

**QUALITY ASSURANCE PROJECT PLAN
FOR HYDRAULIC FRACTURING WASTE WATER
SOURCE APPORTIONMENT STUDY**

**U. S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
NATIONAL EXPOSURE RESEARCH LABORATORY**

June 25, 2012

APPROVED BY:

<u>15/</u> _____ Gary Norris, Branch Chief, Principal Investigator	<u>6/29/2012</u> _____ Date
<u>15/</u> _____ Matthew Landis, Principal Investigator	<u>6/25/2012</u> _____ Date
<u>15/</u> _____ Chris Impellitteri (NRMRL, Cincinnati), Project Lead	<u>6/30/2012</u> _____ Date
<u>15/</u> _____ Stephen Kraemer (NERL, Athens), Project Lead	<u>6/29/2012</u> _____ Date
<u>15/</u> _____ Roy Fortmann, Acting HEASD Division Director	<u>6/25/2012</u> _____ Date
<u>15/</u> _____ Michelle Henderson, NERL, Director of Quality Assurance	<u>6/26/2012</u> _____ Date

A2 Table of Contents

List of Figures	3
List of Tables	3
List of Appendices	3
Notice.....	4
List of Abbreviations	5
SECTION A. PROJECT MANAGEMENT.....	7
A3 Distribution List	7
A4 Project/Task Organization	8
A5 Problem Definition/Background	11
A6 Project/Task Description.....	12
A7 Quality Objectives and Criteria for Measurement Data.....	14
A8 Special Training/Certification	17
A9 Documents and Records.....	17
SECTION B. MEASUREMENT/DATA ACQUISITION	19
B1 Sampling Process Design	19
B2 Sampling Methods	22
B3 Sample Handling and Custody	23
B4 Analytical Methods	25
B5 Quality Control.....	26
B6 Instrument/Equipment Testing, Inspection, and Maintenance	28
B7 Instrument Calibration and Frequency.....	28
B8 Inspection/Acceptance of Supplies and Consumables	29
B9 Non-Direct Measurements	30
B10 Data Management	30
SECTION C. ASSESSMENT AND OVERSIGHT	30
C1 Assessments and Response Actions	30
C2 Reports to Management	32
SECTION D. DATA VALIDATION AND USABILITY	32
D1 Data Review, Verification, and Validation	32
D2 Verification and Validation Methods.....	32
D3 Reconciliation with User Requirements	33
REFERENCES.....	35

List of Figures

Figure 1. Hydraulic Fracturing Waste Water Source Apportionment Study Research Team.....9

List of Tables

Table 1. HF Wastewater Source Apportionment Study Research Team Personnel Responsibilities.....10
Table 2. Elements, Ions and Isotopes to be analyzed in Stream Waters.....14
Table 3. Target quantitative Data Quality Indicators for Inorganic Elements by Inductively Coupled Plasma Optical Emission Spectroscopy.....16
Table 4. Target quantitative Data Quality Indicators for Inorganic Ions by High Resolution Inductively Coupled Plasma Mass Spectrometer.....16
Table 5. Target quantitative Data Quality Indicators for Inorganic Ions by Ion Chromatography.....17
Table 6. Waste Water Treatment Facility and Receiving Stream Information.....20
Table 7. Sample collection schematic.....21
Table 8. Sample Holding Times and Storage.....24
Table 9. Volume Allotments for Sample Analyses.....24
Table 10. Analytical Quality Control Elements27
Table 11. Schedule of Audits.....31

List of Appendices

APPENDIX A: List of Operating Procedures Used.....36
APPENDIX B: Quality Assurance Project Plan Deviation Report.....37
APPENDIX C: Chain of Custody Form.....38

Notice

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 quality assurance/quality control activities and technical requirements that will be used during the research study. EPA plans to publish the research study results in a draft report, which will be reviewed by the EPA Science Advisory Board. The final research report would be considered the official Agency dissemination. Mention of trade names or commercial products in this planning document does not constitute endorsement or recommendation for use.

List of Abbreviations

AMD	Acid Mine Drainage
BP	Barometric Pressure
CMB	Chemical Mass Balance
CFUB	Coal Fired Utility Boiler
COTS	Commercial off-the-shelf
COTW	Commercially Owned Treatment Works
CFS	Cubic Feet per Second
CPVC	Chlorinated Polyvinyl Chloride
DaVIs	Data Visualization
DBP	Disinfection Byproduct
DI	Deionized
DQO	Data quality objective
ECAB	Environmental Characterization and Apportionment Branch
EPA	Environmental Protection Agency
ERD	Ecosystems Research Division
GPD	Gallons per day
GWERD	Ground Water and Ecosystem Research Division
HEASD	Human Exposure and Atmospheric Sciences Division
HF	Hydraulic fracturing
HR- ICPMS	High Resolution Magnetic Sector Field Inductively Coupled Plasma Mass Spectrometer
IC	Ion Chromatography
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IDL	Instrument Detection Level
IO	Immediate Office
LDR	Linear Dynamic Range
MS	Mass spectrometry
MDL	Method detection limit
MQL	Method quantification limit
Milli-Q	ASTM Type II Laboratory Water (18.2 Ω -cm)
NCC	National Computer Center
NERL	National Exposure Research Laboratory

NRMRL	National Risk Management Research Laboratory
OGWDW	Office of Ground Water and Drinking Water
ORD	Office of Research and Development
ORP	Oxidative/Reduction Potential
OSP	Office of Science Policy
PARCC	Precision, accuracy, representativeness, completeness, and comparability
PDW	Public Drinking Water
PI	Principal Investigator
PLS	Partial Least Squares
PMF	Positive Matrix Factorization
POTW	Publically Owned Treatment Works
PPM	Policies and Procedures Manual
QA	Quality assurance
QAM	Quality Assurance Manager
QATS	Quality Assurance Tracking System
QC	Quality control
QAPP	Quality assurance project plan
ReSCUE	Reduction and Species Clustering Using Episodes
RSB	Regulatory Support Branch
RSD	Relative standard deviation
SOP	Standard operating procedure
SRM	Standard Reference Material
SRMD	Standards and Risk Management Division
SRRB	Standards and Risk Reduction Branch
TDS	Total dissolved solids
THM	Trihalomethane
TIMS	Thermal Ionization Mass Spectrometer
TSCA CBI	Toxic Substances Control Act Confidential Business Information
USGS	United States Geological Survey
WQMB	Water Quality Management Branch
WSWRD	Water Supply and Water Resources Division
WWTF	Waste Water Treatment Facility

SECTION A. PROJECT MANAGEMENT

A3 Distribution List

NAME	PROJECT TITLE / POSITION	PHONE
EPA, ORD, NERL, HEASD, ECAB		
Gary Norris	Branch Chief/Principal Investigator/Project Manager	(919) 541-1519
Matthew Landis	Principal Investigator/Project Team Lead	(919) 541-4841
Kasey Kovalcik	Branch QA Representative	(919) 541-7888
EPA, ORD, NERL, HEASD, Immediate Office		
Roy Fortmann	Acting HEASD Division Director	(919) 541-1021
Myriam Medina-Vera	Acting HEASD QA Manager and Deputy Director	(919) 541-5016
EPA, ORD, NERL, Immediate Office		
Jennifer Orme-Zavaleta	Director	(919) 541-2106
Jewel Morris	Deputy Director	(919) 541-2107
Andrew Gillespie	Associate Director for Ecology & NERL HF Coordinator	(919) 541-7989
Michelle Henderson	Director of Quality Assurance	(513) 569-7353
EPA, ORD, NERL, ERD, RSB		
Stephen Kraemer	Principal Investigator for Scenario Evaluation and Modeling Project	(706) 355-8340
EPA, ORD, NRMRL, WSWRD, WQMB		
Christopher Impellitteri	Principal Investigator for Produced Water Treatment and Disposal Project	(513) 487-2872
EPA, ORD, NRMRL, GWERD		
David Jewett	HF Team Technical Lead	(580) 436-8703
Jim Weaver	Hydraulic Modeler	(580) 436-8550
EPA, ORD, OSP		
Stephen Watkins	HF Project Quality Assurance Manager	(202) 564-3744
Jeanne Briskin	HF Team Project Lead	(203) 564-4583
EPA, Region 3		
Ronald Landy	Region 3 ORD Liaison	(410) 305-2757
Amy Bergdale	Field Technician	(304) 234-0285

A4 Project/Task Organization

The Hydraulic Fracturing Waste Water Source Apportionment project is managed and implemented by the National Exposure Research Laboratory's (NERL) Human Exposure and Atmospheric Sciences Division (HEASD) of the EPA Office of Research and Development (ORD). The Hydraulic Fracturing Waste Water Source Apportionment project supports the Produced Water Treatment/Disposal and Scenario Evaluation and Modeling studies within the national EPA ORD Hydraulic Fracturing Study. The Produced Water Treatment/Disposal Project Lead is Chris Impellitteri (National Risk Management Research Laboratory (NRMRL), Cincinnati) whereas the Scenario Evaluation and Modeling Project Lead is Stephen Kraemer (NERL), Athens, GA. The NERL Coordination Lead is Andrew Gillespie. Matthew Landis is the Source Apportionment Project Team Lead and Gary Norris is the Source Apportionment Project Manager, both from HEASD. The Project Team Lead will be responsible for maintaining and updating the official approved quality assurance project plan (QAPP). Analyses will be conducted by HEASD's Environmental Characterization and Apportionment Branch (ECAB) in Research Triangle Park, NC. Myriam Medina-Vera and Kasey Kovalcik are the Acting HEASD Quality Assurance Manager and ECAB Branch Quality Assurance Representative/Inorganic Laboratory Manager, respectively. **Figure 1** summarizes the roles of the NERL HF Source Apportionment project team members. **Table 1** summarizes the responsibilities for the NERL HF source apportionment study research team.

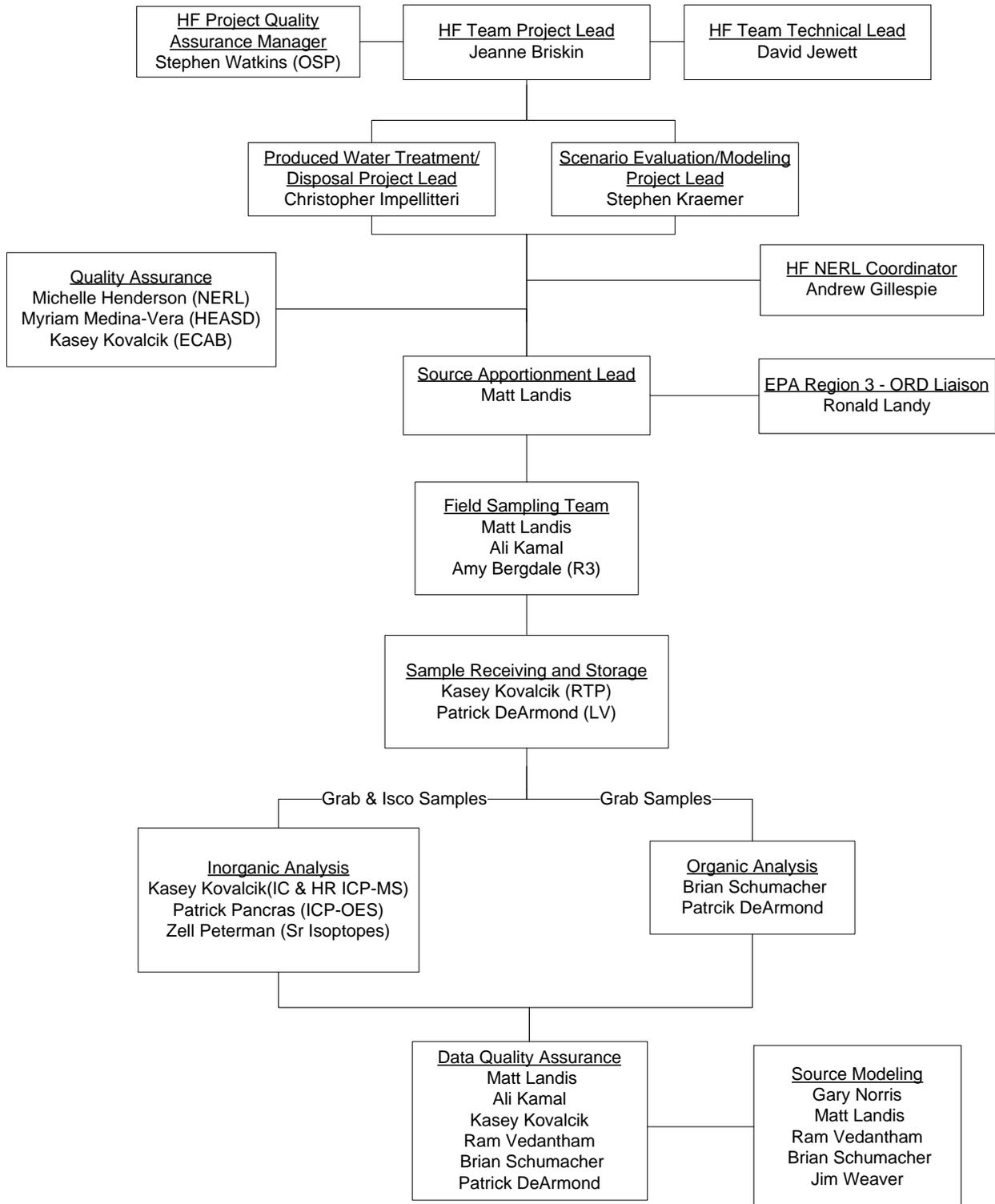


Figure 1. Hydraulic Fracturing Waste Water Source Apportionment Study Research Team

Table 1: HF Waste Water Source Apportionment Study Research Team Personnel Responsibilities

Personnel	Responsibilities
Principal Investigators	
Matthew Landis	<u>Project Team Lead</u> responsible for (i) development of study plan, (ii) coordination of sample collection and analysis, (iii) outreach coordination with commercial treatment facilities, (iv) field sample campaign logistics, (v) development of field safety plan, (vi) field study lead, (vii) field sample custody, (viii) project timeline and schedules, and (ix) review, approval, and maintaining/updating approved QAPP.
Gary Norris	<u>Project Manager</u> responsible for coordination with HEASD and NERL, project budget, schedules, and source apportionment modeling lead and review and approval of these tasks as found in the QAPP.
Stephen Kraemer	<u>Principal Investigator</u> for Scenario Evaluation and Modeling project responsible for review and approval of sampling strategy and data as found in the QAPP.
Christopher Impellitteri	<u>Principal Investigator</u> for Produced Water Treatment and Disposal project responsible for review and approval of sampling strategy and data as found in the QAPP.
Scientific and Field Staff	
Kasey Kovalcik	<u>Inorganic Laboratory Manager</u> responsible for (i) evaluation and modification of analytical SOPs for IC and HR-ICPMS, (ii) IC, ICP-OES, and HR-ICPMS sample analysis, (iii) QA review of IC, ICP-OES, and HR-ICPMS data, and (iv) lab sample custodian.
Zell Peterman	USGS scientist responsible for TIMS Sr isotope analysis.
Ali Kamal	Responsible for (i) development of SOPs for operation of field sampling equipment (Isco samplers, YSI multi-probe, Onset in river sondes), (ii) development of chain-of-custody and sample tracking SOP, (iii) participating as a field sampling team member, (iv) back-up lab sample custodian, (v) back-up field sample custodian, and (vi) database manager.
Ram Vedantham	Responsible for (i) development of project Microsoft Access database, (ii) back-up database manager, and (iii) source apportionment modeler.
Amy Bergdale	Responsible for (i) field study river and treatment facility reconnaissance, (ii) grab sample collection, and (iii) installation of Region 3 in river sondes.
Patrick DeArmond	Sample receiving and storage of HF samples; Organic analysis of samples.
Brian Schumacher	Organic analysis of HF samples.

Table 1 (continued): HF Wastewater Source Apportionment Study Research Team Personnel Responsibilities

Project Coordination	
Ronald Landy	ORD Liaison responsible for coordination between ORD and EPA Region 3.
Andrew Gillespie	NERL Liaison responsible for coordination between NERL and EPA OSP.
Jeanne Briskin	HF Team Project Lead responsible for overall project coordination.
David Jewett	HF Team Technical Lead responsible for coordination of data collection and analysis.
Quality Assurance	
Kasey Kovalcik	ECAB QA Representative responsible for ECAB Branch level review and approval of SOPs related to this study.
Myriam Medina-Vera	HEASD Quality Assurance Manager responsible for division level review and approval of QAPPs and associated SOPs related to this study.
Michelle Henderson	NERL Quality Assurance Manager responsible for laboratory level review of QAPPs and SOPs related to this study.
Stephen Watkins	HF Project Quality Assurance Manager responsible for OSP project level review of QAPPs related to this study.
Modeling	
Ram Vedantham	Source Apportionment Modeler responsible for model applications and development.
Jim Weaver	Hydraulic Modeler responsible for chemical transport modeling support.

A5 Problem Definition/Background

Hydraulic Fracturing (HF) is a method of extracting natural gas from unconventional hydrocarbon reservoirs, such as coal beds and shales. During HF of shale plays, an average of 3 to 5 million gallons of fracturing fluid (water with chemical additives such as lubricants, anti-scaling agents, surfactants, proppants, and biocides) are injected into the horizontal well bores of a gas-bearing geologic formation (e.g. shale), typically at depths ranging from 500 to 3,000 meters. The impact of this pressurized fluid creates vertical fractures in the gas-reservoir formation, through which natural gas can migrate. As the pressure of the fracturing fluid injection is reduced, the fractures relax into the proppants and the fluid is pumped up through the bore hole to the surface. The fluid that is recovered at the surface is termed "flowback" and contains the chemical components of the original fracturing fluid, and some chemical components of the gas-reservoir formation, including salts and hydrocarbons. Typically, only 10-30% of the fracturing fluid is recovered as flowback water from shale formations. Since flowback water is the early return fluid and only interacts with gas-bearing formation for a short period of time, flowback water is compositionally similar to the initial fracturing fluid. During well production, small amounts of water (generally less than 50 gallons per day¹) are brought to the surface with the gas stream and are termed "produced" water. Produced water has a much longer time to interact with the target gas-bearing formation. In this time, water-soluble compounds, natural gas, and other hydrocarbons are entrained from the target formation into the produced water. Wells produce organic condensates and gas with these waters throughout the lifetime of the well.

A series of chemicals that have been found in produced waters are provided in Table E2 of the U.S. EPA

HF Study Plan¹. Produced waters are also highly saline, up to ten times the salinity of sea water, with particularly high bromide concentrations in produced waters from the Marcellus Shale play. High bromide concentrations are of significant concern due to the propensity of bromides to react with aromatic organic compounds to produce carcinogenic trihalomethanes (THM) and other disinfection byproducts (DBP) from drinking water treatment processes. Flowback and produced waters are often stored in above-ground storage tanks or in surface impoundments. During storage, it appears that microbial activity changes the organic composition of impounded fluids. These fluids are visibly distinct from fresh flowback and produced waters, and are referred to as “blackwater”.

Hydraulic fracturing wastewaters are either recycled and reused at other HF wells or are disposed of through deep-well injection, publicly owned waste water treatment works (POTWs), or commercially owned waste water treatment works (COTWs). Deep-well injection has historically been the most common disposal method for saline drill wastes, but other disposal methods have become more common as the hydraulic fracturing industry has expanded. Currently, there are industrial research efforts to develop effective methods for the recycling of hydraulic fracturing wastewaters at zero-discharge plants. Meanwhile, fracturing wastewater is disposed of at COTWs and publicly POTWs. Most waste water treatment facilities (WWTFs) (including both COTWs and POTWs) are designed to filter and flocculate solids and consume biodegradable organic species, but have not been designed to manage the organic and inorganic chemical compounds contained in shale gas fracturing wastewaters. This project will evaluate the inorganic composition of river water upstream and downstream of WWTFs processing hydraulic fracturing wastewaters to elucidate any potential impacts of the WWTF discharges.

Additionally, public drinking water (PDW) intakes are often located in river systems with discharges from WWTFs and a variety of other industrial and/or urban discharges, and it is critical to evaluate sources of contamination at those drinking water intakes. Especially in areas with water quality concerns, it is important to discern whether HF wastes or a variety of other potential contamination sources such as coal-fired utility boilers (CFUB), acid mine drainage (AMD), and road salt are negatively impacting water quality. This project will provide source profile characteristics and data for Source Apportionment Modeling using statistical receptor models to quantitatively determine sources contributing to impaired water quality in rivers upstream of public drinking water intakes in western Pennsylvania (EPA Region 3).

A6 Project/Task Description

The three primary objectives of this project are to (1) quantify the inorganic chemical composition of discharges in two river systems from commercial waste water treatment facilities receiving oil/gas well flow back and produced water, coal-fired electric utilities, acid mine drainage, storm water runoff of roadway deicing material, and other industrial sources; (2) investigate the impacts of the discharges by simultaneously collecting multiple upstream and downstream samples to evaluate transport and dispersion of inorganic species; and (3) estimate the impact of these sources on downstream bromide and chloride levels in public drinking water supply system intakes using mathematical models. Stream water samples will be collected upstream and downstream of two WWTFs currently processing hydraulic fracturing wastewaters (described in Section B1). Specifically, automatic water samplers (Teledyne Isco, model 6712) will be deployed at five sites in the river systems containing each WWTF, for a total of ten sampling sites. Sample site locations are discussed more thoroughly in Section B1. Briefly, one Isco sampler will be deployed at a site upstream of each WWTF to assess the background conditions of the stream water, without influence of the WWTF. One Isco sampler will be deployed inside each of the two participating WWTFs to sample the facility effluent directly. Two Isco samplers will be deployed downstream of each WWTF. The first downstream sampler will be located at a proximal point determined to represent a zone in which the WWTF effluent is effectively well mixed in the river (see

Section B1.1). The second downstream sampler will be located approximately equidistant between the first downstream location and the closest PDW intake. Finally, there will be a sampling site in the nearest PDW intake downstream of each WWTF. Daily composite samples will be collected at each of the ten sites described above, with two daily composite samples collected at the PDW intake sites. Collocated Isco samples will be collected at one site per sampling campaign to provide replicate precision of the field measurements (e.g., spring – at a river sampling site; summer – at a PDW sampling site; fall – at a river sampling site). Automatic water samples will be collected according to EPA NERL/HEASD Standard Operating Procedure for the Teledyne Isco 6712 Portable Automatic Sequential Water Sampler (ECAB-136). On the other hand, samples for source characterization (including HF flowback waters, HF produced waters, POTW effluent, CFUB discharge, AMD, and road deicing material stormwater runoff) will be collected manually following EPA NERL/HEASD SOP Manual Collection of Hydraulic Fracturing Wastewater Samples (ECAB-132.0). A minimum of 3 water samples will be collected per source sample collection site. Specifications for the source sample collection sites are provided in section B1.1.

Each river water and source sample will be analyzed for the suite of elements and ions listed in **Table 2**. Inorganic ion and element concentrations will be determined by ion chromatography (IC), inductively coupled plasma optical emission spectroscopy (ICP-OES), and high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) (see SOPs listed in Appendix A). Additionally, strontium (Sr) isotope analyses will be determined on a subset (approximately 20%) of samples by thermal ionization mass spectrometry (TIMS). Samples on which Sr isotope analyses will be performed will be selected to corroborate source apportionment modeling results.

Three two-week intensives will be conducted to assess river conditions under different flow regimes (spring, summer, autumn). The spring intensive is scheduled for April 30 – May 14, 2012, the summer intensive will be conducted in August 2012, and the autumn intensive in October 2012. Sondes will be deployed at each river sampling location and will monitor temperature and conductivity (Total Dissolved Solids (TDS)) from April through October to provide data to evaluate the representativeness of the intensive study periods.

This project will be completed in three phases: sample collection, sample analysis, and source apportionment modeling. The first two phases are described in this QAPP, and the third phase will be described in a separate NERL/HEASD modeling QAPP. In Phase 1, river water samples will be collected by EPA ORD/NERL/HEASD personnel by automated stream water samplers in the Allegheny River and Blacklick Creek located in western Pennsylvania, and samples will be shipped (within one week of collection) to the EPA in Research Triangle Park, NC for laboratory analysis. Additionally, representative samples of HF wastes, WWTF effluents, CFUB discharge, AMD, and road salt runoff will be collected in Pennsylvania or West Virginia by EPA Region 3 or EPA ORD/NERL/HEASD personnel and shipped to Research Triangle Park, NC for laboratory analysis. In Phase 2, 15 mL aliquots of stream water samples and source characterization samples will be analyzed using existing methods for sample preparation and instrument usage of the IC, ICP-OES, and HR-ICP-MS (see **Table 2** and Appendix A). A 500 mL working archive of each sample will be retained in a locked and monitored 4°C refrigerator. If selected (based on source apportionment modeling), a 250 mL aliquot of the working archive will be shipped to the USGS in Denver, CO for Sr isotope analysis using TIMS. Phase 2 analyses will provide definitive measurements including PARCC parameters (precision, accuracy, representativeness, completeness, and comparability), of the elements of interest. Rigorous Quality Assurance/Quality Control (QA/QC) will be implemented and assessed as described in the SOPs associated with this QAPP. Data from Phase 2 ultimately will be utilized to support the third phase, which is conducting source apportionment receptor modeling.

Table 2. Elements, Ions and Isotopes to be analyzed in Stream Waters

Element	Instrument Used	Element (con't)	Instrument Used (con't)
Ag	HR-ICP-MS	Nd	HR-ICP-MS
Al	ICP-OES	Ni	HR-ICP-MS
As	HR-ICP-MS	P	ICP-OES
B	ICP-OES	Pb	HR-ICP-MS
Ba	ICP-OES	Pd	HR-ICP-MS
Be	HR-ICP-MS	Pt	HR-ICP-MS
Bi	HR-ICP-MS	Rb	HR-ICP-MS
Ca	ICP-OES	S	ICP-OES
Cd	HR-ICP-MS	Sb	HR-ICP-MS
Ce	HR-ICP-MS	Sc	HR-ICP-MS
Co	HR-ICP-MS	Se	HR-ICP-MS
Cr	HR-ICP-MS	Si	ICP-OES
Cs	HR-ICP-MS	Sm	HR-ICP-MS
Cu	ICP-OES, HR-ICP-MS	Sn	HR-ICP-MS
Fe	ICP-OES, HR-ICP-MS	Sr	HR-ICP-MS
Gd	HR-ICP-MS	Tb	HR-ICP-MS
Ge	HR-ICP-MS	Th	HR-ICP-MS
K	ICP-OES	Ti	ICP-OES
La	HR-ICP-MS	Tl	HR-ICP-MS
Li	ICP-OES	U	HR-ICP-MS
Mg	ICP-OES	V	HR-ICP-MS
Mn	ICP-OES, HR-ICP-MS	W	HR-ICP-MS
Mo	HR-ICP-MS	Y	HR-ICP-MS
Na	ICP-OES	Zn	ICP-OES
Ion	Instrument Used	Isotope Ratio	Instrument Used
Ca ²⁺	IC	⁸⁷ Sr: ⁸⁶ Sr	TIMS
K ⁺	IC		
Li ⁺	IC		
Mg ²⁺	IC		
NH ₄ ⁺	IC		
Na ⁺	IC		
Br ⁻	IC		
Cl ⁻	IC		
F ⁻	IC		
NO ₂ ⁻	IC		
NO ₃ ²⁻	IC		
PO ₄ ³⁻	IC		
SO ₄ ²⁻	IC		

A7 Quality Objectives and Criteria for Measurement Data

Field sampling requires (i) cleaned sample bottles and collection supplies, (ii) the use of established clean handling techniques during deployment and collection, (iii) proper documentation and chain of custody, and (iv) proper packaging and preservation of samples.

To ensure the integrity of collected samples according to this QAPP, sample bottles will be prepared according to methods detailed in EPA NERL/HEASD SOP Manual Collection of Hydraulic Fracturing Wastewater Samples (ECAB-132.0), and samples and field blanks will be collected by EPA ORD/NERL/HEASD staff using EPA NERL/HEASD Standard Operating Procedure for the Teledyne Isco 6712 Portable Automatic Sequential Water Sampler (ECAB-136.1) and as described in Section B of this QAPP. Additionally, collocated replicate samples will be collected for 10% of the samples collected throughout the course of the three field campaigns (42 days). After collection, the samples will be analyzed for the elements, ions, and isotopes presented in **Table 2** using IC, ICP-OES, HR-ICP-MS, or TIMS following the methods listed in Appendix A. For each element and each instrument, there are data quality objectives (DQOs) that will be met (see write-up below, sampling plan, and SOPs). The primary DQOs for this project are to precisely and accurately characterize the inorganic composition of (i) river waters downstream of WWTFs processing HF waste waters, and (ii) each source type; and to provide data appropriate for source apportionment modeling in the rivers of interest. The study DQOs will be assessed using the data quality indicator (DQI) PARCC parameters outlined below, including the method/instrument sensitivity parameters presented in **Tables 3-5**. Generally, ICP-OES is appropriate to measure element concentrations in the $\mu\text{g/L}$ to mg/L range and HR-ICP-MS is appropriate to measure element concentrations in the ng/L to $\mu\text{g/L}$ range. IC is appropriate to measure ion concentrations in the $\mu\text{g/L}$ to mg/L range. Specific MDLs are presented in **Tables 3-5** below. Instrument biases and analytical interferences will be addressed and corrected as directed in each analytical SOP.

Precision is the relative agreement among individual measurements and provides an estimate of random error. Precision for elemental concentrations using each instrument will be expressed as relative standard deviation (RSD) for replicate measurements. Usable data will have instrument RSD less than 15% of the mean value otherwise it will not be included in the dataset.

Accuracy is the agreement of the data with the true value. Generally, accuracy is the evaluated by difference between the mean of measurements and the global population mean or assumed true value. Measurement accuracy can be diminished by systematic errors inherent in the method, such as mass and/or charge interferences. Standard reference materials (SRMs) will be measured multiple times during each analytical session to evaluate the accuracy possible for each method. Sample data will be valid only if SRMs are reported within 15% of their published value.

Representativeness is the degree to which a subset of samples is characteristic of the total data set, and the degree to which the total data set describes the total possible data sets. Representativeness within the river water data set will be assessed through the monitoring of river conditions. As mentioned in Section A6, five (5) sondes with each measuring water temperature and conductivity will be deployed in each river domain for the seven (7) months during which the three sampling campaigns will occur (April through November 2012) as detailed in NERL/HEASD Standard Operating Procedure for the HOBO U24 Conductivity Logger and HOBO Data Shuttle (ECAB-137.1). Comparison of the average stream velocity and TDS during the sampling campaigns with the same parameters during non-sampling weeks will help to inform whether or not river conditions during the intensive sampling campaigns are representative of typical river conditions. Representativeness of the source sample data set will be evaluated by direct comparison of concentrations from randomly selected samples of the same type (e.g., acid mine drainage or flowback water) collected during the same intensive. External extrapolated representativeness of the sample set will be evaluated by comparison of the mean and range of concentrations measured in this study with published data of similar sample types, if available.

Completeness will be defined as the proportion of valid, usable data out of the total data collected. It is expected that at least 85% of the data will be usable and will be described as complete.

Comparability is confidence with which a data set can be evaluated against an external data set. When different preparation methods are employed, a direct comparison of SRM measurements will be assessed. Data sets will be compared only if SRM measurements agree within 10%.

Table 3. Target quantitative Data Quality Indicators for Inorganic Elements by Inductively Coupled Plasma Optical Emission Spectroscopy.

Element	MDL/IDL (ppb)*	Element (con't)	MDL/IDL (ppb) (con't)
Ag	4.17	Mo	20.83
Al	20.83	Na	500
As	10.42	Ni	4.17
B	8.33	P	41.67
Ba	4.17	Pb	8.33
Be	4.17	S	374
Ca	20.83	Sb	10.42
Cd	4.17	Se	10.42
Co	4.17	Si	41.67
Cr	4.17	Sn	8.33
Cu	4.17	Sr	4.17
Fe	20.83	Ti	20.83
K	500	Tl	10.42
Li	10.42	V	4.17
Mg	20.83	Zn	10.42
Mn	4.17		

Table 4. Target quantitative Data Quality Indicators for Inorganic Ions by High Resolution Inductively Coupled Plasma Mass Spectrometer.

Isotope	MDL/IDL (ppb)	Isotope (con't)	MDL/IDL (ppb) (con't)
Ag107	0.0480	Ni60	0.0125
Al27	0.6000	P31	0.1000
As75	0.0100	Pb208	0.0200
Ba147	0.3000	Pd105	0.0150
Be9	0.0120	Pt195	0.0250
Bi209	0.0750	Rb85	0.0350
Ca44	4.000	Rh103	0.0180
Cd111	0.0350	S32	4.000
Ce140	0.0025	Sb121	0.0150
Co59	0.0100	Sc45	0.1000
Cr52	0.0030	Se77	0.1000
Cs133	0.0100	Si28	8.000
Cu63	0.0200	Sm147	0.0025
Dy163	0.0025	Sn118	0.1000
Fe57	0.1000	Sr88	0.0500
Gd157	0.0025	Tb159	0.0025
Ge72	0.0100	Th232	0.3500
K39	0.4500	Ti47	0.0080
La139	0.0025	Tl205	0.0300
Li7	0.0350	U238	0.0125
Mg24	0.3500	V51	0.0015
Mn55	0.0100	W182	0.0125
Mo95	0.2000	Y89	0.0020
Na23	1.6000	Z66	0.1500
Nd146	0.0025		

Table 5. Target quantitative Data Quality Indicators for Inorganic Ions by Ion Chromatography.

Ion	LOQ (ppm)	Ion (con't)	LOQ (ppm) (con't)
Br ⁻	0.0500	Ca ²⁺	0.500
Cl ⁻	0.0500	K ⁺	0.100
F ⁻	0.0100	Li ⁺	0.025
NO ₂ ⁻	0.0500	Mg ²⁺	0.100
NO ₃ ⁻	0.0500	NH ₄ ⁺	0.200
PO ₄ ³⁻	0.100	Na ⁺	0.100
SO ₄ ²⁻	0.0500		

A8 Special Training/Certification

Special Training

To achieve the stated quality objectives noted in Section A7, trained and experienced U.S. EPA employees and contractors will be responsible for supplies, sample collection, sample preservation, and sample analysis. Experienced and trained EPA scientists will perform all necessary sample preparation (e.g., digestion, filtration, dilution) and sample analysis (using IC, ICP-OES, and HR-ICPMS) procedures. Each scientist participating in this project has demonstrated proficiency with the specific analytical procedures tasked, and the HEASD QA Manager is to maintain records of all training and documented analyst proficiency.

QA/QC Training

Training regarding the contents of this QAPP will be provided by the Division QA Manager and Project Manager. Contents of this training will include:

- logistics and requirements of sampling and sampling receipt and sample handling
- field and laboratory documentation requirements
- laboratory data review requirements
- deviation and change requirements

Regular Staff Meetings

Weekly staff meetings for personnel listed in Figure 1 will occur, as needed, to ensure all staff are kept informed of the status of the project, problems encountered are discussed, and resolution or improvement of procedures are carried out.

A9 Documents and Records

Laboratory activities will be documented according to the NERL Integrated Information and Quality Management Plan (IIQMP) Appendix 6 “NERL Scientific Record Keeping Policy”² and the ORD SOP on paper laboratory records³. In keeping with these policies, all paper and electronic laboratory records will be kept up to date; they will be maintained and organized such that continued research and data acquisition is not contingent upon a specific researcher. Each researcher involved in the project will maintain a laboratory notebook and any associated electronic data records. The Project Manager, will review researcher notebooks on a weekly basis. Notebooks and other documentation will be reviewed during regular lab reviews by the division QA Manager.

Electronic copies of all current QA documents, such as this QAPP, SOPs, and audit reports, will be kept in the NERL Quality Assurance Tracking System (QATS) database and uploaded by the HEASD QA Manager. The Project Manager, will be responsible for distribution of the current version of the QAPP

and will retain copies of all management reports, memoranda, and correspondence between project personnel identified in A4. Additionally, this QAPP will be made available to the public on the EPA Hydraulic Fracturing website.

Documents provide direction and guidance for performing work and making decisions. Conversely, records provide testimony of work and decisions that have occurred.

Hardcopy Records - Hardcopy records will be maintained in accordance with ORD Policies and Procedures Manual (PPM) 13.2³. These records include, but are not limited to, information regarding preparation and treatment of standards, samples, field and laboratory blanks, calibration standards, and quality controls. Researchers will maintain the records in designated laboratory notebooks. All samples will be recorded in the laboratory notebook by a unique sample ID. The date of all laboratory and field activities and the signatures/initials of the researcher writing the records will be recorded. The location of electronic data generated from analysis of samples will also be recorded in the laboratory notebook, expressed as a data management path. For example: EPA Computer Number; Hard Drive / Folder Name (Program name) / Subfolder Name (Project name) / Item Folder Name / File name with extension.

Electronic Records created or converted from hardcopies and/or generated by electronic devices, shall be maintained in a manner that maximizes the integrity and accessibility of the data. All electronic data and notes shall be cross-referenced in a hardcopy notebook to record the date and location and facilitate retrieval. Data may be transferred to electronic spreadsheets for analysis and presentation. Electronic Records will be backed up to an external database once every week.

Research Record Retention: The laboratory notebook and records will be retained in the laboratory (or office area) where these operations are performed until the conclusion of the study. At the end of the research study, the research records shall be archived in a manner consistent with the appropriate EPA National Records Management Records Disposition Schedule.

Records and documents that will be produced in conjunction with this project include:

- Raw Data
- Field notebooks
- Sample documentation sheets
- Chain-of-custody forms
- Laboratory notebooks
- Instrument logbooks and maintenance records
- Progress reports
- Documentation of audits
- Project interim report
- Project final report
- Standard operating procedures

Disposition

Record-keeping will be permanent according to EPA Records Schedule 501:

Non-electronic project files

- Including documentation related to the formulation and approval of the research plan, selection of the research methodology, quality assurance project plans, raw data, laboratory notebooks, project- or study-related correspondence, copies of interim reports showing data tabulation results

and interpretations, copies of the final reports, peer reviews, and quality assurance assessments.

- Records will be made permanent.
- Inactive records will be closed upon completion of the project.
- Twenty (20) years after file closure, files will be transferred to the National Archives.

Electronic project files

- Including documentation related to the formulation and approval of the research plan, selection of the research methodology, quality assurance project plans, raw data, laboratory notebooks, project- or study-related correspondence, copies of interim reports showing data tabulation results and interpretations, copies of the final reports, peer reviews, and quality assurance assessments.
- Records will be made permanent.
- Inactive records will be closed upon completion of the project.
- Twenty (20) years after file closure, files will be transferred to the National Archives.

Project work papers and administrative correspondence

- Including completed questionnaires or other documents used for data collection, drafts or copies of interim progress reports, and other work papers created in the course of the study.
- These files will be classified as disposable.
- Inactive records will be closed upon completion of the project.
- Three (3) years after file close, files will be destroyed.

Maintenance, calibration, and inspection of equipment records

- These files will be classified as disposable.
- Inactive records will be closed upon completion of the project.
- Five (5) years after file close, files will be destroyed.

SECTION B. MEASUREMENT/DATA ACQUISITION

B1 Sampling Process Design

B1.1 Site Selection

The NERL Source Apportionment study team outlined a study plan to investigate two different waste water treatment facilities discharging treated HF waste water from Paleozoic formations (with special interest in Devonian, Silurian, and Ordovician formations) into public waterways. The hydraulic fracturing wastewaters treated at the WWTFs may include drilling mud, flowback water, produced water, and formation water. In order to assess impacts of HF wastes treated at WWTFs in a variety of conditions, the study will include sampling campaigns during different river flow regimes, including anticipated high-flow river conditions during the spring and low-flow river conditions during the summer and fall. River flows will be estimated from the USGS gauging stations nearest the participating WWTFs, stations 03025500 and 03042000. The study will include one WWTF discharging into a large river system, and one discharging into a small river system. Other selection criteria for participating WWTFs included: (i) a minimum total discharge from a POTW of 400,000 gallons per day (GPD), (ii) a minimum total discharge from a COTW of 40,000 GPD, (iii) presence of public drinking water (PDW) intake downstream (<65-85 km), and (iv) no major additional tributaries between the WWTF discharge and the PDW intake. Through consultations with EPA Region 3 research partners, two candidate facilities that met the site selection criteria were proposed and subsequently accepted by the study team. Details concerning facility A and facility B are detailed below in **Table 6**.

Table 6: Waste Water Treatment Facility and Receiving Stream Information

	Facility A	Facility B
Approximate Discharge Volume (GPD)	50,000	67,000
Receiving Stream	Allegheny River	Blacklick Creek
Receiving Stream 2010 Mean Daily Flow (cubic feet/second (cfs))	1640	327
Nearest Downstream Drinking Water Intake (km)	51	90

In order to assess any potential impacts of HF wastewaters processed through WWTFs on receiving surface waters and public drinking water supplies, five sites in the river systems encompassing each WWTF will be sampled. The exact locations of sampling sites are contingent upon river reconnaissance by EPA Region 3 research partners and USGS local river experts, who will report to the Source Apportionment study team regarding issues including shore slope and vegetative density, shore access and land ownership, shipping lanes and boat traffic (particularly on the Allegheny River upstream and downstream of Facility A), and the locations of other industrial discharges into the study waterways. Assuming reasonable access, the five sampling locations will include one site upstream of each WWTF, one site within each WWTF discharge, and three sites downstream of each WWTF including one site in the nearest downstream PDW intake.

The upstream site will be located as close to the WWTF as possible while ensuring that no back-flow from the WWTF discharge could reach the sampling location. The purpose of the upstream sampling site is to provide the background chemical composition of each river of interest. The Allegheny River is one of the four largest rivers in Pennsylvania, and has several industrial operations along its banks. The sampling site upstream of Facility A, discharging into the Allegheny River, is critical to assess contaminant loads that are unrelated to the subject WWTF. Blacklick Creek, which is a small tributary to the Conemaugh River, has much less industrial activity along its upstream reaches than the Allegheny but is impacted by AMD. It is anticipated that the upstream sampling location in Blacklick Creek and in the Allegheny River will demonstrate different baseline conditions for the rivers receiving discharge from the two participating WWTFs.

Each participating WWTF has indicated its willingness to allow EPA personnel to conduct sampling directly from its effluent. This sampling will provide information regarding the characteristics (source profile) of the discharge that will be used to interpret source apportionment modeling results (briefly described in section B4).

Three sampling locations will be selected downstream of each WWTF. The first downstream site will be located at a distance downstream that is sufficient for the discharge plume to be fully mixed in the receiving stream, but that is near enough to the discharge site that compounds with the propensity to precipitate will likely still be suspended solids. Hydrodynamic transport modeling, conducted by EPA NRMRL's Ground Water and Ecosystems Research Division (GWERD) will inform the most appropriate zone for this sampling in each river system. The second downstream sampling site in each river system will be at an intermediate distance between the WWTF discharge location and the location of the nearest downstream PDW intake. The third downstream sampling site will be in the nearest public drinking water (PDW) intake downstream of each participating WWTF. As noted in **Table 6**, the nearest PDW intakes are 51 km and 90 km downstream of Facility A and Facility B, respectively. During the spring sampling intensive, a second Isco sampler will be collocated at one of the PDW intake sampling sites. During the summer sampling intensive, the collocated sampler will be at one of the river sampling sites, and during the fall sampling intensive, the collocated sampler will be at one of the WWTF discharge sites. Obtaining collocated replicate samples at these sites will inform us of sampling uncertainty and therefore

strengthen the modeling output confidence. The data gathered from the PDW intake site samples will be used to generate source apportionment receptor modeling, described in section B4.

B1.2 Automated Sample Collection Scheme for River Water Daily Composite Samples

At each sampling site, an automated water sampler (Teledyne Isco, model 6712) will be deployed. Each Isco sampler will collect one daily composite sample by drawing two 400 mL aliquots per day (09:00 and 12:00 EST). At each PDW intake sampling site, the Isco samplers will take two daily composite samples. One of the daily composite samples will be treated like daily composite samples from other sites (e.g., acidified, filtered, and allocated for analysis), and the other daily composite sample from each Isco sampler at each PDW intake site will be filtered prior to acidification at the laboratory (described in section B4). **Table 7** summarizes the general sampling scheme. Each sample must provide sufficient material for analysis and the sample integrity must not be compromised.

Table 7: General sample collection scheme (with collocated sampler at PDW intake at Facility A)

Sampler Position	Facility A		Facility B	
	# Isco samplers	# Daily Composites	# Isco samplers	# Daily Composites
Upstream	1	1	1	1
WWTF	1	1	1	1
Downstream 1	1	1	1	2
Downstream 2	1	1	1	1
PDW Intake	2	2	1	2

Field bottle blanks, known as a “field blanks”, will be collected in each Isco sampler during the study to represent a minimum of 10% of collected samples. Field blanks are collected by placing an uncapped empty bottle in the sampler that will not receive sample water, but will be open and exposed in the sampler in an identical manner as the actual sample bottles (48-96 hours). The field blanks are then capped and handled exactly as the river water daily composite samples (see NERL/HEASD SOP ECAB-136.1). Source characterization samples will be collected as described in section B1.3. These source samples will also be acidified, filtered, and allocated like the river water daily composite samples described above.

B1.3 Manual Grab Sample Collection Scheme for Source Characterization Samples

In addition to characterizing the effluent from WWTF discharges detailed in **Table 6**, the study also aims to characterize other potential sources of halides to the study river systems and develop corresponding source profiles. Known sources that will be manually sampled are HF flowback, HF produced waters, POTW effluent, CFUB discharge, AMD, and road deicing material stormwater runoff. These sources will be manually sampled by EPA NERL/HEASD and Region 3 personnel. Samples of raw HF wastewaters will be collected directly in trucks carrying HF wastes from an HF well site to a disposal facility. Samples of CFUB discharge will be collected in effluent streams flowing out of CFUB facilities. Samples of AMD will be collected in sluices and/or streams that have previously been identified as impacted by AMD and are hydrologically connected to active or historical mining locations. Samples of road deicing material runoff will be collected from drainages on roads, ideally from open drainage pipes on bridge overpasses. Each source characterization sample will be collected in a location with one unambiguous source. A minimum of three and a maximum of six samples of each type (HF flowback, HF produced waters, POTW effluent, CFUB, AMB, road salt runoff) will be collected. Efforts will be taken to collect samples from multiple physical locations in the region in order to provide a range of geochemical compositions associated with each waste. Bottle trip blanks will be collected during each sampling campaign to document background contributions. It is anticipated that the

inorganic chemical composition of each source type will vary by location. This variability will be assessed through comparison of samples collected at different times and locations.

B2 Sampling Methods

River water samples will be collected using Isco model 6712 automated water samplers. Detailed instructions for sample labeling are found in NERL/HEASD Standard Operating Procedure for the Tracking of Hydraulic Fracturing Waste Water Source Apportionment Field Study Samples (NERL SOP ECAB-138.1), and instructions on sample collection are provided in NERL/HEASD Standard Operating Procedure for the Teledyne Isco 6712 Portable Automatic Sequential Water Sampler (NERL SOP ECAB-136.1). Briefly, Isco samplers will be positioned on flat surfaces on river banks. When access to river banks is not feasible, Isco samplers will be positioned on bridge abutments or docks. Each Isco sampler is equipped with an 8 m Teflon lined polyethylene inlet tube with a chlorinated polyvinyl chloride (CPVC) inlet strainer. The inlet strainers will be placed as near to the highest-flow section of the river as is logistically reasonable while also ensuring that the Isco samplers are secure and the sample uptake line is unobstructed. The inlet strainers will be placed into PVC protective housings, zip tied to a cinder block, and placed in the river to minimize visibility to pedestrians and boaters. Each Isco will also be equipped with 24 acid-cleaned 1 L polypropylene bottles. The Isco samplers will draw 400 mL river water twice a day (09:00 and 12:00 EST) into one bottle to create an 800 mL daily composite sample. Daily composite samples will be collected for fourteen consecutive days during each intensive. At the sampling locations in the PDW intakes, each Isco sampler will collect two daily composite samples by drawing 400 mL river water into two different bottles twice a day (09:00 and 12:00 EST). The two daily composite samples will be labeled U (unfiltered) and F (filtered), respectively. Each sample will have a unique barcode label, described in section B3. Field blanks will be collected leaving the bottle uncapped for the duration of each sample collection-to-gathering interval, capping and shipping it to EPA in Research Triangle Park along with other samples (see section B3).

Within one week of sample collection, the EPA/ORD/NERL/HEASD Source Apportionment study field team will gather samples from each Isco sampler. Upon retrieval of each sample, the sample barcode will be scanned and a custody seal will be placed across the cap and top of each bottle to ensure that the integrity of the sample is maintained throughout transport. All samples will be stored in coolers with ice packs prior to and during transport as the samples are sent to EPA in Research Triangle Park, NC. Sample shipping and storage procedures are detailed in NERL/HEASD Standard Operating Procedure for the Tracking of Hydraulic Fracturing Waste Water Source Apportionment Field Study Samples (NERL SOP ECAB-138.1) and described in section B3.

Samples for source characterization of HF flowback and produced waters will be collected from trucks carrying the HF waste water or from storage tanks at the treatment facilities. Detailed instructions for sample collection are provided in NERL/HEASD SOP Manual Collection of Hydraulic Fracturing Wastewater Samples (ECAB-132.0). Briefly, an acid-cleaned polyethylene dipper will be (i) submerged in the fluid inside the truck top tank hatch or (ii) positioned under the storage tank discharge in the treatment facility manhole. The dipper will be used to pour HF waste fluids into 1L acid-cleaned, labeled polypropylene bottles for analysis. Samples for source characterization of WWTF effluent, CFUB discharge, AMD, and road salt runoff will be collected by placing the dipper in the effluent or discharge pipe and then pouring that liquid into 1L acid-cleaned, labeled polypropylene bottles. Each sample will have a unique Sample ID (see example in Section B3) and include the date and location of collection, and initials of the collector. Clean bottles that will be opened and closed in the field will serve as “field blanks” and be transported back to ECAB with all of the regular samples. Upon collection of each sample, a custody seal will be placed across the cap and top of the bottle to ensure that the integrity of the

samples is maintained during transport. All samples and field blanks will be stored in coolers with ice packs for storage prior to and during transport. Photographs will be taken during every grab sample collection to document the location and conditions under which the sample was collected as well as to obtain a visual record of the sample (e.g., if it was clear, murky, colored, etc.).

If problems with sample collection occur, such as field safety concerns or human interferences, the sample collector will determine whether or not it is safe to proceed with sample collection. Whether the sample collector deems it safe or unsafe to proceed, the sample collector will provide a report including a description of the safety or interference concerns to the Project Manager within 24 hours of the incident.

At the time of sample retrieval a member of the field team will measure the (i) river water temperature, conductivity, pH, oxidation/reduction potential (ORP), and barometric pressure (BP) using a hand-held YSI multi-parameter probe, as detailed in NERL/HEASD Standard Operating Procedure for the YSI Model 556 Multi Probe System (ECAB-135.1); and (ii) depth and velocity of the river flow using a portable velocity sensor, as detailed in NERL/HEASD Standard Operating Procedure for the Swiffer Model 3000 Stream Velocity Meter (ECAB-145.0). Data from both instruments are electronically logged, but will also be recorded immediately in field notebooks. The primary objective of this portion of the HF Waste Water Source Apportionment project is to characterize each sample by the elements and ions listed in **Table 2**. The other data collected (e.g., sample location, temperature, pH, ORP, BP, conductivity, river water depth, river water velocity) will be used to provide context for the sample analyses.

B3 Sample Handling and Custody

Sample tracking and chain of custody will be maintained using a new two-dimensional bar code tracking system being developed by ECAB. All aspects of sample bottle preparation, weighing, deployment, collection, extraction, analysis, and archive storage will be tracked by a Microsoft Access based searchable data system created and administered by ECAB. Wasp Barcode Technologies (Plano, Texas) bar code making software will be used to generate labels in the lab for sample bottles that will be used to track each sample. The label will identify the acid clean batch and bottle ID numbers (e.g., acid cleaning batch, bottle ID, A001B01). Each time the bottle is handled, it will be scanned and all pertinent information will be recorded such as date, time, person, action (e.g., cleaned, weighed, deployed, retrieved, shipped, received, poured off, analyzed), and data (e.g., weight, analysis result). In the laboratory, WASP model WWS450 bar code scanners will be utilized, and in the field AML (Euless, Texas) model M5900 portable data terminal scanners will be used. A second bar code label will be affixed to each sample after collection identifying the study area, sampling intensive, Isco sampler ID, Isco bottle position, and sequential sample ID number (e.g., BKLK-SPR-S03-P03-U03). These labels will be generated prior to the study and will be a part of the site notebook. Data will be uploaded into the field laptop system on a daily basis from both laboratory and field operators.

In the field, samples will be collected according to the procedures outlined in NERL/HEASD Standard Operating Procedure for the Teledyne Isco 6712 Portable Automatic Sequential Water Sampler (ECAB-136.1). All samples will be properly labeled as noted in Section B2. Within one week of collection, samples will be removed from the Isco samplers, have their barcodes scanned, be double-bagged, be placed in an ice packed cooler, and then shipped overnight via a common carrier (e.g., UPS), as described in NERL/HEASD Standard Operating Procedure for the Tracking of Hydraulic Fracturing Waste Water Source Apportionment Field Study Samples (ECAB-138.1). Upon receipt at the EPA Research Triangle Park, NC facility, sample barcodes will be scanned and samples will be stored by EPA research staff personnel in a locked 4°C refrigerators, to which only the principal investigators and select analysts will

have access. **Table 8** lists the maximum sample holding times at each step between sample collection and analysis. Sample custody documentation will be maintained through the two-dimensional bar code system being developed by ECAB.

Table 8: Sample Holding Times and Storage

Sample Location	Sample Holding Times	Storage Conditions
Field Retrieval	<1 week	Ice Packed Cooler
Shipping	<3 days	Ice Packed Cooler
Storage Before Analysis	See respective analytical SOPs	4°C Refrigerator
Archival Samples	5 years	4°C Refrigerator

At the EPA in Research Triangle Park, NC, research staff will pour a 15 mL aliquot of each sample to be processed for IC analysis, as detailed in NERL/HEASD SOP Operation and Maintenance of the Element 2 High Resolution Inductively Coupled Plasma Mass Spectrometry Instrument (ECAB-098.1) in a Class 100 clean room. The researcher will then separate the “F” set of composite samples collected at the PDW intake sites. The “F” samples will be filtered (0.2 – 0.45µm, Teflon membrane) prior to being acidified and UV extracted as described below. All other samples will be weighed, and subsequently acidified with Optima grade Nitric Acid to a final concentration of 2% HNO₃ (v/v). Acidified samples will be stored at room temperature in a locked laboratory space for a minimum of seven days to allow for leaching of particles into solution. After the initial seven day leach, acidified samples will be exposed to UV radiation in a UV light chamber for two days. After UV exposure, organic matter will be degraded, particles will be leached, and the elements of interest (see **Table 2**) will be aqueous. The samples will then be filtered (0.2-0.45µm, Teflon membrane) into 15 mL centrifuge tubes for ICP-OES and HR-ICPMS analysis, and a 500 mL acid-cleaned polypropylene working archive bottle. **Table 9** lists the sample volume that will be allocated for each analytical technique. Excess sample will be disposed of in appropriately labeled hazardous waste containers. For additional detail on the previous procedures, see NERL/HEASD Standard Operating Procedure for the Tracking Hydraulic Fracturing Waste Water Source Apportionment Field Study Samples (ECAB-138.1). Sample storage times at the EPA prior to sample analysis are listed in each respective analytical SOP. Archived samples will be available for future analysis by the EPA or other approved personnel, including the USGS in Denver, CO, for at least five years. Proper documentation will be maintained, security of samples ensured, and analyst procedures documented.

Table 9: Volume Allotments for Sample Analyses

Analytical Technique	Volume (mL)
IC	15
ICP-OES	15
HR-ICPMS	15
Working Archive (including 250 mL sample for TIMS)	500

Sample chain-of-custody records will be electronically generated and stored in an ECAB Microsoft Access database for each sample acquired. Chain-of-custody records will include the date and describe the condition and details of each sample when they are received by each party (e.g., cleaning, deployment, collection, shipment, acidification, filtering, pour off, and analysis). The records will be maintained throughout the course of the study, from sample collection through shipping, storage, and analysis. Custody records will include:

- Project name

- Scanned initials of sample collector(s)
- Sample number, date and time of collection, and date and time of retrieval
- Location of sample location (latitude, longitude)
- Type of sample location (upstream, downstream, etc)
- Sample volume
- Digital bar code scans of individuals ID badges involved in sample weighing, deployment, collection, filtration, acidification, pour off, dilution, and analysis
- Signatures of individuals involved in sample shipping and receiving (**Appendix C**)
- If applicable, the air bill or other shipping tracking number

EPA National Geospatial Data Policy and Procedures (NGDPP)

Whenever applicable, this research will adhere to the *EPA National Geospatial Data Policy* (NGDP)⁴ and the *EPA National Geospatial Data Policy Procedure for Geospatial Metadata Management*.⁵ These policies and procedures outline the responsibilities and requirements for collecting and managing geospatial data used by federal environmental programs and projects within the jurisdiction of the U.S. Environmental Protection Agency (EPA).

B4 Analytical Methods

One of the primary objectives of this project is to assess through source apportionment modeling whether or not HF wastewaters treated and discharged from WWTFs are significant sources of bromides (Br⁻) and chlorides (Cl⁻) at downstream PDW plants in EPA Region 3. To this end, the inorganic chemical composition of river water samples will be characterized comprehensively using a series of analytical methods, including chromatographic, spectroscopic, and mass spectrometric techniques.

B4.1 Sample Analysis

ECAB's Inorganic Laboratory Manager (**Table 1**) is responsible for ensuring the all chemical analysis SOPs are followed, all analytical quality control elements are attained (**Table 10**), and laboratory notebooks are properly maintained (Section B6). The analytical methods for HF samples include: (i) major anions and cations by IC, as described in NERL/HEASD SOP Ion Chromatographic Analysis of Aqueous Inorganic Species (ECAB-131.0), (ii) major elements using ICP-OES, following NERL/HEASD SOP Inductively Coupled Plasma Optical Emission Spectroscopic (ICP-OES) Analysis of Elements (ECAB-140.0), and (iii) minor elements by HR-ICP-MS, as described in NERL/HEASD SOP Operation and Maintenance of the Element 2 High Resolution Inductively Coupled Plasma Mass Spectrometry Instrument (ECAB-098.1). For each of these instruments, user manuals will also be readily accessible for supplemental information as referenced in the SOP for instrument procedures. Zell Peterman at the U.S. Geological Survey (USGS) in Denver, CO, is responsible for quantifying strontium (Sr) isotopic composition in a subset of samples using TIMS following the method detailed in the technical procedures titled "YMPB USGS Technical Procedure: Rb-Sr Isotope Geochemistry" (YMPB-USGS-GCP-12, R0). Instructions for corrective action following potential failures of any of these methods are included in their respective SOPs.

For each method and analyte, a calculated MDL and linear dynamic range (LDR) will be made according to procedures as outlined by McDougall et al.,⁶ and EPA Method 200.7.⁷ In brief, a series of seven multi-element standards ranging in concentrations from low to high will be analyzed. Retention times, absorptions, and masses will be determined, and linear regression will be performed on the data sets.

MDLs will vary by compound, and are calculated as the product of (i) the standard deviation of seven replicate analyses of a low concentration matrix specific sample and (ii) the Student's t value for a 99% confidence interval and a standard deviation estimate with n-1 degrees of freedom (3.14 for seven replicates). Method quantification limits (MQLs) are calculated as twice the MDLs. Instrument calibration procedures are detailed in Section B7.

Where possible, data will be compared to published results.

B4.2 Source Apportionment Modeling

Data gathered through analyses described above will be used to support receptor source modeling. Specifically, samples collected at public drinking water intakes will be evaluated using source apportionment modeling to discern the contributing sources of Br⁻ and Cl⁻ to those stream waters. EPA receptor models are software tools that are used to reduce a large number of individual environmental measurements from samples (such as stream water) into source types (such as hydraulic fracturing wastewater or acid mine drainage) using mathematical algorithms. Source types are distinguished by unique compositions and the models provide quantitative estimates of the source type contributions and robust uncertainty estimates. Receptor models require a comprehensive analysis of environmental samples to provide a sufficient number of constituents to identify and separate the impacts of different source types. Analysis of major ions and inorganic trace elements, as detailed above, will accomplish the needs for robust receptor modeling.

EPA-implemented models and commercial off-the-shelf (COTS) software will both be used to analyze study data. EPA models include receptor (e.g., Unmix, and Positive Matrix Factorization (PMF), Chemical Mass Balance (CMB)) and hybrid (e.g., ReSCUE, EPA DaVIS) models. COTS software includes Partial Least Squares (PLS) and SigmaPlot. These models have been used to evaluate a wide range of environmental data for air, soil, and sediments, and the models can be used to evaluate data from emerging issues such as HF impacts to drinking water. The receptor models have a minimum data requirement to evaluate mathematical relationships (> 40 samples) and a comprehensive set of species measurements including key tracer species from natural and industrial contaminant sources. Other approaches, including EPA CMB and PLS, can be used to evaluate smaller data sets from 1 sample for CMB to 15 samples for PLS.

The selected modeling efforts will be described in a separate modeling QAPP.

B5 Quality Control

Evaluation of field and laboratory blanks, calibration standards, internal standards, standard reference materials (SRMs), continuing calibration verification (CCV), and sample replicates will be performed throughout the study. Collocated replicate sample collection will be conducted at one collection site, comprising 10% of the total samples collected. Replicate analyses will be conducted for 10% of samples collected, and CCVs will comprise no less than 10% of all samples analyzed. Quality control elements are described in **Table 10**. Established analytical methods that are suitable to the matrix of interest (river water) will be instituted. Analytical instrument performance will be assessed daily or more frequently if necessary.

Table 10. Analytical Quality Control Elements

QC Check	Frequency	Precision	Accuracy	Corrective Action
Calibration	At the beginning of each analytical session	RSD < 15%	$r^2 > 0.99$	Samples will not be analyzed until calibration achieves criteria
Standard Reference Materials	At the beginning and end of each analytical session	RSD < 15%	±15% of certified value	Samples will not be analyzed until calibration achieves criteria. All valid samples will be bracketed by SRM that meet criteria.
Laboratory Blank	At the beginning and end of each analytical session	N/A	< MQL	Inspect the system and make any necessary repairs; reanalyze the blank; recalibrate the instrument if criteria are not achieved. All valid samples will be bracketed by blanks that meet criteria.
Continuing Calibration Verification	10% of analyses	RSD < 15%	±15% of certified value	Inspect the system and make any necessary repairs; reanalyze the standard; recalibrate the instrument if criteria are not achieved. All valid samples will be bracketed by SRM that meet criteria.
Internal Standard Addition	100% ICP-OES and HR-ICP-MS	RSD < 15%	±15% of certified value	Review data and known interferences; if interference is present, describe in logbook and notebook, and flag recovery; if no known interference is present, inspect instrument and analyze a laboratory blank and a laboratory check-standard; reanalyze sample. Sample data is valid only when QC is achieved.
Laboratory Replicates	10% of analyses	RSD < 15%	N/A	Inspect instrument and analyze a laboratory blank and a laboratory check-standard; reanalyze sample. All valid samples will be bracketed by SRM that meet criteria.

The instrument detection limit (IDL) will be determined by the concentration of each analyte in laboratory blank solutions, and is equal to three times the standard deviation of the analyte concentration in blank solutions. The method detection limit (MDL) will be determined for each analyte at a 99 percent level of confidence that the concentration of the analyte is greater than zero, as detailed in section B4.

Sample data will be considered valid only if analyte concentrations are measured above the MDL and

within the acceptable method range. The acceptable method range will be determined by the linearity of calibration standards, and is not to exceed the highest concentration standard nor be less than the lowest concentration standard. In addition to these measurement requirements, data will be considered valid if it meets all data quality objectives (DQOs) set for each of the data quality indicators detailed in section D3.

In addition to the analyses performed, 500 mL of each sample will be archived. Archived samples will be considered “working archives”, available for future analysis by approved laboratories. Archived samples will be filtered (0.2-0.45 μm , Teflon membrane) and stored in a locked refrigerator kept at 4°C.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

As noted in their respective SOPs, routine maintenance will be conducted and preventative maintenance will be scheduled as needed on the IC, ICP-OES, HR-ICPMS, and TIMS, based on the requirements for the analytes of interest. Instruments will be officially inspected annually. Any deficiencies found during instrument inspections will be remedied to ensure that the instrument meets manufacturer’s instrument performance specifications (as noted in instrument manuals), and to ensure that this study’s DQOs are met. Spare parts for each instrument will be located in their laboratories or will be ordered as needed. An instrument maintenance log book will be maintained in the laboratory with each instrument. All maintenance activities and problems will be documented in instrument logbooks.

Instrument performance will be monitored daily and may require system maintenance including cleaning and troubleshooting. Monitoring of chromatographic and mass spectral peak shapes, instrument apparent sensitivity, and linear response will be monitored and adjusted daily per instrument manufacturer specifications. Each instrument’s criteria for proper performance can be found in the manufacturer’s operating manuals as referenced in their respective SOPs. Performance issues, troubleshooting and remedies taken will be noted in the instrument logbook.

B7 Instrument Calibration and Frequency

IC, ICP-OES, HR-ICPMS, and TIMS will be used to measure elements, ions, and isotopes of interest in the sample fluids. Each instrument has unique optimal operating conditions, and the initial conditions will be based on each instruments SOP specifications.

For each instrument, calibrations will be conducted using certified multi-element standards. Each instrument will use the manufacturer-provided software to implement its calibration. The calibration processes are described in the appropriate methods and SOPs: NERL SOP ECAB-098.1, NERL SOP ECAB-131.0, NERL SOP ECAB-140.0, and USGS SOP YMPB-USGS-GCP-12 R0 (see Appendix A). Calibrations will be conducted using at least five (5) concentrations of analyte. The range of concentrations will be analyte and instrument dependent. Element specific retention times and calibration curves will be conducted prior to each analytical session and will be performed additionally as required by QA replicate analysis or calibration check standards. Instrument calibrations will be documented in instrument output data files.

All instruments will be maintained according to the manufacturers’ maintenance specifications. Balances will be calibrated and certified annually by an outside vendor and will be routinely checked with certified weights. The HR-ICPMS lab manager verifies the accuracy and precision of pipettes, calibrated annually according to Eppendorf guidelines, and records the results in a laboratory notebook. If a pipette fails, it is returned to the vendor for repair and calibration. Sample storage unit (refrigerators and freezers)

temperatures will be continuously monitored and recorded using Dickson (Addison, IL) model FT520 NIST traceable temperature recorders. If any sample storage unit fails, samples will be moved to a working unit until the failed unit is fixed or replaced.

B8 Inspection/Acceptance of Supplies and Consumables

Reagents will be purchased of the highest purity required to fulfill laboratory requirements. Standard preparations, reagent, and chemical lot numbers will be recorded in sample and standard preparation log books or in laboratory notebooks. Supplies, equipment, and consumables may include, but are not limited to, the following.

B8.1 Field Equipment

- Isco samplers
- Sample bottles
- Solar arrays
- Batteries
- YSI Multi-probe
- HOBO Sondes
- Swiffer velocity probe
- Barcode scanner
- Coolers with ice

B8.2 Laboratory Consumable Supplies

- Pipette tips
- Beakers, volumetric flasks
- 1 L polypropylene bottles
- 15 mL polyethylene centrifuge tubes
- Lab tape
- Permanent markers
- Powder-free vinyl clean room gloves

B8.3 Laboratory Equipment

- Class 100 clean room
- Class 100 exhausting hood
- Class 100 clean bench
- Microgram balance
- 2000 g balance
- Variable volume standard pipettors (0.5 -10 μL , 20-200 μL , 100-1000 μL)
- Refrigerators with locks and temperature monitoring devices
- Milli-Q water purification system
- Ion chromatograph (Dionex ICS-2000, or equivalent)
- Inductively coupled plasma optical emissions mass spectrometer (PerkinElmer 4300DV, or equivalent)
- High resolution magnetic sector field inductively coupled plasma mass spectrometer (Thermo Finnigan E2, or equivalent)
- Thermal ionization mass spectrometer (VG-MM54E, or equivalent)

B8.4 Chemicals and Reagents

- Optima grade nitric acid
- ASTM Type II water (Millipore Water, R • 18.2 MΩ-cm)
- Liquid argon
- Calibration standards, as noted in each analytical SOP

B9 Non-Direct Measurements

The strontium (Sr) isotopic composition of samples will be analyzed at the USGS laboratory in Denver, Colorado under the direction of Dr. Zell Peterman, as described in the YMPB USGS Technical Procedure: Rb-Sr Isotope Geochemistry (YMPB-USGS-GCP-12, R0) document. Clean laboratory facilities will be used for sample preparation prior to analyses using TIMS. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of each sample will be determined within an uncertainty (2 SD) of ± 0.00002 . Additionally, the Sr concentration will be determined using HR-ICPMS with a RSD <5%. The USGS determination of Sr concentrations will provide inter-laboratory comparison of measurements and provide an estimate of accuracy. Other stable isotope ratios, such as O, H, and C also can be determined at the USGS in Denver, Co. If these data prove useful, this QAPP will be amended to include the appropriate SOPs and QA/QC documentation.

B10 Data Management

Data will be managed according to the NERL IIQMP's (2005) Section 8 and Appendix 6⁽²⁾. A daily laboratory notebook will be maintained to document all experiments conducted, including information regarding sample identification, masses, volumes, standards concentrations, and sample calculations. Estimates of uncertainty will also be included where appropriate. Data acquired under computer control, will be recorded in electronic spreadsheets, and maintained on at least one hard drive. Electronic data and information will be cross-referenced in the hardcopy notebook(s). Electronic data will be automatically backed up weekly to access-restricted servers by the National Computer Center (NCC), as per usual at EPA RTP. Data will be processed using SAS. Ali Kamal, Ram Vedantham, Matthew Landis and Kasey Kovalcik, will be responsible for data processing and compilation. Data that has been passed through Quality Assurance will be posted to an access-restricted virtual drive to be available to the national EPA HF Study team.

SECTION C. ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

This project will have a Technical Systems Audit (TSA) and a Performance Evaluation (PE) audit performed at the method testing stage for each matrix. The findings and the corrective actions of the PE analyses will be reported to the HF Project Quality Assurance Manager (QAM) in the form of a report with a copy to the HEASD Quality Assurance Manager (QAM).

As noted earlier, data will be evaluated at the bench level by the analyst. Audits of Data Quality (ADQs) will be performed quarterly by the Division Quality Assurance Manager and a report will be submitted to Gary Norris, the HF Source Apportionment Project Manager, for further dissemination as necessary. The Principal Investigators (PIs) will independently evaluate the data as needed for reporting purposes.

A surveillance audit will be conducted during the PE by the HEASD QAM.

A schedule of the applicable audits is listed in **Table 11**. Reports for each audit will be submitted by the auditor to the PI. If any unsatisfactory findings are identified in these audits, a response with corrective actions will be prepared by the Principal Investigator and submitted to the HF Project QAM (with a copy to the HEASD QAM). The PI shall ensure the corrective actions are performed by the due dates as indicated in the response report and provide quarterly status reports on the corrective actions to the HF Project QAM (with a copy to the HEASD QAM).

Table 11. Schedule of Audits

Type of Audit	Frequency	Details
TSA	Conducted during method testing, specifically during optimization of method parameters	Performed by HEASD QAM
TSA	Conducted during matrix sample collection	Performed by EPA Region 3 Staff or HEASD QAM or appropriate designee.
PE	Conducted during method testing, specifically during optimization of method parameters. PE samples will consist of NIST SRMs with analytes of interest, where possible.	Provided blind by the HEASD QAM. The results will be reviewed by the HEASD QAM.
Surveillance audit	Conducted during PEs	Performed by HEASD QAM
ADQ	Conducted quarterly	Performed by HEASD QAM

C2 Reports to Management

As noted in Section C1, the auditors will provide audit reports to the PI after each audit is conducted. The PI will be responsible for providing responses to any unsatisfactory findings noted in the audit reports, ADQ reports, and quarterly status reports. Audit reports, responses to audit reports, ADQ reports, and quarterly status reports of corrective actions will be provided to the HF Project QA Manager with a copy sent to the HEASD Division Director. Tracking and closure of unsatisfactory findings are the responsibility of the HEASD QAM.

Field sampling trip reports will be provided to the Project Manager.

SECTION D. DATA VALIDATION AND USABILITY

D1 Data Review, Verification, and Validation

This QAPP will inform each action of this project. All persons participating in this project will adhere to the procedural requirements of the QAPP including adhering to the criteria to accept, reject, or qualify project data.

Proper sample collection technique will be verified by the PIs and validated by other senior scientists with experience collecting trace level environmental samples.

This QAPP will be reviewed at least annually to ensure that the project will achieve its intended purposes and the QAPP details all relevant information. All of the authors and original reviewers will participate in the annual review of the QAPP. The Principal Investigators will be responsible for ensuring that data are of adequate quality to support this project. The project will be modified as directed by the project management team. The Principal Investigators will be responsible for the implementation of changes to the project and will document the effective date of all changes made.

It is anticipated that modifications of the project will need to be made, perhaps in a short time-frame. The project's management team will authorize all changes or deviations in the operation of the project. Deviations will be documented using the Deviation Report found in Appendix B, and these will be disseminated to those on the QAPP distribution list by the Principal Investigator. All verification and validation methods will be noted in the analysis provided in the final project report.

D2 Verification and Validation Methods

Data will be reviewed by the Division QAM to verify how they were recorded, transformed, analyzed, and qualified. The Division QAM will ensure that PARCC parameters were employed (see Section A7) and the DQOs (see Section A7) achieved. The data will be validated by a senior analyst with expertise in the methodologies utilized to confirm that the DQOs were achieved and the data are appropriate to meet the goals of this project. Data will be deemed accessible if it is verified and validated as having met all DQOs. If DQOs are not met, the project staff (Ali Kamal or Kasey Kovalcik) will confer with project management (Matthew Landis and Gary Norris) and continue iterative method development.

D3 Reconciliation with User Requirements

The calculation of data quality indicators will be based on the following equations:

D3.1 Precision

Precision will be determined through the use of field duplicates and duplicate quality control samples. The Relative Standard Deviation (RSD) will be calculated and used as an indicator of precision. The following formula should be used to calculate precision:

$$\%RSD = (s/y)*100\%$$

Where:

%RSD = relative standard deviation

s = standard deviation

y = mean of replicate analyses

The uncertainty of a sample concentration is twice the standard deviation of replicate analyses. If a secondary source of uncertainty, such as weighing error, is larger than the standard deviation of replicate analyses, then the uncertainty of a sample concentration will reflect the larger uncertainty.

D3.2 Accuracy

Accuracy will be assessed through the analysis of standard reference materials (SRMs). Accuracy will be recorded as the percent recovered (%R) through the method. Measurements will be deemed accurate if $95\% < \%R < 105\%$. The following formula will be used to determine %R:

$$\%R = (C_M/C_{SRM})*100\%$$

Where:

%R = percent recovery

C_M = measured concentration of standard reference material

C_{SRM} = certified concentration of standard reference material

D3.3 Completeness

Data completeness will be expressed as the percentage of valid data obtained from the measurement system. For data to be considered valid, it must meet all the acceptable criteria, including accuracy and precision, as well as any other criteria required by the prescribed analytical method. The target completeness percentage is $>90\%$. The following formula will be used to calculate completeness:

$$\%C = V/n$$

Where:

%C = percent completeness

V = number of measurements judged valid

n = total number of measurements

D3.4 Method Detection Limit

The Method Detection Limit (MDL) will be calculated using a modified EPA method 200.7, where matrix-specific samples will be substituted for the fortified reagent water to simulate the various actual sample matrixes. The MDL is calculated by:

$$MDL = t_{(n-1, 1-\alpha)} * S$$

Where:

MDL = method detection limit

$t_{(n-1, 1-\alpha)}$ = Student's t -value for a 99 percent confidence level and a standard deviation estimate with $n-1$ degrees of freedom (3.14 for seven replicates)

S = standard deviation of seven replicate analyses

If analyses do not meet DQOs based on the criteria detailed above, the methods employed will be deemed unsatisfactory and further method development will ensue.

REFERENCES

1. Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, EPA/600/R-11/122, November 2011, Office of Research and Development, US EPA, Washington, DC.
2. The NERL Information Integrated Information and Quality Management Plan (IIQMP) Appendix 6 “NERL Scientific Record Keeping Policy”, December 2005.
<http://intranet.epa.gov/nerlintr/qa/qs.html> [URL accessed August 24, 2011].
3. ORD Policies and Procedures Manual, Section 13.02 “Paper Laboratory Records” signed in to policy December of 2006, last accessed in June 2009: [Section 13.2: Paper Laboratory Records](#) [URL accessed August 24, 2011].
4. US Environmental Protection Agency, CIO Policy Transmittal 05-022, Classification No. 2121, Policy Title: *EPA National Geospatial Data Policy*, August 24, 2005.
http://www.epa.gov/nerlesd1/gqc/pdf/epa_natl_geo_data_policy.pdf [URL accessed August 11, 2011].
5. US Environmental Protection Agency, CIO Policy Transmittal 08-004, Classification No. CIO 2131-P-01-0, Policy Title: *EPA National Geospatial Data Policy Procedure for Geospatial Metadata Management*, October 25, 2007. <http://www.epa.gov/geospatial/docs/2131.pdf> [URL accessed August 11, 2011].
6. McDougall, D. et al., Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry, *Anal. Chem.* 52, 2242-2249, 1980.

APPENDIX A: List of Operating Procedures

Organization Responsible	Reference #	Title	QAPP Section	No Change	Updated	New	Comments
Environmental Protection Agency	ECAB-136.1	Standard Operating Procedure for the Teledyne Isco 6712 Portable Automatic Sequential Water Sampler	A6, A7, B2, B3		<input checked="" type="checkbox"/>		Updated inlet set-up configuration and collection sample timing
Environmental Protection Agency	ECAB-132.0	Manual Collection of Hydraulic Fracturing Wastewater Samples	A6, A7, B2	<input checked="" type="checkbox"/>			
Environmental Protection Agency	ECAB-138.1	Standard Operating Procedure for the Tracking of Hydraulic Fracturing Waste Water Source Apportionment Field Study Samples	B2, B3		<input checked="" type="checkbox"/>		Updated new tracking operations
Environmental Protection Agency	ECAB-135.1	Standard Operating Procedure for the YSI Model 556 Multi Probe System	B2		<input checked="" type="checkbox"/>		Updated calibration procedures
Environmental Protection Agency	ECAB-137.1	Standard Operating Procedure for the HOBO U24 Conductivity Logger and HOBO Data Shuttle	A6, A7		<input checked="" type="checkbox"/>		Updated data download and sonde launching procedure
Environmental Protection Agency	ECAB-098.1	Operation and Maintenance of the Element 2 High Resolution Inductively Coupled Plasma Mass Spectrometry Instrument	A6, A7, B3, B4, B7	<input checked="" type="checkbox"/>			
Environmental Protection Agency	ECAB-131.0	Ion Chromatographic Analysis of Aqueous Inorganic Species	A6, A7, B4, B7	<input checked="" type="checkbox"/>			
Environmental Protection Agency	ECAB-140.0	Inductively Coupled Plasma Optical Emission Spectroscopic (ICP-OES) Analysis of Elements	A6, A7, B4	<input checked="" type="checkbox"/>			
Environmental Protection Agency	ECAB-145.0	Standard Operating Procedure for the Swoffer Model 3000 Stream Velocity Meter	B2			<input checked="" type="checkbox"/>	
Geological Survey	YMPB-USGS-GCP-12, R0	YMPB USGS Technical Procedure: Rb-Sr Isotope Geochemistry	A6, A7, B4, B7, B9	<input checked="" type="checkbox"/>			

APPENDIX B: Quality Assurance Project Plan Deviation Report

QAPP TITLE AND DATE: QAPP for Hydraulic Fracturing Waste Water Source Apportionment Study

DEVIATION NUMBER:

DATE OF DEVIATION:

DESCRIPTION OF DEVIATION:

CAUSE OF DEVIATION:

IMPACT OF DEVIATION ON THE PROJECT:

CORRECTIVE ACTION:

ORIGINATED BY:

Date

ACKNOWLEDGED BY:

ECAB Branch Chief, Principal Investigator

Date

HEASD Quality Assurance Manager

Date

Required Distribution: All individuals listed in Table 1 of Section A4.

APPENDIX C: Chain of Custody Form

**SHIPPING CHAIN-OF-CUSTODY FORM
HF SPRING STUDY**

2 OF 2

Tracking Number	
1ZA5E77501 9917 8778	
COOLER ID	COOLER 06
DATE PREPARED	5/16/2012
TIME PREPARED	8:00
PREPARED BY	ASK

CONFIRM (Initials)

SAMPLE ID	BOTTLE ID	SHIPPED	RECEIVED	NOTES
1	BKLLK-SPR-S05-P05-U14	A002B12		
2	BKLLK-SPR-S05-P06-F14	A002B01		
3	BKLLK-SPR-S05-P07-U15	A002B08		
4	BKLLK-SPR-S05-P08-F15	A002B18		
5	GRAB-7	A000B23		
6	GRAB-8	A000B14		
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				

CUSTODY TRANSFER		LAUNCH LOGGER BEFORE SHIPPING? <input type="checkbox"/>	
SHIPMENT PREPARED BY	DATE	SHIPMENT RECEIVED BY	DATE
SIGNATURE		SIGNATURE	
PRINT NAME		PRINT NAME	
LOGGER ID/TEMP SHIPPED		LOGGER ID/TEMP RECEIVED	
TRANSFER FROM	DATE	TRANSFER TO	DATE
SIGNATURE		SIGNATURE	
PRINT NAME		PRINT NAME	
TRANSFER FROM	DATE	TRANSFER TO	DATE
SIGNATURE		SIGNATURE	
PRINT NAME		PRINT NAME	