QUALITY ASSURANCE PROJECT PLAN
Category I Research Project

Formation of Disinfection By-Products from Hydraulic Fracturing Fluid Constituents

EPA QA Log Number: W-16436

U.S. Environmental Protection Agency
Contract No. EP-C-11-006
Work Assignment No. 3-64 (2-64)

Prepared by:

Pegasus Technical Services, Inc.
5050 Section Avenue
Cincinnati, Ohio 45219

Prepared for:

Christopher A. Impellitteri, Ph.D. Principal Investigator
Craig L. Patterson, P.E., Work Assignment Manager

U.S. Environmental Protection Agency
National Risk Management Research Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268

Revision 4
December 9, 2013

SECTION A - PROJECT MANAGEMENT

A1 TITLE APPROVAL SHEET

Pegasus Technical Services, Inc. Project Team Concurrences:

1. Brahm Prakash, Shaw Environmental & Infrastructure, Inc.
   Work Assignment Leader

/s/	1/17/14
Signature	Date

2. Steven Jones, ASQ CQA/CQE, Shaw Environmental & Infrastructure, Inc.
   Pegasus Contract Quality Assurance Manager

/s/	1/15/14
Signature	Date

3. Raghuraman Venkatapathy, Ph.D., Pegasus Technical Services, Inc.
   On-Site Technical Manager

/s/	1/17/14
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/	1/15/14
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, Quality Assurance Manager

/s/	1/27/14
Signature	Date

Project Staff Concurrences:

1. Robert Grosser

/s/	1/17/14
Signature	Date

2. Joshua Kickish

/s/	1/17/14
Signature	Date

3. Colin White

/s/	1/17/14
Signature	Date

4. Pablo Campo-Moreno

/s/	1/17/14
Signature	Date

5. Shahram Ghasemzadeh

/s/	1/17/14
Signature	Date

6. Gune Silva

/s/	1/15/14
Signature	Date

7. Jill Webster

/s/	1/15/14
Signature	Date

8. Nancy Shaw

/s/	1/15/14
Signature	Date

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.

A2 TABLE OF CONTENTS

A Project Management **2**
A1 Title and Approval Sheet **2**
A2 Table of Contents **6**
A2.1 Acronyms/Definitions **9**
A3 Distribution List **10**
A4 Project/Task Organization **12**
A5 Problem Definition/Background **19**
A6 Project/Task Description **20**
A6.1 Evaluation of the effects of high TDS upon chlorination of HF-impacted waters 20
A6.2 Project Schedule 26
A7 Quality Objectives and Criteria **26**
A8 Special Training/Certification **27**
A9 Documents and Records **28**
B Data Generation and Acquisition **30**
B1 Sampling Process Design **30**
B2 Sampling Methods **31**
B3 Sample Handling and Custody **36**
B4 Analytical Methods **37**
B5 Quality Control **38**
B5.1 Precision 38
B5.2 Accuracy 39
B5.3 Comparability 39
B5.4 Sensitivity 39
B5.5 Confirmatory Column Analysis for THMs 40
B6 Instrument/Equipment Testing, Inspection and Maintenance **50**
B7 Instrument/Equipment Calibration and Frequency **50**
B8 Inspection/Acceptance of Supplies and Consumables **50**
B9 Non-Direct Measurements **50**
B10 Data Management **50**

C Assessment and Oversight 52

C1 EPA Assessments and Response Actions 52

C1.1 Assessments 53
C1.2 Corrective Actions 53

C2 Pegasus and Shaw Assessments and Response Actions 53

C2.1 Performance Evaluation (PE) Samples 54
C2.2 Assessments 55
C2.3 Corrective Actions 55
C2.4 Reports to Management 55

D Data Validation and Usability 56

D1 EPA Data Review, Verification and Validation 56

D2 Pegasus and Shaw Data Review, Verification and Validation 57

D3 Data Qualification 58

D4 Reconciliation with User Requirements 60

References 61

Summary of Revision 62

Appendices 63

List of Tables

Table A4.1 Project Roles and Contact Information 18
Table A6.1 List of critical and non-critical parameters 22
Table A6.2 General experimental matrix 25
Table A6.3 Project Schedule 26
Table B1.1 Field Sample Collection 30
Table B2.1 Sample Containers, Preservation and Holding Times 32
Table B2.2 Bench-Scale Reactor Sampling Strategy Summary 33
Table B4.1 Outline of Analysis Methods 37
Table B5.1 Summary of QA/QC Checks 41
Table B10.1 Reporting Units 51
Table D3.1 Data Descriptors 59
Table D3.2 Data Qualifiers 59

List of Figures

Figure A4.1 Pegasus Team Project Organization 16
Figure A4.2 Shaw Team Project Organization 17

A2.1 ACRONYMS/DEFINITIONS

AR	Absolute Range
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
CTR	Cold Temperature Room
DBP	Disinfection By-products
EPA	U.S. Environmental Protection Agency
HASP	Health and Safety Plan
HF	Hydraulic Fracturing
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
Na_2SO_3	Sodium Sulfite
NH_4Cl	Ammonium Chloride
NOM	Natural Organic Material
NRMRL	National Risk Management Research Laboratory
OGWW	Oil & Gas Wastewater
ORD	Office of Research and Development
PE	Professional Engineer
Pegasus	Pegasus Technical Services, Inc.
PI	Principal Investigator
POTW	Publicly Owned Treatment Works
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QMP	Quality Management Plan
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
Shaw	Shaw Environmental & Infrastructure, Inc.
SHEM	Safety, Health, and Environmental Management
SOP	Standard Operating Procedure
SUVA	Specific UV Absorbance
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
T&E	Test and Evaluation
THM	Trihalomethanes
TSA	Technical System Assessment
TSS	Total Suspended Solids
WA	Work Assignment
WSWRD	Water Supply and Water Resources Division
WWTF	Wastewater Treatment Facilities

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

Pegasus Technical Services, Inc.

Karen Koran, Ph.D.	Project Manager
Raghuraman Venkatapathy, Ph.D.	On-Site Technical Manager
Steven Jones, ASQ CQA/CQE	Contract Quality Assurance Manager
Brahm Prakash	Work Assignment Leader
Robert Grosser, Ph.D.	Project Scientist
Joshua Kickish	Project Scientist
Colin White	Project Scientist

Shaw Environmental & Infrastructure, Inc.

E. Radha Krishnan, P.E.	Program Manager
Gune Silva, Ph.D.	Project Leader
Jill Webster	Project Scientist
Nancy Shaw	Project Scientist

University of Cincinnati

George Sorial, Ph.D.	Project Manager
Pablo Campo-Moreno, Ph.D.	Project Leader
Shahram Ghasemzadeh	Project Scientist

A4 PROJECT/TASK ORGANIZATION

The overall project management and distribution of responsibilities among the project personnel are described in this section. Figures A4.1 and A4.2 show the project organization chart and Table A4.1 presents the project roles and responsibilities of the various project staff.

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 EPA Office of Water and wastewater treatment utilities in EPA Region 3.

Mr. Craig L. Patterson, **P.E.,** EPA ORD/NRMRL/WSWRD at the EPA Test and Evaluation (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) 2-64 under EPA Contract EP-C-11-006 and ensuring that the data deliverables received from Pegasus Technical Services, Inc. (Pegasus) satisfies the project objectives. Mr. Patterson is also responsible for overall technical direction of WA 3-02 (EPA Contract EP-C-09-041) and ensuring that the data deliverables received from Shaw Environmental & Infrastructure, Inc. (Shaw) satisfies the project objectives.

Mr. Kit Daniels, EPA ORD/NRMRL/WSWRD at EPA AWBERC serves as the EPA Project Scientist. Mr. Daniels is responsible for collection, preservation, transportation, processing and distribution of field samples. He is also responsible for maintaining a chain of custody form for the samples. Mr. Daniels may also prepare and deliver samples to the EPA T&E Facility at the direction of the EPA WA Manager or the PI.

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 AWBERC in Cincinnati, Ohio serves at the WSWRD Associate Division Director.

Dr. John Olszewski, EPA ORD/NRMRL/WSWRD at EPA AWBERC serves as the EPA WSWRD Quality Assurance (QA) Manager with the responsibility for QA review of the 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. Michael Moeykens and Mr. Stephen Wright, U.S. Environmental Protection Agency (EPA), at the Andrew W. Breidenbach Environmental Research Center (AWBERC) in Cincinnati, Ohio serve as the Project Officer for EPA Contract No: EP-C-11-006 (awardee: Pegasus Technical Services, Inc.) under which this QAPP is being written.

Dr. Karen Koran, with Pegasus serves as the Pegasus Project Manager for the Pegasus Contract and is responsible for overall management of Pegasus Contract activities conducted by Pegasus and Pegasus subcontractors.

Dr. Raghuraman Venkatapathy, with Pegasus serves as the Pegasus On-Site Technical Manager for the Pegasus Contract and is responsible for management of the Pegasus On-Site Program, supervision of On-Site Pegasus Team Staff, providing Pegasus Team staff training on the requirements of this QAPP, and maintaining personnel training and qualification records for the On-Site WA Leaders and staff. Dr. Venkatapathy will serve as the main point of contact for receiving samples from the field sampling team, and shipping samples to the EPA T&E Facility and other labs for sample analysis. He is also responsible for ensuring that this QAPP and WA 2-64 deliverables receive an internal full, independent, and documented review by conducting the actual review, ensuring that review comments are adequately addressed prior to final delivery or use of the document, and ensuring that environmental data generated under WA 2-64 are performed in accordance with this QAPP.

Mr. Steven Jones, ASQ CQA/CQE, with Shaw, a subcontractor to Pegasus for WA 2-64, serves as the Contract QA Manager for the Pegasus Contract. Mr. Jones also serves as the Shaw QA Manager for the Shaw T&E Facility Contract (EPA Contract EP-C-09-041). Mr. Jones is responsible for oversight of Quality Management Plan (QMP) quality program implementation for both contracts, QA review of WA 2-64 and WA 3-02 documents and deliverables, providing guidance for and verifying implementation of quality program requirements as described in this QAPP, and conducting project assessments. Under the Pegasus Contract, Mr. Jones reports to the Pegasus President and CEO and is organizationally independent of WA 2-64 project data collection efforts. Under the Shaw T&E Facility Contract, Mr. Jones reports to the Shaw Corporate Quality Manager and is organizationally independent of the WA 3-02 project data collection efforts.

Mr. Brahm Prakash with Shaw, a subcontractor to Pegasus for WA 2-64, serves as the On-Site WA Leader for this Pegasus On-Site WA and is responsible for trihalomethanes (THM), free chlorine, pH, and conductivity analyses. The On-Site WA Leader is also responsible for coordinating the submittal of deliverables to the Pegasus On-Site Technical Manager and Contract QA Manager for review, maintaining project records, including chain of custody forms for received samples, receiving samples from the EPA, preparation of samples for shipment and analysis, maintaining documentation for standard preparation and sample analysis, performing

sample analysis, verifying that analytical data generated meets the requirements of this QAPP, data entry/reporting, and ensuring that deliverables are peer reviewed prior to submittal to EPA.

Dr. Robert Grosser, Mr. Joshua Kickish and Mr. Colin White with Pegasus will serve as project scientists. They will conduct the day-to-day experiments described in this QAPP under the direction of the On-Site Technical Manager. At the conclusion of each experimental time point, the Project Scientists will transfer the THMs, pH, conductivity and free chlorine analysis samples to Mr. Prakash for analysis along with appropriate chains of custody. They will also transport the remaining samples (alkalinity, anions, DOC, TDS/TSS and TOC) in hard-sided coolers (maintained at 4 ± 2 ºC) as well as appropriate chains of custody to EPA's T&E Facility (point of contact: Dr. Gune Silva) or to the University of Cincinnati (UC; point of contact: Dr. Pablo Campo-Moreno) for their analysis. While anion samples will always be delivered to T&E, and alkalinity samples will always be delivered to UC, the remaining samples (DOC, TSS/VSS and TOC) will be delivered to either T&E or UC, depending on the work load of the analysts at the two facilities. Dr. Grosser and Mr. White will also be responsible for SUVA analysis.

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 Team deliverables to EPA. Mr. Krishnan is also responsible for ensuring that environmental data generated by the Shaw Team for this project under WA 3-02 are performed in accordance with this QAPP, that deliverables receive an internal full, independent, and documented review by conducting the actual review, and ensuring that review comments are adequately addressed prior to final delivery or use of the document.

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 WA 2-64 (under EPA/Pegasus Contract EP-C-11-006) samples that are shipped/delivered to the EPA T&E Facility for sample processing/analysis. All samples at the T&E Facility will be processed under WA 3-02 of EPA/Shaw Contract EP-C-09-041. 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 and Ms. Nancy Shaw with Shaw at the EPA T&E Facility serves as the Shaw Project Scientists. Ms. Webster is responsible for Ion Chromatography (IC), total organic carbon (TOC), total dissolved solids (TDS) and total suspended solids (TSS) analyses that will be performed for this WA. Ms. Webster will be responsible for preparation of samples for analysis, maintaining documentation for standard preparation and sample analysis, sample analysis, implementing the QA/QC requirements for sample analyses as specified in this QAPP, and data entry/reporting. Ms. Nancy Shaw will provide support for TDS and TSS analyses as needed.

Dr. Pablo Campo-Moreno with UC serves as the WA Leader for the experiments and analyses being performed at UC, and is responsible for project planning and coordination of day-to-day activities that are conducted by the UC staff, and overseeing the activities conducted by the UC staff to ensure implementation of the requirements as stated in this QAPP. Dr. Campo-Moreno is the primary point of contact for all WA 2-64 samples that are shipped/delivered to UC for sample processing/analysis. The WA Leader is also responsible for coordinating the submittal of deliverables to the Pegasus On-Site Technical Manager and Pegasus Contract QA Manager for review, ensuring that the UC staff received training on the requirements of this QAPP, maintaining project records, including chain of custody forms for received samples, sample analysis, verifying that data generated by the UC staff meet the requirements of this QAPP, data reporting, and ensuring that deliverables are peer reviewed prior to submittal to EPA.

Mr. Shahram Ghasemzadeh, with UC serves as the UC Project Scientist. Mr. Ghasemzadeh will be responsible for assisting the UC WA Leader with the maintenance of instruments, preparation of samples for analysis, maintaining documentation for standard preparation and sample analysis, sample analysis for alkalinity, DOC, TDS/TSS and TOC, implementing the QA/QC requirements for sample analyses as specified in this QAPP, and data entry/reporting.

Figure A4.1 Pegasus Team Project Organization

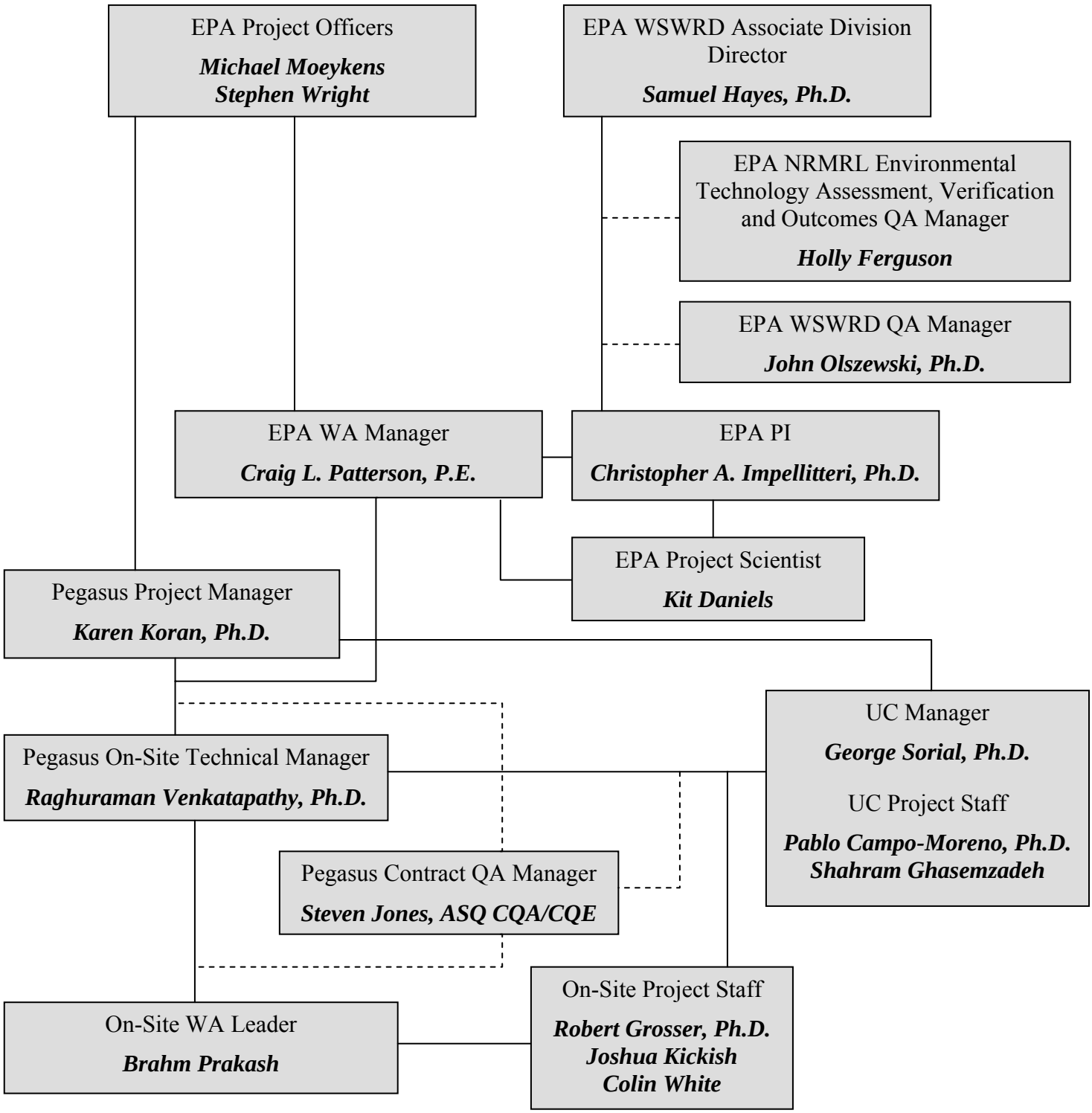

Figure A4.2 Shaw Team Project Organization

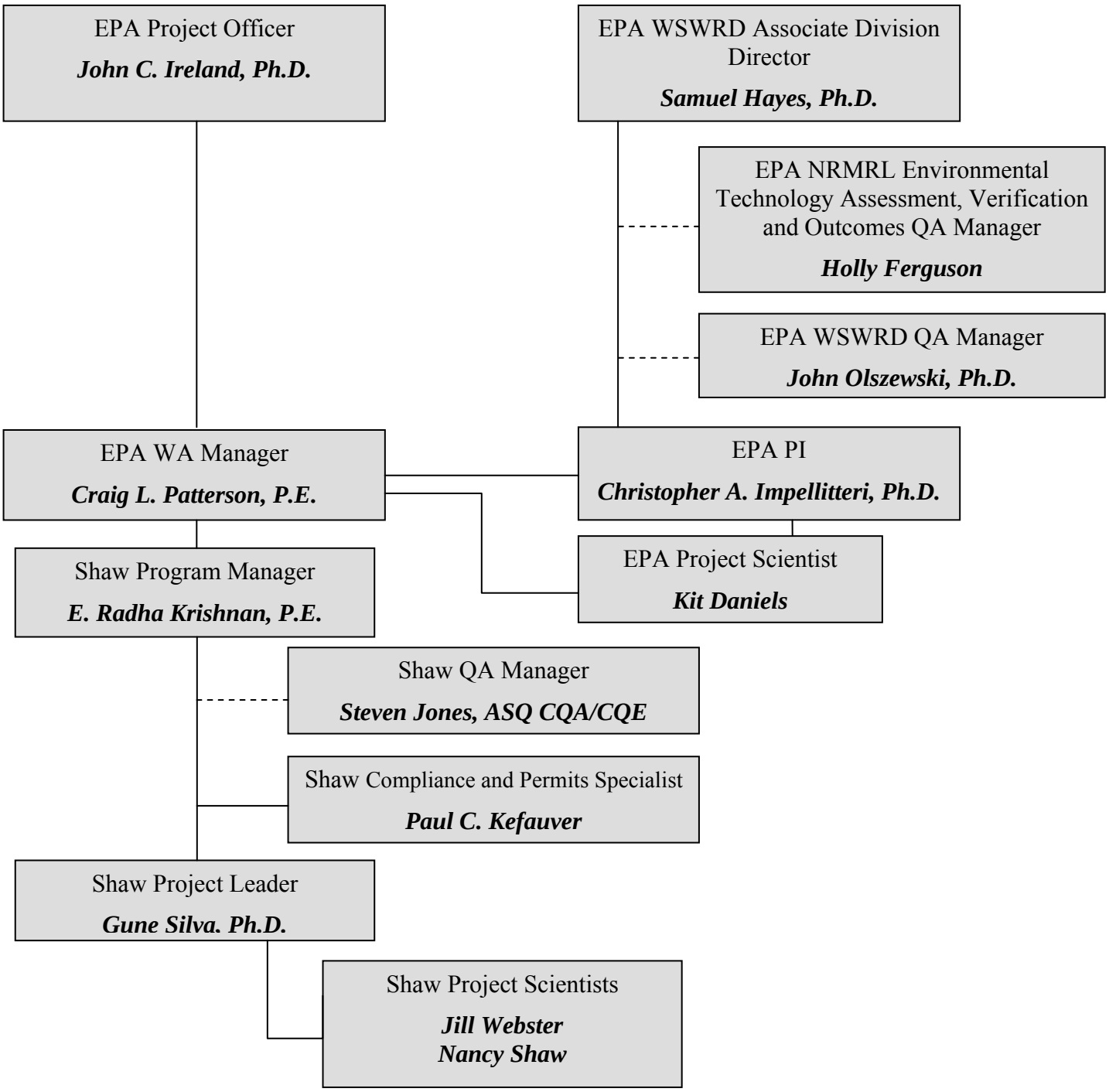

Table A4.1 Project Roles and Contact Information

Name of Person/Affiliation	Project Role	Phone Number, email
Christopher A. Impellitteri, Ph.D./ EPA	PI	513-487-2872 Impellitteri.Christoper@epa.gov
Craig L. Patterson, P.E./ EPA	WA Manager	513-487-2805, Patterson.Craig@epa.gov
Kit Daniels/ EPA	Project Scientist	513-569-7018, Daniels.Kit@epa.gov
Samuel Hayes, Ph.D. /EPA	WSWRD Associate Division Director	513-569-7514, Hayes.Samuel@epa.gov
John Olszewski, Ph.D./ EPA	WSWRD QA Manager	513-569-7481, Olszewski.John@epa.gov
Holly Ferguson/ EPA	NRMRL Environmental Technology Assessment, Verification and Outcomes QA Manager	513-569-7944, Ferguson.Holly@epa.gov
Michael Moeykens/ EPA	Pegasus Contract Project Officer	513-569-7196, Moeykens.Michael@epa.gov
Stephen Wright /EPA	Pegasus Contract Project Officer	513-569-7610, Wright.Stephen@epa.gov
Karen Koran, Ph.D. /Pegasus	Project Manager	513-569-7304, Koran.Karen@epa.gov
Steven Jones, ASQ CQA/CQE/ Pegasus Subcontractor (Shaw)	Pegasus Contract QA Manager/ Shaw QA Manager	513-782-4655, Steven.Jones@shawgrp.com
Raghuraman Venkatapathy, Ph.D./ Pegasus	On-Site Technical Manager	513-569-7077, Venkatapathy.Raghuraman@epa.gov
Brahm Prakash/Pegasus Subcontractor (Shaw)	On-Site WA Leader	513-569-7945, Prakash.Brahm@epa.gov
Robert Grosser, Ph.D./Pegasus	On-Site Project Staff	513-569-7529, Grosser.Robert@epa.gov
Joshua Kickish/Pegasus	On-Site Project Staff	513-569-7485, Kickish.Joshua@epa.gov
Colin White/Pegasus	On-Site Project Staff	513-569-7708, White.Colin@epa.gov
E. Radha Krishnan, P.E. /Shaw	Program Manager/Project leadership/peer review	513-782-4730, Radha.Krishnan@shawgrp.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
Nancy Shaw/Shaw	Project Scientist	513-569-7996, Shaw.Nancy@epa.gov
George Sorial, Ph.D./ Pegasus Subcontractor (UC)	UC Manager	(513) 556-2987, sorialga@ucmail.uc.edu
Pablo Campo-Moreno/ Pegasus Subcontractor (UC)	UC WA Leader	(513) 556-3637, campomp@ucmail.uc.edu
Shahram Ghasemzadeh/ Pegasus Subcontractor (UC)	UC WA Support Staff	(513) 556-3640 ghasemsm@mail.uc.edu

A5 PROBLEM DEFINITION/BACKGROUND

Hydraulic fracturing (hydro-fracking, 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. This flow-back water typically contains high levels of dissolved solids (including chloride and bromide salts), heavy metals, and hydrocarbons from natural sources as well as chemical additives from various stages of the oil and gas exploration process. In general, treatment of water from oil and gas exploration activities has occurred through either admixture to normal wastewater inputs or post-treated wastewater. However, to date, the impacts of such inputs, and in particular, the effects of high TDS levels on subsequent water disinfection have not been ascertained. The elevated TDS levels are of particular concern because wastewater treatment is not effective at their removal.

Literature studies on the effects of bromide ions under chlorination disinfection conditions have demonstrated increased propensity for the formation of brominated disinfection by-products (DBPs) upon reaction with natural organic material (NOM), and although the highest levels were observed upon ozonation, chlorination/chloramination also produce brominated DBPs.[1,2] Brominated DBPs are considerably more toxic than corresponding chlorinated DBPs, in addition to being of higher molecular weight (which would mean reduced concentrations would be needed to exceed maximum concentration limits), and it is accordingly of interest to EPA to assess and quantify the effects of flowback water on DBP generation.

HF techniques produce a large quantity of wastewaters which may be sent to wastewater treatment facilities (WWTFs), or treated on site for reuse. In any treatment scenario, there is a final waste product that must be managed. In some regions, wastewaters from oil and gas exploration activities (hereafter referred to as OGWW) were treated by publically owned treatment works (POTWs) either by mixing at the headwaters or blended with the POTW effluent. Since 2011, volumes of OGWW treated by POTWs have drastically declined. Currently, the bulk of oil and gas wastewater treated for discharge to surface water is performed by commercial WWTFs; however, the industry is rapidly moving toward zero discharge and reuse technologies. The impact of effluent discharge into surface water sources on drinking water treatment has not yet been evaluated, nor is it clear at this point the extent of dilution upon arrival at drinking water input streams. The results of this study will be used for refinement of the conditions employed in treating high TDS containing waters.

Accordingly, the research objective for this project is to evaluate the effects of high TDS and NOM upon chlorination of oil and gas exploration impacted waters and the formation of disinfection by-products such as THMs. As part of conducting the experiments described in this QAPP, OGWW was collected from 5 sources in the Marcellus Shale Region of the Eastern United States. Prior to conducting experiments with these waters, the water samples will be

analyzed for several variables including DBPs, TOC, anions, TDS, TSS, pH, free chlorine and conductivity. Since the main aim of this project is to determine the effect of high TDS and NOM upon chlorination of OGWW and since the aim is not to determine the values of these variables for waters that are representative of their respective field locations, the water samples will be shipped to EPA AWBERC in coolers without any preservatives. The results of these analyses will not be reported in any product; they will only be used to provide information needed to design the chlorination experiments. All samples will be analyzed prior to start of the experiments (time = 0) to provide a baseline against which the results of the experiments described under this QAPP will be compared.

A6 PROJECT/TASK DESCRIPTION

A6.1 Evaluation of the effects of high TDS upon chlorination of HF-impacted waters

It is known that the amount and type of TDS and halide content in water can influence aqueous chemistry, particularly upon water treatment/disinfection. This is particularly true with water which has been impacted by wastewater input from a variety of industrial/resource extraction processes. In this component of the study, we will evaluate the effect of chlorination on WWTF effluent water samples while varying TDS and NOM (as measured by TOC). These effluent water samples (hereafter referred to as WWTF effluent) are obtained from the effluent of wastewater treatment plants that have treated OGWW (hereafter referred to as WWTF influent). In addition to WWTF influent (originating from the trucks bringing OGWW to the WWTF for treatment), Ohio River water (hereafter referred to as surface water) is obtained to serve as a matrix diluent. Waters (WWTF influent, WWTF effluent) from five sources in the Marcellus Shale Region will be used for this study. The five sampling sites include Mt. Pleasant, PA (WWTF influent and effluent), Josephine, PA (WWTF influent and effluent), Williamsport, PA (WWTF influent and effluent), Warren-WWTF, OH (WWTF effluent) and Warren-Patriot, OH (WWTF influent and effluent). The WWTF influent and effluent samples were collected on August 19, 2013 (Mt. Pleasant), 20 (Josephine), 21 (Williamsport) and 22 (Warren) and stored in a refrigerated truck. In addition, 60 liters of surface water sample were obtained from Josephine, PA, at a point upstream of the effluent discharge point into the Blacklick Creek. Since the main aim of this project is to determine the effect of high TDS and NOM upon chlorination of OGWW, and since the aim is not to determine the values of these variables for waters that are representative of their respective field locations, the water samples were shipped to EPA AWBERC in a refrigerated truck without any preservatives. In addition, due to large amounts of surface water (~380 liters) required to conduct the experiments described in this study is more than the amount (60 liters) collected in the field, and because it would be beneficial to conduct all experiments using the same surface water matrix, approximately 420 liters of surface water from the Ohio River was collected prior to the start of the experiments described in this study. For this study, Ohio River water was collected on October 31, 2013 from a sampling port

connected to the intake pump at the Richard Miller water treatment facility in California, OH, and transported by a flat-bed truck to EPA AWBERC. All WWTF influent, WWTF effluent and surface water samples were stored in Cold Temperature Room 613 upon arrival at EPA AWBERC (4 ± 2 ºC). As with the WWTF influent and effluent samples, no preservatives were added to the surface water (Ohio River water) sample. The containers used for sample collection are listed in Table B1.1.

Formation of THMs has been shown to be dependent on a variety of factors in source water, including the character of NOM, the presence and concentration of halogen salts, temperature, water treatment methods and pH. The components of this study include assessing THM formation potentials taking place in WWTF effluent water to be obtained from five sources, which can have their own characteristics, including endogenous levels of TOC, anions, TSS and TDS. WWTF influent waters are not expected to be used in any of the experiments described in the QAPP; however, these waters will be collected and analyzed to determine endogenous levels of TOC, anions, TDS, TSS and THMs in case these waters need to be used in the experiments in place of WWTF effluent samples (e.g., when bromide concentrations in the effluent are low, and only influent waters can be used to meet the desired bromide levels in the experiments). All experiments in this study will be conducted with deionized (DI) water or surface water (with and without fortification with WWTF effluent), which may also contain endogenous levels of TOC, anions, TDS, TSS and THMs. Hence, all water samples that are to be used in conducting the experiments will be analyzed for the presence of THMs, and background concentrations of TDS and TOC prior to the start of the experiments in this section to ensure that background effects are properly taken into consideration while evaluating the effects of high TDS on chlorination of OGWW. Other variables that will be measured for all water samples include pH, conductivity, anions concentration, alkalinity, Specific Ultraviolet Absorbance SUVA (absorbance at 254 nm to measure the aromatic characteristics of dissolved organic matter), TSS and free chlorine. The parameters that will be evaluated for this study are shown in Table A6.1. Since the samples are not being preserved in the field, and since some analyses will not be conducted within their respective holding times, the analyses values will not be considered representative of field values at any time during this study and will not be reported as such.

The enhanced formation of disinfection by-products as a result of high halide levels in water has been previously documented in the literature (Chowdhury, S.; Champagne, P.; McLellan, P.J.; 2009) (Yang, G.; Shang, C.; 2004). Elevated levels of dissolved bromide, in particular, have been implicated in the formation of brominated DBPs, which demonstrate significantly higher toxicity than chlorinated equivalents. As such, it is of interest to assess the implications of high chloride and bromide levels on THM formation. In addition, the use of five water sources from areas impacted by resource extraction techniques will assist in determining whether variances in HF water chemistry have an impact on THM formation in conjunction with elevated halide concentrations. Table A6.1 lists the THMs for this study.

Table A6.1 List of critical and non-critical parameters that will be evaluated for this study

THMs	**CAS Number**	**Measurement Importance**
Bromodichloromethane	75-27-4	Critical
Bromoform	75-25-2	Critical
Chloroform	67-66-3	Critical
Dibromochloromethane	124-48-1	Critical
Anions	**CAS Number**	**Measurement Importance**
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
NOM		**Measurement Importance**
TOC		Critical
General Chemistry Water Parameters		**Measurement Importance**
Free Chlorine		Critical
pH		Critical
Alkalinity		Non-critical
SUVA		Non-critical
Conductivity		Non-critical
TDS		Non-critical
TSS		Non-critical

Bench-scale experiments using 1 L reactors (amber glass jars) on stir plates will be performed to assess the effects of elevated bromide and chloride levels on disinfection by-product (DBP) (THMs) formation in several water matrices. Experiments in this study will focus on water samples including: de-ionized water, de-ionized water fortified with commercially-available NOM, surface waters and WWTF effluent sources. All experiments will be conducted in EPA AWBERC Lab 682 or in Lab 674-676. Anions, alkalinity, DOC, TDS and TOC will be analyzed off site at the EPA T&E Facility or at UC. THM samples will be analyzed on site in EPA AWBERC Lab 668, while the remaining variables will be analyzed in EPA AWBERC Lab 682 or 674-676.

Chlorination of water samples (Appendix A) will be performed to explore the effects of halogen ion content on overall formation of THMs. This will be accomplished through analysis for THM formation using EPA Method 551.1, following disinfection of water samples. Variables to be explored include:

- Concentration of disinfectant

- Halogen ion concentration (bromide; Cl:Br ratio of 100:1, or the ratio found in surface water will be maintained in all experimental samples through addition of NaCl)
- Water source (see Table A6.2)
- Duration of disinfection (or contact time)
- TOC concentration

THMs will be assessed in the water matrices (laboratory DI water, WWTF effluent and surface water), with the addition of varying bromide concentrations, varying chlorine disinfectant concentrations and varying the duration of disinfection. Chloride concentrations will be adjusted in each reactor using NaCl to maintain a Cl:Br ratio of 100:1, or the levels found in surface water (whichever is higher). All experiments will start at the time of addition of the disinfectant (time = 0). Surface water samples will be collected from the Ohio River. WWTF influent samples will be collected directly off of the trucks that transport these waters to the WWTFs or at the point of discharge from the trucks into the WWTF. WWTF effluent water samples will be collected from the discharge pipes of the WWTF. Though WWTF influent samples are not expected to be used in any of the experiments described in this QAPP, the influent is being collected in case samples need to be fortified at concentrations higher than those available in the WWTF effluent samples. All source waters (WWTF influent, WWTF effluent and surface water) will be analyzed for ambient THMs, anions, TOC, TDS, TSS, pH, residual chlorine and conductivity to obtain estimates of these values. These estimates will be used to plan the chlorination experiments with these source waters, including approximate amounts of NOM, chloride and bromide to add for each experiment. Since the experiments described in this QAPP are expected to be conducted over the course of 3-4 months, these waters will be analyzed for ambient THMs, anions, TOC, TDS, TSS, pH, residual chlorine, conductivity, alkalinity and SUVA just prior to starting the experiments. The values obtained during this analysis will allow us to estimate the actual amounts of NOM, chloride and bromide to add for each experiment. The remaining variables (THMs, other anions, TDS, TSS, pH, residual chlorine, conductivity, alkalinity and SUVA) will be used to correct for background levels while performing statistical analyses at the conclusion of this study.

TOC in all non-control samples will be adjusted as needed to 5 mg/L using humic acid from a known source such as Sigma-Aldrich. For experimental samples that involve the use of the surface water blended with WWTF effluent, an appropriate amount of the WWTF effluent will be added to surface water to achieve the target bromide concentrations for each experiment (listed under the column entitled ‘Bromide Concentration (mg/L)’ in Table A6.2). For surface waters whose ambient bromide concentrations are lower than 0.05 mg/L, experiments with specific bromide concentrations in surface and surface+OGWW samples will be carried out with 0.05, 0.1 and 0.25 mg/L bromide (last 2 rows of Table A6.2). If the ambient bromide concentration in the surface water is higher than 0.05 mg/L, the three experiments mentioned previously will be conducted with the surface and surface+OGWW samples spiked with 0.05,

0.1 and 0.25 mg/L bromide (final bromide concentration in sample = ambient level + appropriate spike amount). The chloride ion concentration in the water samples for each experiment will be adjusted using NaCl depending on endogenous levels of bromide and chloride in each experimental matrix to keep the bromide:chloride ratio the same in all experiments (similar to those found in the environment; approximately 1:100, or those found in the surface water, whichever is higher).

THM formation will be analyzed using EPA Method 551.1 for all experimental samples. TOC, anions, free chlorine, and pH will also be monitored. Initial analysis will focus on the determination of total THM formation potentials after set reaction times (0, 0.5, 1, 5 or 12 days). Samples will be collected from each of the t=0 triplicate reactors prior to the addition of chlorine (pre time = 0). For time t=0 samples, samples will be collected from each t=0 reactor immediately after the addition of chlorine followed by the addition of a quenching agent. For all other reaction times, samples will be collected from each reactor after the addition of the quenching agent at the appropriate time (approximately 0.5, 1, 5 or 12 days. All quench and sample collection times will be noted in the laboratory notebook). For all experiments, an appropriate amount of 0.1M thiosulfate will be added in excess (~1000x free chlorine concentration) to quench the reaction at the appropriate time. Experiments will be conducted in triplicate at room temperature. In addition, all samples will be buffered at 5 mM using a phosphate buffer, and the pH of all samples will be adjusted to 7.5 prior to the start of each experiment using sodium hydroxide or nitric acid.

A single set of experiments using a given sample matrix, disinfection duration and given bromide concentration is expected to be conducted at any given time. Depending on the number of reactors that can be incorporated in a stir plate, multiple stir plates may have to be used to include triplicate samples for each sample matrix (total 18 reactors per sample matrix/bromide concentration). All reactors in the stir plates will be started at the same time through the addition of free chlorine to the experimental matrix. Each sample location in the stir plate will hold a sample that is to be sacrificed at a given time point (pretime, 0, 0.5, 1, 5 or 12 days). Sample aliquots for each of the variables monitored will then be collected from the appropriate triplicate jars at the appropriate time (one sample aliquot from each of the triplicate jars will be collected for each variable to be analyzed). For samples being analyzed at the EPA T&E Facility, the samples will be preserved using the preservative listed in Table B2.1, and the person preparing the samples will create a chain of custody form for the samples to be transferred for analysis. For each variable to be monitored, two additional sample aliquots will be collected from one of the three triplicate jars at each time point to determine analytical precision and accuracy for that variable. Once the triplicate aliquots are analyzed for that given variable, a %RSD will be calculated for that variable. The %RSD for each variable should meet the criteria listed in Table B5.1. In addition, for TOC, THMs and anions, an additional aliquot of samples will be collected

from a second triplicate jar to perform matrix spike recoveries tests. The recoveries for the analytes of interest should meet the criteria listed in Table B5.1.

The experimental matrix is outlined in Table A6.2:

Table A6.2 General experimental matrix

Sample	TOC Concentration (mg/L)	Initial Chlorination Concentration (mg/L)	Time (days)	Bromide Concentration (mg/L)	Experimental QC
DI Water (Control)	0	0	pretime=0, 0, 0.5, 1, 5, 12	n/a	Triplicate
DI Water	5	5	pretime=0, 0, 0.5, 1, 5, 12	n/a	Triplicate
DI Water	5	5	pretime=0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate
Ohio River surface water	5	5	pretime=0, 0, 0.5, 1, 5, 12	Ambient	Triplicate
Ohio River surface water	5	5	pretime=0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate
Ohio River surface water blended with effluent from Mt. Pleasant	5	5	pretime=0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate
Ohio River surface water blended with effluent from Josephine	5	5	pretime=0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate
Ohio River surface water blended with effluent from Williamsport	5	5	pretime=0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate
Ohio River surface water blended with effluent from Warren-WWTF	5	5	pretime=0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate
Ohio River surface water blended with effluent from Warren-Patriot	5	5	pretime=0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate

Statistical analysis will involve comparing the THM formation in the control matrix (DI water) against the THM formation in each sample matrix/bromide concentration at each time point. It is expected that the high TDS concentrations in the OGWW will have an impact on THM

formation during the disinfection process. The effect of TDS on THM formation will be determined using Analysis of Variance (ANOVA) for each of the critical THMs. The null hypothesis for this analysis is that the THM concentrations in the control (DI water with no chlorination) are not equal to the concentrations in the other experimental matrices. The alternative hypothesis for this analysis is that at least one of the concentrations is equal. All statistical analysis will be carried out at $\alpha = 0.05$ significance level.

A6.2 Project Schedule

Activities for this WA will be performed from October 2012 to April 2014. The project schedule and main activities to be conducted are shown in Table A6.3.

Table A6.3 Project Schedule

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

Monthly progress reports will be submitted by Pegasus and Shaw to the EPA WA Manager. At the conclusion of this study, an interim summary report will be submitted by the Pegasus Team to the EPA WA Manager. Two weeks after receiving comments from EPA, a final report on this study will be submitted to the EPA WA Manager.

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, and storage at cold conditions (at 4±2°C) can help minimize further variability. Additionally, the use of calibrated measuring and weight equipment, appropriate laboratory ware, unadulterated chemicals, using high purity chemicals and solvents 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 performing laboratory research activities at EPA AWBERC and field sampling activities will complete the training required by the EPA Cincinnati Chemical Hygiene Plan. The Health and Safety Plan (HASP) on file also includes information on the project-specific safety training and requirements.

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 also includes information on the project-specific safety training and requirements. 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.

Within one week of endorsement of this QAPP by EPA, the Pegasus On-Site Technical Manager will provide training to the Pegasus Team staff at EPA AWBERC on the QAPP requirements, while the Shaw Project Leader for the Shaw T&E Facility Contract will provide training to the Shaw Team staff at the EPA T&E Facility on the QAPP requirements. QAPP requirements training for EPA staff will be handled by the EPA PI or EPA WA Manager.

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 staff assigned 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 (e.g., the SOP), and if available, 4) satisfactorily analyzing a performance evaluation sample or a second source standard. It is anticipated that performance evaluation samples will be submitted for all analytical methods that will be performed under this QAPP.

Safety training records for EPA and EPA contractor staff are maintained by the EPA Safety, Health, and Environmental Management (SHEM) Office at EPA AWBERC. Training documentation (QA management surveillances, PPMs 13.2/13.4 training) for contract staff at AWBERC will be maintained by the Pegasus QA Manager, documentation for contract staff at T&E will be maintained by the Shaw Project Leader for the Shaw T&E Facility Contract,

documentation for contract staff at UC by the UC Manager, while the EPA PI will maintain the training documentation for EPA staff. Initial demonstration of analyst proficiency (IDAP), MDL and PE sample documentation for the Pegasus Team staff are maintained by the Pegasus On-Site Technical Manager, for the UC Team staff by the UC Manager, and by the Shaw Compliance and Permits Specialist for Shaw Team staff. The EPA PI is responsible for data management, while purchasing documentation for PE samples and standards are maintained by the WSWRD QA Manager, and the EPA WA Manager, respectively.

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 Pegasus QA Manager will provide and/or make available the most current versions of this QAPP to all persons identified in Section A3, Distribution List. The Pegasus QA Manager 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 Pegasus QA Manager 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 WA 2-64 WA Leaders and WA 3-02 Project Leader will submit internally the raw data, including calculations and QA/QC requirements, for QA and Management review at the conclusion of each experimental run. The Pegasus QA or Technical Manager will submit the data to the EPA WA Manager and the EPA PI. Monthly progress reports will be submitted by Pegasus and Shaw 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 at least one final report describing the analytical results of the samples analyzed.

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 Pegasus/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 AWBERC and at the EPA T&E Facility, unless otherwise directed by the EPA WA Manager.

SECTION B DATA GENERATION AND ACQUISITION

B1 SAMPLING PROCESS DESIGN

Field water samples (surface water, and WWTF influent and effluent water) will be collected by the EPA Project Scientist (Kit Daniels) under the supervision and guidance of the EPA WA Manager (Craig Patterson) and PI (Chris Impellitteri). The water samples will be collected from five WWTF locations from the Marcellus Shale Region. The surface water sample will be collected from the Ohio River by Pegasus project staff (Robert Grosser, Joshua Kickish and Raghuraman Venkatapathy). WWTF influent water samples will be collected from sampling ports located on the influent tanks at each of the WWTFs or directly from the trucks. WWTF effluent water samples will be collected from the outflow pipes from the WWTFs. For OGWW sample collection, the sampling valves will be opened and allowed to flow for 30 seconds prior to filling the sample containers. In addition, the containers will be rinsed with the sample 2 times before sample collection. Sample containers and sample volumes for field samples are shown in Table B1.1. Due to challenges in sample procurement, every effort will be made to procure as much sample as possible for continuity in the study.

Table B1.1 Field Sample Collection

Sample	Sample Container	Sample volume	Preservation
Surface water from Ohio River	20 L carboys	420 L	4 ± 2 ºC
Influent from Mt. Pleasant	1 L bottle	1 L	4 ± 2 ºC
Influent from Josephine	1 L bottle	1 L	4 ± 2 ºC
Influent from Williamsport	1 L bottle	1 L	4 ± 2 ºC
Influent from Warren-Patriot	1 L bottle	1 L	4 ± 2 ºC
WWTF Effluent from Mt. Pleasant	5 L carboy	5 L	4 ± 2 ºC
WWTF Effluent from Josephine	5 L carboy	5 L	4 ± 2 ºC
WWTF Effluent from Williamsport	5 L carboy	5 L	4 ± 2 ºC
WWTF Effluent from Warren-WWTF	5 L carboy	5 L	4 ± 2 ºC
WWTF Effluent from Warren-Patriot	5 L carboy	5 L	4 ± 2 ºC

The samples that will be collected from the field WWTF locations will be used for the bench-scale reactor experiments to evaluate the effects of high TDS upon chlorination of OGWW, as described in Section A6 of this QAPP. Determining the concentrations of analytes/compounds at the time of field sample collection is not a study objective for this project. Field samples will not be pH adjusted at the time of collection. All samples will be transported from the field to the EPA AWBERC facility and stored under cold preservation (4 ± 2 ºC) until use in experiments.

B2 SAMPLING METHODS

A one-time sampling event from each of the five WWTF locations is planned for this study. In addition, a one-time sampling event for collecting Ohio River water is also planned for this study. The quantities of sample to be collected for each matrix/analysis, as shown in Table B1.1, reflect quantities needed to complete all tests for this study.

All water samples will be analyzed for THMs, anions, TOC, free chlorine, pH, conductivity, TDS and TSS in addition to alkalinity and SUVA to obtain approximate background concentrations prior to start of any experiments (pre time = 0) to serve as the control for that experiment. The quantity of sample required for this analysis as well the preservation techniques to be used is shown in Table B2.1. Each analysis will be conducted in triplicate. In addition, for THMs, anions, TOC and TDS, a separate aliquot of the sample will be spiked with the appropriate analyte(s) at 1/4 – 1/2 the concentration of the highest calibration standard, depending on the background concentration of the analytes expected in each sample. Spike recoveries for this matrix spike should meet the criteria listed in Table B5.1.

For the bench-scale reactor experiments to assess the effects of elevated bromide and chloride levels on THMs formation, sampling containers and volumes as well as preservation techniques are shown in Table B2.1, and the monitoring parameters are shown in Table B2.2. Prior to the start of each experiment (pre time = 0), the samples will be analyzed for all parameters. At other time points (t = 0, 0.5, 1, 5, 12 days), the samples will be analyzed for THMs, anions, pH, TOC, alkalinity, SUVA and free chlorine. All experimental samples will be quenched with sodium thiosulfate prior to sample collection to stop the reaction at the appropriate time. One set of samples will be collected for each analyte from each triplicate reactor for each time point (experimental replicate). For each variable to be monitored, two additional sample aliquots will be collected from one of the three triplicate jars at each time point to determine analytical precision and accuracy for that variable. Once the triplicate aliquots are analyzed for that given variable, a %RSD will be calculated for that variable. The %RSD for each variable should meet the criteria listed in Table B5.1. In addition, for TOC, THMs, SUVA and anions, an additional aliquot of samples will be collected from a second triplicate jar to perform matrix spike recoveries tests. The recoveries for the analytes of interest should meet the criteria listed in Table B5.1. For THMs, though the method states that samples can be extracted within 14 days of collection, the samples will be extracted within a week of the day of sample collection from the experiments; the extracted samples will be analyzed within 14 days. TOC, anions, TDS and TSS analyses will be performed within two days of sample collection. Alkalinity and SUVA analyses will be performed on the day of sample collection.

Table B2.1 Sample Containers, Preservation and Holding Times for Analysis of Samples from Each Experiment

Parameter	Sample Container	Preservation	Max. Holding Time
THMs	60 mL Amber Vial	4 drops 0.1 N sodium sulfite per 60 mL vial, headspace free, 4±2°C	14 days for sample; 14 days for extracts
TOC	40 mL Amber Vial	Cool @ 4±2 ^{0}C, Acidified using 4 drops of H_2SO_4 or H3PO_4 to pH≤ 2; headspace free	28 days
Anions	15 mL Centrifuge tube	Cool @ 4±2 ^{0}C	28 days (except PO_4, NO_3^-& NO_2^- 48 hrs)
TSS	125 mL HDPE bottle	Cool @ 4±2 ^{0}C	7 days
TDS	125 mL HDPE bottle	Cool @ 4±2 ^{0}C	7 days
Free Chlorine	60 mL vial	None	Analyze Immediately
pH	60 mL Vial	None	Analyze Immediately
Conductivity	60 mL Vial	None	Analyze Immediately
Alkalinity	60 mL Amber Vial	None	Analyze Immediately
SUVA	60 mL Vial	Cool @ 4±2 ºC; DOC sample acidified to pH < 2 after filtration	48 hrs for UVA, 28 days for DOC

Table B2.2 Bench-Scale Reactor Sampling Strategy Summary

Sample/ Measurement Location	Condition	TOC Conc. (mg/L)	Initial Chlorination Conc. (mg/L)	Time (days)	Bromide Concentration (mg/L)	Experimental QC	Analysis	Total Number of Samples*
Laboratory (baseline)	DI Water	0	0	pretime = 0, 0, 0.5, 1, 5, 12	n/a	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	24 24 24 18 18 18 24
Reactor	DI Water	5	5	pretime = 0, 0, 0.5, 1, 5, 12	n/a	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	24 24 24 18 18 18 24
Reactor	DI Water	5	5	pretime = 0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	72 72 72 54 54 54 72
Reactor	Ohio River Surface Water	5	5	pretime = 0, 0, 0.5, 1, 5, 12	Ambient	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	24 24 24 18 18 18 24

Sample/ Measurement Location	Condition	TOC Conc. (mg/L)	Initial Chlorination Conc. (mg/L)	Time (days)	Bromide Concentration (mg/L)	Experimental QC	Analysis	Total Number of Samples*
Reactor	Ohio River Surface Water	5	5	pretime = 0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	72 72 72 54 54 54 72
Reactor	Ohio River Surface Water blended with effluent from Mt. Pleasant	5	5	pretime = 0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	72 72 72 54 54 54 72
Reactor	Ohio River Surface Water blended with effluent from Josephine	5	5	pretime = 0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	72 72 72 54 54 54 72
Reactor	Ohio River Surface Water blended with effluent from Williamsport	5	5	pretime = 0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	72 72 72 54 54 54 72

Sample/ Measurement Location	Condition	TOC Conc. (mg/L)	Initial Chlorination Conc. (mg/L)	Time (days)	Bromide Concentration (mg/L)	Experimental QC	Analysis	Total Number of Samples*
Reactor	Ohio River Surface Water blended with effluent from Warren-WWTF	5	5	pretime = 0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	72 72 72 54 54 54 72
Reactor	Ohio River Surface Water blended with effluent from Warren-Patriot	5	5	pretime = 0, 0, 0.5, 1, 5, 12	0.05, 0.1, 0.25	Triplicate	THMs Anions TOC Free Chlorine pH Alkalinity SUVA	72 72 72 54 54 54 72

* In addition to these samples, for each variable to be monitored, two additional sample aliquots will be collected from one of the three triplicate jars at each time point to determine analytical precision and accuracy for that variable. Once the triplicate aliquots are analyzed for that given variable, a %RSD will be calculated for that variable. The %RSD for each variable should meet the criteria listed in Table B5.1. In addition, for TOC, THMs, SUVA and anions, an additional aliquot of samples will be collected from a second triplicate jar to perform matrix spike recoveries tests (LFSM). The recoveries for the analytes of interest should meet the criteria listed in Table B5.1. The samples required for LFSM is included in the 'Total number of samples' column in the Table. Spike recoveries have to meet the criteria listed in Table B5.1.

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 environmental samples will store the samples at 4 ± 2 ºC during shipment to the EPA. Table B1.1 provides the sample containers and the amount of sample to be collected from each water source. Except for temperature control, no other preservation techniques will be used for sample shipment from the field to EPA AWBERC. The sample containers will be stored in the EPA AWBERC 613 CTR (cold temperature room) until being used in the experiments.

A chain-of-custody (Appendix B) 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.

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 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.

The field surface water and WWTF influent and effluent water samples to be used in the study will be transported in hard-sided coolers from the field site on ice or in a refrigerated truck and padded with adequate packaging material to protect the samples from breaking during shipment. All containers used to collect the samples will be labeled. This label will contain the sample location, date and time of sampling. A laboratory notebook will be used by the field sampling team to record the details of the field sampling event. The samples will be transported from the field site to EPA AWBERC by the field sampling team.

Upon receipt at EPA AWBERC, samples will be stored at 4±2 °C in CTR 613 until processed. Aliquots will be prepared and then transferred to the respective laboratories for analysis along with a chain-of-custody form. Larger samples will be thoroughly mixed via agitation prior to collection of sub-samples to deliver to appropriate experiments. Sample labeling will be maintained as mentioned above. A laboratory notebook will be used to record the details that will be signed, dated, and witnessed. Prior to starting the experiments, the collected samples will be analyzed for all variables. Samples will be stored for a period not exceeding the maximum holding time (Table B2.1). Samples that are transferred from EPA AWBERC to another facility for analysis (e.g., the EPA T&E Facility or UC) will be packaged in hard-sided coolers on ice and transferred

with a second chain-of-custody form (Appendix B). The results from the analyses of these samples are for informational purposes only, and will not be formally reported.

For samples collected from the bench-scale reactors (see Table B2.2), samples will be labeled to include the collection date, condition (DI, SW, SW+E P1, SW+E P2, etc.), TOC concentration, time (days), initial chlorine concentration, bromide concentration, and analysis. These samples will be analyzed within a week of collection for all variables except pH, conductivity and free chlorine. For these three variables, the samples will be analyzed immediately upon sample collection.

B4 ANALYTICAL METHODS

The methods for analysis are summarized in Table B4.1.

Table B4.1 Outline of Analysis Methods

Parameter	Measurement	Instrument	Analytical Method	Target MDL[1]	Analysis Location
THMs -Bromodichloromethane -Bromoform -Chloroform -Dibromochloromethane	Critical	HP 6890 Series GC-ECD	EPA Method 551.1 (Appendix C)	0.5 µg/L	EPA AWBERC
Anions -Bromide -Chloride	Critical	Ion Chromatograph (IC), using AS-18 Dionex chromatography column	EPA Method 300.1 (Appendix F)	0.5 mg/L	EPA T&E Facility
Anions -Fluoride -Nitrite/Nitrate -Phosphate -Sulfate	Non-critical			0.5 mg/L	
Free Chlorine	Critical	HACH DR/2500 Spectrophotometer	HACH Method 8021 (Appendix E)	0.21 mg/L	EPA AWBERC
pH	Critical	HACH Illuminator Module pH Meter	Standard Method 4500B (Appendix D)	--	EPA AWBERC
TOC	Critical	Teledyne Tekmar Fusion UV/Persulfate TOC Analyzer	EPA Method 415.3 (Appendix G)	1 mg/L	EPA T&E Facility
TOC	Critical	TOC-V CSH Total Organic Carbon Analyzer, Shimadzu	Standard Method 5310B (Appendix L)	1 mg/L	UC
Conductivity	Non-critical	Thermo Scientific Orion 5-Star temperature compensated pH /ISE/DO/ Conductivity meter	Standard Method 2510B (Appendix H)	--	EPA AWBERC

Parameter	Measurement	Instrument	Analytical Method	Target MDL[1]	Analysis Location
TDS	Non-critical	--	Shaw T&E SOP 510 (Appendix I)	--	EPA T&E Facility
TDS	Non-critical		Standard Method 2540 D (Appendix M)		UC
TSS	Non-critical	--	Shaw T&E SOP 509 (Appendix J)	--	EPA T&E Facility
TSS	Non-critical		Standard Method 2540 D (Appendix M)		UC
Alkalinity	Non-critical	-	EPA Method 310.1 (Appendix N)	--	EPA AWBERC
SUVA	Non-critical	Teledyne Tekmar Fusion UV/Persulfate TOC Analyzer	EPA Method 415.3 (Appendix G)	1 L/mg-M	EPA T&E Facility
SUVA	Non-critical	TOC-V CSH Total Organic Carbon Analyzer, Shimadzu	Standard Method 5310B (Appendix L)	1 L/mg-M	UC

[1] MDLs required to meet project objectives. Actual MDLs should be below the target MDL to meet project objectives. The method reporting limit (MRL), calculated as actual MDL * 5, should be close to the lowest calibration standard for each analysis. The actual MDL and QL will be included in all applicable lab reports.

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. All analytical data will be collected in accordance with the QA/QC procedures specified in this QAPP. Table B5.1 summarizes the QA/QC checks, acceptance criteria, and corrective actions for each analysis. The data quality indicators for the analyses are defined in Sections B5.1 through B5.4. Section B5.5 mentions the criteria that will be used to determine the target THM analytes using a confirmatory column.

B5.1 Precision

Precision is broadly defined as the scatter within any set of repeated measurements. For samples that are measured in duplicate, precision will be calculated as relative percent difference (RPD).

$$RPD = (C1-C2) / ((C1+C2) / 2) * 100 \quad (1)$$

where C1 and C2 are the two measurements. For samples that are measured in triplicate or higher, the precision will be measured as the relative standard deviation (RSD).

$$RSD = (S / SM) * 100 \quad (2)$$

where S is the standard deviation, and SM is the sample mean. Precision of the measurements that cannot be calculated with Equations (1) and (2) will be determined by absolute range (AR).

$$AR = |C1 - C2| \quad (3)$$

where C1 and C2 are the two measurements.

B5.2 Accuracy

Accuracy is broadly defined as how close the analyses will come to the true concentration in the sample. The accuracy of measurements, incorporating a standard reference material or a second source standard, will be calculated as percent recovery.

$$\% \text{ Recovery} = 100\% * (Cs/Cmst) \quad (4)$$

where Cs is the measured concentration of the standard and Cmst is the actual concentration of the standard. The accuracy of the analyses that use matrix spikes will be calculated by

$$\% \text{ Recovery} = 100\% * (Csp - Cmsa) / Cac \quad (5)$$

where Csp is the measured concentration of the spiked aliquot, Cmsa is the measured concentration of the sample, and Cac is the actual concentration of the spiked aliquot.

The accuracy of the samples that cannot be determined with Equations (4) and (5) will be calculated by the measurement bias.

For matrix spikes, it is recommended that spiking concentrations be approximately 50% of the anticipated sample concentration. In no cases should the sample concentrations be greater than four times the spike concentration.

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. MDLs (EPA, 1986) 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 five times the MDL will be flagged and not included in statistical analyses.

B5.5 Confirmatory Column Analysis for THMs

Sample components are identified by comparison of retention times of target analytes to retention data from the calibration standard analysis. If the retention time of an unknown compound corresponds within limits to the retention time of a standard compound, then identification is considered positive. The width of the retention time window used to make identifications is based on measurements of actual retention time variations of the standards in that particular batch. Three times the standard deviation of a retention time can be used to calculate the suggested retention size for a target analyte. Since EPA Method 551.1 used a retention time window of 1% of the total analyte retention time, the larger of 1% of retention time or three times the standard deviation of the retention time of the standards in that batch will be used to determine the retention time windows for all target analytes in that batch.

Each data report (described in Section D2) for the confirmatory column will include the retention times for all target analytes, internal standards and surrogates for all calibration standards, check standards, blanks and samples in an analysis batch. The analyst will calculate the retention time window for all target analytes using the criteria described above. The retention times of the target analytes in the samples will be checked against the calculated retention time window. If there are no peaks within the calculated retention time window for a particular target analyte, the analyte will be listed as ‘not present’, and vice versa.

Table B5.1 Summary of QA/QC Checks

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
THMs	Critical	Initial calibration	7 point calibration	With every sequence	RSD for curve < 0.25	Prepare new standard curve; Re-calibrate; Reanalyze affected samples.
		Quality Control Sample (QCS)	Externally prepared from source different than calibration standards	Following instrument calibration	+/- 20% of the expected values	Recalibrate Instrument. Analysis cannot proceed without a passing QCS.
		Laboratory Reagent Blank (LRB)	Prepared and treated as sample, including exposure to lab glassware, equipment, reagent, etc.	Prior to analyzing any samples, with each extracted sample set, and required with any reagent change.	The LRB should not produce peaks within the retention time window for any analytes.	If this occurs, the source of contamination must be identified and removed before processing samples.
		Initial Demonstration of Capability (IDC)	Uses 7 replicate prepared Lab Fortified Blanks (LFB) approx 50 times the estimated detection limit	Following procedural calibration standard analysis and any subsequent calibration.	Mean recoveries must be within +/- 20% of the actual value and the standard deviation must be less than 15%.	Analyze for source of error. Repeat procedure with 8 fresh samples until satisfactory performance has been demonstrated.
		Method Detection Limits (MDLs)	Statistically derived using 7 replicates prepared LFB at 2-5 times estimated signal to noise ratio	Prior to analysis of non-IDC samples.	1/10th spike concentration < MDL < spike concentration	Repeat using spike level that will meet criteria.
		Continuing Calibration Check (CCC)	Uses LFBs prepared at 2 different concentration levels to verify calibration curve	Calibration checks are required every 10 samples and at the beginning and end of each analytical batch	Analyte recoveries must be within +/- 20% of the expected values.	Re-analyze CCC to determine if responses are repeated. If standards cannot be met, instrument must be re-calibrated, and previous samples re-analyzed, or analyte results are outside of the acceptable limits and must be reported as suspect.

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
		Laboratory Fortified Sample Matrix (LFSM)	Add known concentrations of analytes to a sample	Once for each reaction time point	Analyte recovery must be of +/- 25% of expected values.	Matrix induced bias is assumed, and data reported as suspect. If the unfortified matrix has background levels higher than the fortified matrix, a duplicate must be prepared at a higher concentration. If not possible, the data for the sample from which the LFSM was prepared should not be reported.
		Analysis replicates	Samples collected from same reactor; tests variability in analytical method	Once for each reaction time point using triplicate samples	RSDs must be < 25% for all analytes	Analysis must be repeated. If failure is repeated, sampling must be repeated or analytes are reported as suspect.
		Extraction precision / Surrogate Recovery	Aqueous samples are fortified with surrogate before extraction	All samples and standards	Surrogate recovery must be +/- 20% of the mean response from the initial calibration standards	Repeat analysis, if this fails, repeat extraction and analysis, if this fails, data is reported as suspect. Consecutive failures could also indicate the need to recalibrate.
		Internal Standard Recovery	Aqueous samples are fortified with an internal standard after extraction	All samples and standards	I.S. response should not deviate from mean I.S. response of the past five continuing calibration standards by >20%	Optimize instrument performance and inject a 2^{nd} aliquot of that extract. If it passes, report results for that aliquot. Otherwise, follow Section 9.9 in the method.

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
		Confirmatory Column Analysis	Qualitative confirmation of the analytes is conducted on a secondary column	All samples for which a positive result is observed on the primary column	Analytes should be present in the retention window (3 x standard deviation or 1% of expected retention time, whichever is greater for particular analyte) for the confirmatory column	Repeat analysis using the confirmatory column or another instrument.
pH	Critical	Initial calibration	2 point calibration	Daily when in use prior to sample analysis	±0.1 pH units of the actual concentration for calibration verification	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.
		Calibration verification	3 pH units different from the second pH buffer	Immediately after calibration, after every 10 samples and at the end	±0.1 pH units of the actual concentration	Re-calibrate if verification is outside of ± 0.1 pH unit acceptance criteria
Free Chlorine	Critical	Instrument verification	SpecCheck Secondary Standards Kit	Daily when in use prior to sample analysis and at end of batch	See kit-specific acceptance criteria listed on the Certificate of Analysis for secondary standard kit[1]	Re-analyze batch
		Check standard	Standard additions/ sample spike method	Beginning of analysis	±10 % of the actual concentration	Correct matrix interferences Reanalyze samples
Anions	Critical	Initial calibration	Calibration	With every sequence	Initial calibration needs to be verified with an initial calibration check and the QCS	Prepare new standard curve; Re-calibrate

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
		Initial calibration check	An individual calibration standard	Analyzed immediately after the calibration curve	±25 % of the true value (QL to 10x QL) ±15% of the true value (>10x QL)	Re-calibrate
		Continuing and end calibration check	An individual calibration standard	After every 10 samples	± 25 % of the true value (QL to 10x QL) ±15 % of the true value (Greater than 10x QL)	Re-analyze CCC to determine if responses are repeated. If standards cannot be met, instrument must be re-calibrated, and previous samples re-analyzed, or analyte results are outside of the acceptable limits and must be reported as suspect.
		Instrument Performance check solution (IPC)	Calculate the Peak Gaussian Factor (GPF)	One per batch	0.8 – 1.15	Repeat analysis
		Laboratory reagent blank (LRB)	An aliquot of reagent water	Every 10 samples	< MDL	If this occurs, the source of contamination must be identified and removed before processing samples.
		Quality control sample (QCS)	A source external to the lab and different from the source of calibration	After initial calibration	±15 % of the true value	Recalibrate Instrument. Analysis cannot proceed without a passing QCS.
		Surrogate	Add same concentration of surrogate	With each calibration and sample	Recovery of 90-115%	Repeat analysis, if this fails, data is reported as suspect. Consecutive failures could also indicate the need to recalibrate.

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
		Analysis replicates	Samples collected from same reactor; tests variability in analytical method	Once for each reaction time point using triplicate samples	RSDs must be < 20% for all analytes	Analysis must be repeated. If failure is repeated, sampling must be repeated or analytes are reported as suspect.
		Laboratory fortified blank (LFB)	An aliquot of reagent water spiked with a known amount of analytes	One per batch	±25% of the true value (QL to 10x QL) ±15% of the true value (>10x QL)	Recalibrate Instrument.
		Laboratory Fortified Sample Matrix (LFSM)	Add known concentrations of analytes to a sample	Once for each reaction time point	Analyte recovery must be of +/- 25% of expected values.	Matrix induced bias is assumed, and data reported as suspect. If the unfortified matrix has background levels higher than the fortified matrix, a duplicate must be prepared at a higher concentration. If not possible, the data for the sample from which the LFSM was prepared should not be reported.
Total Organic Carbon (TOC)	Non-Critical	Initial calibration	Calibration	A new calibration curve is generated when fresh standards are made and/or when CCCs fail QC criteria	Calibration curve must have $R^2 \geq 0.99$ before proceeding with analysis	Prepare new standard curve; Re-calibrate
		Laboratory Blank (LB)		One LB with each analysis batch	TOC must be ≤ 0.35 mg/L	If this occurs, the source of contamination must be identified and removed before processing samples.

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
		Continuing calibration checks (CCC)	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 Mid-CCC ±20 % of the true value High-CCC ±15 % of the true value	Re-analyze CCC to determine if responses are repeated. If standards cannot be met, instrument must be re-calibrated, and previous samples re-analyzed, or analyte results are outside of the acceptable limits and must be reported as suspect.
		Laboratory Fortified Sample Matrix (LFSM)	Add known concentrations of analytes to a sample	Once for each reaction time point	Analyte recovery must be of +/- 30% of expected values.	Matrix induced bias is assumed, and data reported as suspect. If the unfortified matrix has background levels higher than the fortified matrix, a duplicate must be prepared at a higher concentration. If not possible, the data for the sample from which the LFSM was prepared should not be reported.
		Quality control sample (QCS)	A second source calibration verification standard	The QCS should be analyzed immediately after calibration	Analyzed value of 1-5 mg/L QCS must be within ±20 % of the true value	Recalibrate Instrument. Analysis cannot proceed without a passing QCS.
		Analysis replicates	Samples collected from same reactor; tests variability in analytical method	Once for each reaction time point using triplicate samples	RSDs must be < 20% for all analytes	Analysis must be repeated. If failure is repeated, sampling must be repeated or analytes are reported as suspect.

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
Conductivity	Non-Critical	Initial calibration	2 point calibration	Initially	±10 % of the actual concentration for mid-point standard	Re-calibrate
		Initial calibration verification	Run mid-point standards	One immediately after calibration	±10 % of the actual concentration	Re-calibrate
		Precision	Sample duplicate	Once for each reaction time point using triplicate samples	≤ 15% RPD	Redo duplicate Investigate problem
		Continuing Calibration Verification	Secondary source standard	Every 10 samples	100 ± 15 % recovery	Investigate problem Re-prepare standard Re-run samples as required
TSS	Non-Critical	Accuracy	Check Standard	One per analysis batch	±25 % of the actual concentration	Investigate problem Re-prepare QCs Re-run samples as required
		Precision	Sample duplicate	Once for each reaction time point using triplicate samples	≤ 20 % RPD	Re-analyze Investigate the problem
		Contamination check	Method Blank	One per batch	<2.0mg/L	Re-analyze Investigate the problem
TDS	Non-Critical	Accuracy	Check Standard	One per batch	±25 % of the actual concentration	Investigate problem Re-prepare QCs Re-run samples as required
		Precision	Sample duplicate	Once for each reaction time point using triplicate samples	≤ 20% RSD	Re-analyze Investigate the problem
		Contamination check	Method Blank	One per batch	<2.0mg/L	Re-analyze Investigate the problem

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
Alkalinity	Non-Critical	QA/QC criteria for pH is applicable				
		Accuracy	Check Standard	One per batch	±20 % of the actual concentration	Investigate problem Re-prepare QCs Re-run samples as required
		Precision	Sample duplicate	Once for each reaction time point using triplicate samples	≤ 20% RSD	Re-analyze Investigate the problem
SUVA	Non-Critical	QA/QC criteria for TOC is applicable; samples need to be filtered prior to DOC analysis				
		Spectrophotometer Performance check	Check Standard	Once prior to starting a batch	±10 % of the expected absorbance	Investigate problem Re-prepare QCs Re-run check until it passes
		Laboratory Blank (LB)		Once every 20 samples in sequence	UVA ≤ 0.01 cm^{-1}	If this occurs, the source of contamination must be identified and removed before processing samples.
		Lab Fortified Blank (LFB)	Add known concentrations of analytes to a blank	Once every batch	±20 % of the actual concentration for a 1-5 mg OC/L spike	Investigate problem Re-prepare QCs Re-run samples as required
		Filter blank	Lab reagent water filtered through a 0.45 μm filter	Once per sequence	UVA ≤ 0.01 cm^{-1}	If this occurs, the source of contamination must be identified and removed before processing samples.
		Precision	Sample duplicate	Once for each reaction time point using triplicate samples	≤ 20% RSD	Re-analyze Investigate the problem

Parameter	Measurement	QC Check	Method	Frequency	Acceptance Criteria	Corrective Action
		Lab Fortified Sample Matrix (LFSM)	Add known concentrations of analytes to a sample	Once every batch	±30 % deviation for a 1-5 mg OC/L spike	Investigate problem Re-prepare QCs Re-run samples as required

[1] The free chlorine concentrations and acceptance criteria for the HACH SpecCheck Secondary Standards are lot specific. For instrument verification checks, record the lot number, expiration date, and model specific standard concentrations with acceptance measurement ranges for the SpecCheck Standards on the datasheet or research notebook that is use to report free chlorine results.

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 instrument. 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 is discussed in Table B5.1 and will be performed at the frequency listed in the table.

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 them. 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.

B9 NON-DIRECT MEASUREMENTS

Non-direct data such as computer databases and programs will not be used in this study. However, during the manuscript preparation process study, results will be compared to reported data in the literature only where direct comparison is possible.

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 analyst who performs the analysis. Printed data from equipment runs will be filed separately in a three-ring binder(s) and labeled "WA-2-64" 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	Unit
THMs	µg/L
Anions	mg/L
TOC	mg/L
Free Chlorine	mg/L
pH	pH units
Conductivity	µS/cm
TDS	mg/L
TSS	mg/L
Alkalinity	mg/L $CaCO_3$
SUVA	SUVA or L/mg-M

SECTION C ASSESMENT 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). 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 only on laboratory activities since only bulk samples are collected in the field. 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 Management Team or by QA support contractors with oversight by the QA Management 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 Management Team or by QA support contractors with oversight by the QA Management 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 EPA WA Manager 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 Management 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 Management Team shall send documentation to the PI and his supervisor that the audit is closed. Audit reports and responses shall be maintained by the PI in the project file and the QA Management Team in the QA files, including QLOG.

C1.1 Assessments

Detailed checklists are based on the procedures and requirements. The laboratory audit will take place when samples are in the laboratory's possession and are in the process of being analyzed.

Laboratory TSAs will focus on the critical target analytes and will be conducted on-site at EPA AWBERC, UC and the EPA T&E Facility laboratories run by Pegasus, UC and 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.

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 Management Team 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 PEGASUS AND SHAW ASSESSMENTS AND RESPONSE ACTIONS

The Pegasus Contract QA Manager will conduct assessments of WA 2-64 and WA 3-02, respectively, to verify compliance with the requirements of this QAPP. Assessment activities include Technical System Assessments (TSAs), readiness reviews, and surveillances.

The three types of WA assessments are discussed below.

A Readiness Review will be conducted prior to the initiation of a WA, either by the Pegasus Contract QA Manager or by EPA). The Readiness Review is initiated to ensure that all personnel, training, equipment, supplies, and procedures are available for environmental data to be collected in accordance with the governing QAPP.

TSAs are thorough, systematic, and qualitative assessments of overall implementation of requirements in accordance with the WA QAPP and related quality documents. The TSA may include assessment of field sampling, laboratory operations, equipment, procedures, records management, or technology application in support of environmental data operations.

Surveillances will be incorporated into the assessment program to provide a less formal independent evaluation of items, activities, or processes for conformance with specific requirements. Performance areas that may be reviewed during surveillances include:

- Training and qualification of personnel
- SOPs
- Work performance
- Verification activities
- Documents and records
- Purchased items and services
- Measuring and test equipment.

The minimum QA/QC practices for ORD Laboratories, as discussed in Subsection 2.1.5, will be included in the periodic surveillance review cycle and assessed during scheduled laboratory surveillances. EPA, at their discretion, may also conduct assessments to verify compliance with the requirements of this QAPP.

Assessment activities that will be conducted by EPA include the submittal of PE samples (including double blind PE samples), readiness reviews, TSAs and ADQs (as described in Section C1). Pegasus, UC and Shaw will fully cooperate with EPA for EPA-conducted assessments.

C.2.1 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 Pegasus/UC/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 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 Pegasus/UC/Shaw prior to submittal to EPA for approval and reporting.

C2.2 Assessments

The Pegasus Contract 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 Pegasus 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 responsible individual, as determined by the Pegasus On-Site Technical Manager or Shaw Program Manager, and submitted to the Pegasus Contract QA Manager. Corrective actions will be implemented by the individual(s) identified on the Corrective Action Plan form. The Pegasus Contract QA Manager will track corrective actions to closure and notify management 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 Pegasus Contract QA Manager and distributed to the WA/Project Leader and responsible manager. A response is prepared for QA assessment findings by the WA/Project Leader to the Contract 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 Pegasus Contract QA Manager through closure. When all findings of the assessment have been closed, notice is sent by the Pegasus Contract QA Manager to the WA/Project Leader and responsible 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. In addition, sample preservation and holding times will be evaluated against requirements provided in Table B.2.1.

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 upon approval by the NRMRL Lab Director.

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 contractor laboratories shall contact the PI and the 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 the WA Manager 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 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 (see D2) 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 PEGASUS AND SHAW DATA REVIEW, VERIFICATION, AND VALIDATION

Data verification and 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 data summary sheet.

A complete verification (100% of the data) is conducted by knowledgeable personnel other than the analyst, as assigned by the Project Leader, QA Manager, or On-Site Technical Manager. 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. The Pegasus Contract QA Manager is

responsible for ensuring that assigned data validators are sufficiently independent to perform the validation.

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 K.
- 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 may be recommended 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 D3.1 and D3.2.

Table D3.1 Data Descriptors

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

Table D3.2 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.

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, precision, and completeness will be performed. All analyses will be required to meet data quality objectives before formulation of the final report and/or manuscript. 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.

Sample data will be presented in tabular format or in figure. 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

Chowdhury, S.; Champagne, P.; McLellan, P.J. Models for predicting disinfection byproduct (DBP) formation in drinking waters: A chronological review. *Water Research*. **2009**, *407*, 4189-4206.

Yang, G.; Shang, C. Chlorination Byproduct Formation in the Presence of Humic Acid, Model Nitrogenous Organic Compounds, Ammonia, and Bromide. *Environ. Sci. Technol.* **2004**, *38*, 4995-5001.

EPA (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. EPA (ed), Washington DC.

EPA (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.

SUMMARY OF REVISION

Revision Number	Revision Date	Description of Change
3	05/16/2013	Approved for implementation.
3.1	05/16/2013	Page change revision (see cover page, and pages 6 and 43). Added Summary of Revision to Table of Contents and on page 57; Corrected the anions LFSM acceptance criteria (Table B5.1, page 43) from ±20% to ±25% to align with Section 9.4.1.4 of EPA Method 300.1.
4	01/03/2014	Updated personnel since original list of personnel were insufficient to complete the experiments on time (pages 10 – 18). Added UC staff to list of personnel since part of the analyses (alkalinity, DOC, TDS/TSS and TOC) may be conducted at UC. Changed experimental protocol to use stir plates instead of jar testers as the use of jar testers would take too much time to complete the experiments (pages 22 and 24). Only 60L of surface water was obtained from a single sampling site (as opposed to the original plan of obtaining surface waters from each of the 5 sampling sites). Since this volume of water was insufficient to complete all the experiments described in this QAPP, and since using different water matrices may affect DBP formation in different ways, a decision was made by the EPA PI to use Ohio River water as a surface water source (page 20). Included alkalinity and SUVA as analytes at the request of the EPA PI. Included information on sampling sites (page 20); updated tables A6.2, B1.1 and B2.2to reflect actual samples. Addressed comments raised during the TSA conducted by Rebecca Shircliff (Neptune and Company, Inc.), Holly Ferguson (EPA/NRMRL) and John Olszewski (EPA/NRMRL) on November 6, 2013, including clarification of criteria for THMs 2nd column confirmation, conductivity QC checks and pH (Table B5.1), number of source waters (page 20), bench-scale reactor sampling (pages 24-25, 31-35), updating MDL for free chlorine (table B4.1), and clarifying roles of contract QA management for training records (section A8). Included Project Staff concurrence page (pages 3-4) Clarified role of Pegasus project personnel (page 14)

APPENDICES

APPENDIX A	SOP for Chlorination of Water Samples	 Appendix A - SOP for Chlorination of Sampl
APPENDIX B	EPA Chain-of-Custody Form	 Appendix B - EPA Chain of Custody For
APPENDIX C	EPA Method 551.1 (DBPs)	 Appendix C - EPA Method 551.1.pdf
APPENDIX D	Standard Method 4500B (pH)	 Appendix D - Standard Method 450
APPENDIX E	HACH Method 8021 (Free Chlorine)	 Appendix E - HACH Method 8021.pdf
APPENDIX F	EPA Method 300.1 (Anions Analysis by IC)	 Appendix F - EPA Method 300.1.pdf
APPENDIX G	EPA Method 415.3 (SUVA)	 Appendix G - EPA Method 415.3
APPENDIX H	Standard Method 2510B (Conductivity)	 Appendix H - Standard Method 251
APPENDIX I	Shaw T&E SOP 510 (TDS)	 Appendix I - 510 Total Dissolved Solids
APPENDIX J	Shaw T&E SOP 509 (TSS)	 Appendix J -509 Total Suspended Solic
APPENDIX K	Example Laboratory Data Report	 Laboratory Data Report.xls

APPENDIX L	Standard Method 5310 B (TOC)	Appendix L - Standard Method 531
APPENDIX M	Standard Method 2540D (Solids)	Appendix M - Standard Method 254
APPENDIX N	EPA Method 310.1 (Alkalinity)	Appendix N - EPA Method 310.1