliance with the requirements of this QAPP. Assessment activities that may be conducted by EPA include the

submittal of PE samples (including double blind PE samples), and conducting TSAs and surveillances. Shaw will fully cooperate with EPA for EPA-conducted assessments.

C2.1 Performance Evaluation (PE) Samples

If PE standards are available for the evaluation of the analytical methods described in this QAPP (shown in Table B4.1), the Shaw Team staff will analyze PE materials received from EPA. The EPA WSWRD QA Manager may also choose to submit PE standards for analysis as an independent assessment of Shaw's performance for a particular analytical method. The PE sample received will be treated and processed as a sample, and will be analyzed in accordance with the analytical methods shown in Table B4.1. All documentation, including sample receipt and storage, raw data, verification and validation of results, are included in the project file, as appropriate. Results will be internally reviewed by Shaw prior to submittal to EPA for approval and reporting.

C2.2 Assessments

The Shaw QA Manager will conduct project assessments (i.e., TSAs, readiness reviews, or surveillances) on a quarterly basis. Assessments will be conducted in accordance with Section 9 of the Shaw QMP. The data may also be assessed by use of a laboratory-focused TSA as detailed in the WA Quality document. The TSA focuses on sample receipt and handling, method parameters, equipment maintenance and calibration, and/or data reduction requirements as specified in the WA Quality document.

C2.3 Corrective Actions

Deficiencies requiring corrective action will be documented on a Corrective Action Plan form by the Shaw Project Leader or designee and submitted to the Shaw QA Manager. Corrective actions will be implemented by Shaw Team staff or the Shaw Project Leader, as appropriate. The Shaw QA Manager will track corrective actions to closure and notify the Shaw Project Leader and Program Manager when closure of items is complete.

C2.4 Reports to Management

Assessment reports will contain the assessment ID; location; purpose and scope; assessment type; assessment date(s); persons contacted; activities observed; and assessment results. Assessment reports are prepared by the Shaw QA Manager and distributed to the Shaw Project Leader and Program Manager. A response is prepared for QA assessment findings by the Project Leader to the Shaw QA Manager within 30 days, unless otherwise specified, after receipt of the final assessment report. Corrective Action Plans are generated in response to assessment findings, logged and tracked by the Shaw QA Manager through closure. When all findings of the assessment have been closed, notice is sent by the Shaw QA Manager to the Project Leader and Program Manager.

SECTION D DATA VALIDATION AND USABILITY

D1 EPA DATA REVIEW, VERIFICATION, AND VALIDATION

Criteria that will be used to accept, reject, or qualify data will include specifications presented in this QAPP, including the methods used and the measurement performance criteria presented in Table B.5.1 (a-e). In addition, sample preservation and holding times will be evaluated against requirements provided in Table B.1.1.

Data will not be released outside of NRMRL until all study data have been reviewed, verified and validated as described in this QAPP. The PI is responsible for deciding when project data can be shared with interested stakeholders in conjunction with the NRMRL Lab Director's approval.

Data verification will evaluate data at the data set level for completeness, correctness, and conformance with the method. Data verification will be done by those generating the data. This will begin with the personnel in the field and the analysts in the laboratory, monitoring the results in real-time or near real-time. The respective laboratories shall contact the PI and/or WA Manager upon detection of any data quality issues which significantly affect sample data. They shall also report any issues identified in the data report, corrective actions, and their determination of impact on data quality.

Data reports are reviewed by the PI and/or WA Manger for completeness, correctness, and conformance with QAPP requirements. All sample results are verified by the PI to ensure they meet project requirements as defined in the QAPP and any data not meeting these requirements are either reanalyzed or appropriately qualified in the data summary prepared by the PI (or in the work assignment deliverables prepared by contractors that will be used by the PI). See Section D3 for the Data Qualifiers. The Contract Laboratory Program guidelines on organic (EPA, 2008) and inorganic (EPA, 2010) methods data review are used as guidance in application of data qualifiers.

Data validation is an analyte- and sample-specific process that evaluates the data against the project specifications as presented in the QAPP. Data validation (i.e., audit of data quality) will be performed by a party independent of the data collection activity. Data summaries for the critical analytes that have been prepared by the PI as well as laboratory data reports and raw data shall be provided to the QAM, who will coordinate the data validation. The validation team shall evaluate data against the QAPP specifications. NRMRL SOP #LSAS-QA-02-0, "Performing Audits of Data Quality" will be used as a guide for conducting the data validation. The outputs from this process will include the validated data and the data validation report (ADQ Report). The report will include a summary of any identified deficiencies, and a discussion on each individual deficiency and any effect on data quality and recommended corrective action.

D2 SHAW DATA REVIEW, VERIFICATION AND VALIDATION

Data verification will be conducted in accordance with Shaw T&E SOP 102, *Data Review and Verification: Bench-Level Review, Data Verification, Data Validation, and Peer Review*. Validation is performed following the guidance provided in the EPA guidance document entitled, *Guidance on Environmental Data Verification and Validation*, EPA QA/G-8.

Initial data assessment is conducted by an analyst who is knowledgeable regarding the WA Quality requirements. The analyst determines that samples have been analyzed, calibration and QC data requirements have been met, and the data are ready for verification. This assessment is documented on the cover of the data summary.

Verification of 100% of the data is conducted by knowledgeable personnel other than the analyst, as assigned by the Shaw Project Leader. This verification is documented on the cover of the data summary. Data verification includes review of the data for completeness, correctness, and technical compliance as summarized below.

- Completeness
    - The data package received contains the documentation listed in the data validation section (below).
    - Forms and other required information have been completed.
    - All expected samples and analyses were reported.
    - Relevant information for each analysis, including QC results and supporting documentation, are included in the data package.
- Correctness
    - Results have been transcribed correctly to the reporting sheets.
    - Correct application of dilution factors.
    - Sample results are supported by valid QC.
    - Missing results and QC outliers have been noted.
- Technical compliance
    - Sample hold times were met.
    - The correct analytical method was used for each analysis, as specified in the QAPP.
    - The samples were properly preserved in accordance with the requested method.
    - Calculations, QC frequencies, and acceptance criteria applied to the data are the same as those specified in this QAPP.

Data validation of 10 percent of analytical data generated is conducted by qualified individuals (or organizations) that are sufficiently independent of those who performed the work, but are collectively equivalent in technical expertise. Data validation is conducted to ensure that activities are technically adequate, competently performed, properly documented, and satisfy

established technical and quality requirements. If significant errors are identified in this 10% check, additional data will be reviewed.

Data validation tasks begin with a review of the QAPP requirements. The data are submitted to the validator in "packets." Each packet contains the data for one sampling event and the following information in the order given here (unless a different submittal packet is agreed to by the validator and the submitter):

- General overview of the data, including information such as the number of samples, the matrix, a brief background on the site and/or system from which the samples originated, and any known problems with the data in general or with specific samples. An example Laboratory Data Summary Report is provided in Appendix Z.
- Field, chain-of-custody, or other pre-analysis information
- Standards data
- Initial calibration data
- Continuing calibration data
- Blank data
- Sample results, including raw data
- QC data.

Additional validation will be conducted if significant anomalies are detected during the 10 percent review. Significant anomalies may include missed holding times, calibration inconsistent with method and/or WA requirements, contaminated blank results, laboratory control samples outside control limits, replicate analysis outside RPD limits, matrix spike/matrix spike duplicate (MS/MSD) results outside recovery limits, or calculation errors.

D3 DATA QUALIFICATION

Data qualification is an integral component of data reporting, review and validation. During data reporting and review, qualifiers are applied to ensure the laboratory has provided data of known quality. During data validation, qualifiers are applied to alert the data end user to quality problems that may impact the usability of the data. Data qualifiers may be assigned to particular sample results based on available information, including: laboratory QC summaries, exceeded holding times, unavoidable analytical interference, laboratory data summary information, etc. The data qualifiers and other data descriptors to be used in this project are below in Table D1.1 and D1.2.

Table D1.1 Data Qualifiers

Qualifier	Definitions
U	The analyte was analyzed for, but not detected above the reported sample quantitation limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
J+	The result is an estimated quantity, but the result may be biased high.
J-	For both detected and non-detected results, the result is estimated but may be biased low.
B	The analyte is found in a blank sample above the quantitation limit, and the concentration in the sample is less than 10 times the concentration found in the blank.
H	The sample was prepared or analyzed beyond the specified holding time. Sample results may be biased low.
*	Relative percent difference of a field or lab duplicate is outside acceptance criteria.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be confirmed.

Table D1.2 Data Descriptors

Descriptor	Definitions
NA	Not Applicable (See QAPP)
NR	Not Reported by Laboratory or Field Sampling Team
ND	Not Detected
NS	Not Sampled

Application Notes for Data Qualifiers:

- If the analyte concentration was less than the Quantitation Limit (<QL), then the B qualifier will not be applied.
- If both an analyte and an associated blank concentration are between the MDL and QL, then the sample results are reported as <QL and qualified with U.
- For samples associated with high Matrix Spike recoveries, the J+ qualifier will not be applied if the analyte is less than the Quantitation Limit (<QL).
- For samples associated with low Matrix Spike recoveries, the J- qualifier will be applied to the analyte with low recovery regardless of analyte concentration (< or > QL).

D4 RECONCILIATION WITH USER REQUIREMENTS

The data will be evaluated to check if they conform to the QA objectives of the project. A statistical assessment for accuracy and precision will be performed. All analyses will be required to meet data quality objectives before formulation of the interim reports. The individual EPA Method or SOPs documenting an analysis will include a discussion of data verification, including ascertaining matrix effects and instrumental biases. Where failures are observed in the individual methods, data will be marked as suspect.

Characterization sample data will be presented in tabular format or in figures. All parameters will be reported along with the mean, standard deviation and range, when applicable. Tabular data summaries will be included in the main discussion of the reports.

REFERENCES

1. U.S. Environmental Protection Agency (1986). 40 CFR Part 136—Guidelines Establishing Test Procedures for the Analysis of Pollutants. Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11. USEPA (ed), Washington DC.

2. U.S. Environmental Protection Agency (1995). Test Methods for Evaluating Solid Waste. Vol. IA: Laboratory manual physical/chemical methods, SW-846, 3rd ed., U.S. Government Printing Office, Washington, DC.

3. U.S. Environmental Protection Agency (2012). GWERD Quality Assurance Project Plan Entitled *Hydraulic Fracturing Retrospective Case Study, Marcellus Shale*, Washington County, PA. Revision 1, January 28, 2012.

REVISION SUMMARY

Revision Number	Revision Date	Section	Description of Change
0	06/06/2013		Approved for implementation.
1	11/06/2013, 12/23/2013 and 01/10/2014	A2	Updated table of contents.
		A2.1	Added new acronyms/definitions.
		A3	Added new project personnel information and addresses
		A4	Added the role of project personnel
		A6.1	Incorporated new analytes and method requirements. Revised the section and added a paragraph to clarify the limitation of each sample digestion and the use of sample metal data in conjunction with PE results.
		A6.2	Added information on limitations of digestion methods and importance of digestion techniques comparison pertaining to current study and the use of metal data in conjunction with PE failures or PE results were not available. Added information on sample preparation as well as delivery for newly adopted analytes. Noted that boron will not be determined for EPA Digestion Method 3052
		B1	Updated analytical laboratory change for VOC analysis from EPA Region 7 to Southwest Research Institute (SWRI) throughout document. Updated field pH/conductivity meters to include the YSI meter in addition to the HANNA. Added new laboratory, point of contact and sample delivery information for additional sludge analyses.
		Table A4.1	Updated organization chart
		Table A6.2	Omitted phosphorus and silica from the target list and added XRD, XRF, SEM, XAS and U to the target list.
		Table A6.3	Updated the project schedule
		Table B1.1	Incorporated new analytes and corrected sample container and preservations. Changed sampling containers for ammonia and TOC from HDPE to amber glass and omitted temperature blank for

			radiological analyses. Added a foot note to indicate the use of current sludge/residual samples for XRD, XRF, SEM, XAS, Ra226, Ra228, alpha, beta and Uranium analyses
		Table B4.1	Incorporated new method requirements
		Tables B5.1a-B5.1f	Updated tables B5.1a-B5.1c including revision of Method 6010C method blank criteria, ammonia initial calibration and accuracy check criteria and pH field duplicate acceptance criteria. Added Table B5.1f QA/QC requirements for analyses.
		Table B5.2	Updated MDL and QL reporting limits
		Appendices	Incorporated method references including ASTM 934-80 for XRD, ASTM D2332 for XRF, ASTM E1508 for SEM, a SOP for XAS and a SOP for U

APPENDICES

APPENDIX A	EPA METHOD 3015A (MICROWAVE ASSISTED LIQUID DIGESTION)	Appendix A - EPA Method 3015A.pdf
APPENDIX B	EPA METHOD 3005a (DISSOLVED METALS)	Appendix B - EPA Method 3005a.pdf
APPENDIX C	EPA METHOD 3050B (HOT PLATE ASSISTED SOLID DIGESTION WITH HNO_3)	Appendix C - EPA Method 3050B.pdf
APPENDIX D	EPA METHOD 3051A (MICROWAVE ASSISTED SOLID DIGESTION WITH HNO_3)	Appendix D - EPA Method 3051A.pdf
APPENDIX E	EPA METHOD 3052 (MICROWAVE ASSISTED SOLID DIGESTION WITH HF/HNO_3 MIXED ACIDS)	Appendix E - EPA Method 3052.pdf
APPENDIX F	EPA CHAIN-OF-CUSTODY FORM	Appendix F - EPA Chain of Custody For
APPENDIX G	EPA METHOD 6010C (METAL ANALYSIS BY ICP-OES)	Appendix G - EPA Method 6010C.pdf
APPENDIX H	EPA METHOD 300.1 (ANIONS ANALYSIS BY IC)	Appendix H - EPA Method 300.1.pdf
APPENDIX I	EPA METHOD 903.1 (RADIUM 226)	Appendix I - EPA Method 903.1.pdf
APPENDIX J	EPA METHOD 904.0 (RADIUM 228)	Appendix J - EPA Method 904 0.pdf
APPENDIX K	EPA METHOD 900.0 (GROSS ALPHA BETA)	Appendix K - EPA Method 900.0.pdf

APPENDIX L	EPA METHOD 8260B (VOC)	 Appendix L - EPA Method 8260B.pdf
APPENDIX M	EPA METHOD 8270D (SVOC)	 Appendix M - EPA Method 8270D.pdf
APPENDIX N	EPA METHOD 8015C (DRO GRO)	 Appendix N - EPA Method 8015C.pdf
APPENDIX O	EPA METHOD 415.3 (TOTAL ORGANIC CARBON)	 Appendix O - EPA_415.3.pdf
APPENDIX P	HACH METHOD 10200 (AMMONIA-NITROGEN ANALYSIS)	 Appendix P - HACH Method 10200.pdf
APPENDIX Q	STANDARD METHOD 4500-H^+ B (pH DETERMINATION USING pH PROBE)	 Appendix Q - Standard Method 45C
APPENDIX R	STANDARD METHOD 2510 B (CONDUCTIVITY DETERMINATION USING CONDUCTIVITY PROBE)	 Appendix R - Standard Method 251
APPENDIX S	SHAW T&E SOP 510 (TDS DETERMINATION)	 Appendix S - 510 Total Dissolved Solids
APPENDIX T	SHAW T&E SOP 509 (TSS DETERMINATION)	 Appendix T - 509 Total Suspended Solic
APPENDIX U	ASTM 934-80 (X-RAY DIFFRACTION)	 Appendix U - XRD ASTM D934-80.pdf
APPENDIX V	ASTM D2332 (X-RAY FLUORESCENCE)	 Appendix V - XRF ASTM D2332.pdf
APPENDIX W	ASTM E1508 (SCANNING ELECTRON MICROSCOPY)	 Appendix W - SEM ASTM E1518.pdf

APPENDIX X	SOP-DR. SCHECKEL (X-RAY ABSORPTION SPECTROSCOPY)	 Appendix X - XAS SOP.pdf
APPENDIX Y	NAREL AM/SOP 1 (ALPHA SPECTROMETRIC OF MULTICHANNEL ANALYZER)	 Appendix Y-NAREL-Actinides Al
APPENDIX Z	EXAMPLE LABORATORY DATA REPORT	 Appendix Z - Example Laboratory [