Water Quality Sampling and Monitoring of the Pawcatuck Watershed.

US Geological Survey Quality Assurance Project Plan

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Quality Assurance Project Plan for: Evaluation of Nutrient Loadings to Pawcatuck River Estuary and Little Narragansett Bay: In Support of Development of a New Watershed-based Approach to Analyzing and Managing Nutrient Impacts to Coastal Estuaries

RAE/EPA Grant #: 6-FULLWG18-CTDEEP-RIDEM
Lead Organization: Connecticut Department of Energy and Environmental Protection
Partner Organization(s): Rhode Island Department of Environmental Management

Water Quality Sampling and Monitoring of the Pawcatuck Watershed

6-FULLWG18-CTDEEP-RIDEM

1.0 Title and Approval Page

Water Quality Sampling Monitoring of the Pawcatuck Watershed
(Project name)

U.S. Geological Survey, Connecticut Water Science Center, East Hartford, Connecticut
(Responsible Agency)

4/26/19
(Date)

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2.0 Document purpose

This Quality Assurance Project Plan (QAPP) supports water quality and stream flow data collection and analysis for the project funded under Southeast New England Watershed Grants Program grant 6-FULLWG18-CTDEEP-RIDEM. The QAPP will cover specifc site, sampling, and analysis information. It also refers to 2 generic QAPPs (appendix 4) which describe the responsibilities and objectives, as well as, the technical and quality assurance tasks related to sample collection and lab analysis of stream water as well as stream-gaging by the United States Geological Survey (USGS). This document incorporates by reference the Generic QAPPs (RFA# - 07279) for routine technical and quality assurance procedures for *Stream-Gaging and Streamflow Computation* and *Surface Water-Quality Sampling for Nutrients*. All procedures and protocols in these documents will be followed unless an alternative approach is explicitly identified in this QAPP.

3.0 Distribution List

Persons listed below will receive copies of the approved QAPP and any subsequent revisions of the QAPP. A complete copy of the original version and all revisions of the QAPP, including the official, approved QA project plan, will be maintained on file by the project QA/QC Officer (Jon Morrison) at the U.S. Geological Survey (USGS) Connecticut Office and will be available upon request.

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Mary Garren and Toby Stover from EPA Region 1 will be provided a copy of this QAPP because of their roles in supporting the 303d and Nutrient programs. Coordination with these programs at the regional level will help to insure project success and support implementation of nutrient management planning and implementation activities in the Pawcatuck watershed in the future. Chelsea Glinka will be provided a copy of this QAPP as she was one of the initial reviewers for this document on behalf of RAE.

3.1 Project Organization

Kaitlin Laabs (Project Manager – USGS) is responsible for all project activities including writing the QAPP, collecting water-quality and flow data, and publishing data. Jon Morrison (Project QA/QC Officer) is responsible for the project quality assurance and quality control activities and for technical and administrative oversight of all the project work.

Project Participants

Name	Title	Organization	Primary Responsibility
Traci Iott	Supervising Environmental Analyst	CTDEEP	Responsible for overall project management and decision making in consultation with RIDEM. Responsible for coordination among all organizations associated with project
TBD	Supervising Environmental Scientist	RIDEM	This position is currently vacant at RIDEM. When filled, this person will work collaboratively on overall project management and decision making in consultation with CTDEEP
Christopher Sullivan	Environmental Analyst III	CTDEEP	Lead Technical Staff. Responsible for project implementation activities.
Heidi Travers	Senior Engineer	RIDEM	Lead Technical Staff. Responsible for project implementation activities
Kaitlin Laabs	Project Manager	USGS	Responsible for all project activities including writing the QAPP, collecting water-quality and flow data, and publishing data
Jon Morrison	QA/QC Officer	USGS	Responsible for the project quality assurance and quality control activities and for technical and administrative oversight of all the project work
Nora Conlon	QA/QC Officer	EPA	Provide review and oversight of project QAPP
Margherita Pryor	Project Officer	EPA	Provide oversight of project with respect to SNEP grant program
Thomas Ardito	Grant Administrator	RAE/SNEP	Administer Grant program and oversee project for consistency with grant requirements

Connecticut Department of Energy and Environmental Protection (CTDEEP)

Applicant organization which was awarded and now implements SNEP Grant 6-FULLWG18-CTDEEP-RIDEM in collaboration with RIDEM, partner organization on the grant. CTDEEP provides point of contact for the project and facilitates collaboration across various organizations associated with this project.

Rhode Island Department of Environmental Management (RIDEM)

Partner organization on SNEP Grant 6-FULLWG18-CTDEEP-RIDEM. Works in collaboration with CTDEEP to implement grant.

United States Geological Survey (USGS)

USGS provides technical services for collection and analysis of water quality and flow data in support of grant project. USGS also provides quality assurance oversight of data collection and analysis,

projects final data results and reports and posts data to National Water Information Service to make the data publicly accessible.

Restore America's Estuaries

Restore America's Estuaries (RAE) has been selected by the Environmental Protection Agency (EPA) to manage the Southeast New England Watershed Grant Program (SNEP) for 2018 and 2019. RAE will oversee fiscal and technical aspects of the grant project.

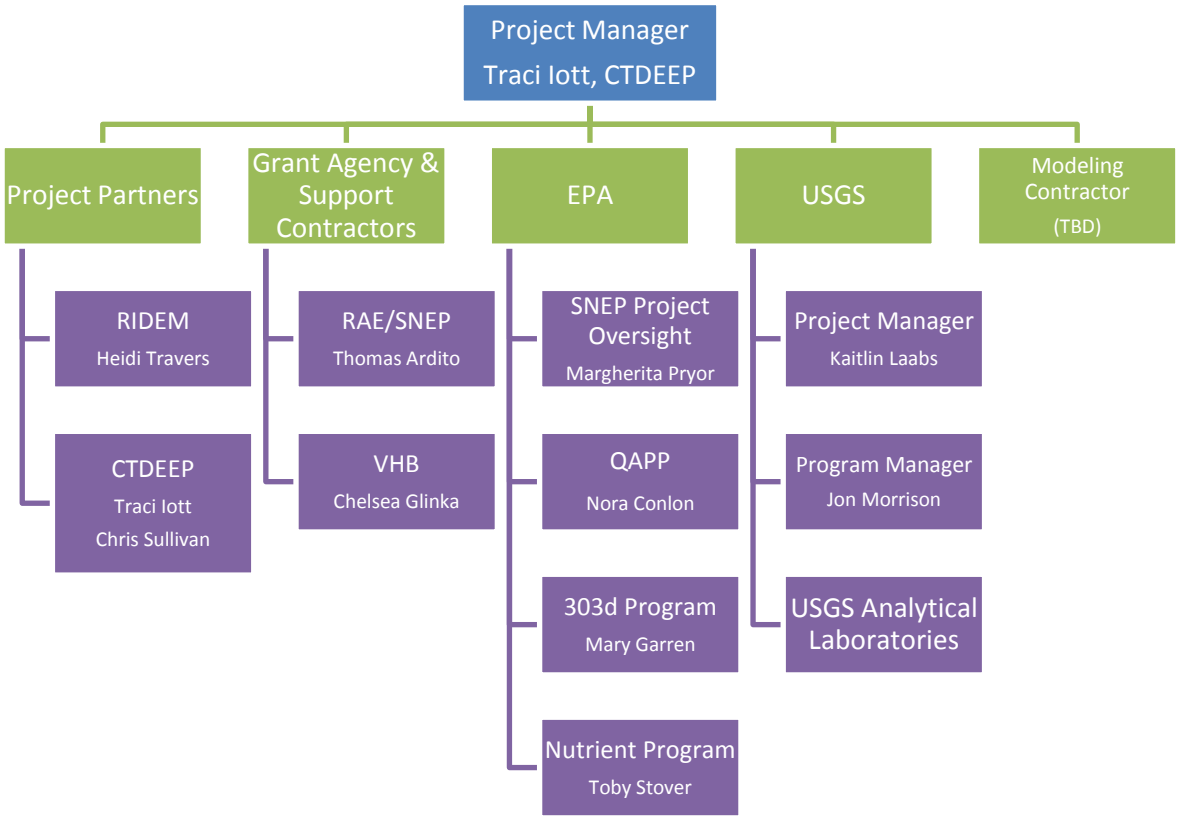
EPA

EPA is the grantor to RAE for the grant money that is being used for this project. The EPA will review and approve this Quality Assurance Project Plan (QAPP). EPA's 303d and Nutrient Program staff provide input to the project within their specific program expertise.

Modeling Contractor

A contractor will be brought on to this project to develop a Hydrological Simulation Program—Fortran (HSPF) watershed model for nutrients, suspended solids, flow and related parameters. This contractor, which has not yet been selected, will use data which is subject to this QAPP. A separate QAPP to cover modeling activities will be prepared at a later date. The model development is not in the scope of this QAPP however and will not begin until after all data has been collected and processed.

Organizational Chart showing relationships and lines of communication among project participants



4.0 Problem Definition/Background/Purpose of Study

Coastal estuaries in Southern New England and New York show the effects of excess nutrients from coastal eutrophication. The effects of excess nutrients include excessive growth of macroalgae, excessive blooms of phytoplankton, hypoxia and oxygen depletion, and deteriorated substrates. Excessive nutrients also contribute to the loss of eelgrass, which provides important underwater habitat and was once commonly found in every bay and harbor in Long Island Sound (Vaudrey and others, 2013; Buzzards Bay National Estuary Program, undated). State and Federal regulators have responded to these nutrient-caused impairments by requiring more stringent permit limits for National Pollutant Discharge Elimination System discharges as waterbody and watershed information indicated they were needed. However, watershed and receiving water-specific information is needed to continue to address nutrient related impacts. In addition, if the sources of nutrients are nonpoint in nature, site-specific information is needed to characterize these sources to support actions to advance their control (Traci Iott, CT DEEP, written commun., June 21, 2018).

The Pawcatuck River and the Pawcatuck River Estuary (PRE) and Little Narragansett Bay (LNB) form part of the boundary between the States of Connecticut and Rhode Island. Both states have identified water quality impairments within these waters related to insufficient oxygen and bacteria. Connecticut has additionally identified impairments associated with nutrient and eutrophication biological indicators. A USGS study by Savoie and others (2017) presented results of long-term water quality monitoring data indicating that nutrient loading from the Pawcatuck River to PRE and LNB decreased during the period between 1975-2015. However, in its latest List of Impaired Waters, CTDEEP documented the disappearance of eelgrass from the estuary, extensive growth of *Cladophora* spp., and mucky, oxygen poor sediment (CT DEEP, 2016). Studies of the eutrophication potential of Long Island Sound (LIS) embayments have identified that the PRE has the highest total load of nitrogen per embayment area of all embayments studied throughout LIS (Vaudrey and others, 2016). Nutrient inputs from large rivers such as the Connecticut, Thames, Housatonic and East Rivers were not evaluated as embayments within that study.

During the summer of 2018, the CTDEEP and RIDEM deployed instrumentation throughout the length of the Pawcatuck River estuary and into Little Narragansett Bay to continuously measure dissolved oxygen and chlorophyll-*a* (among other parameters) and to collect samples for nutrient analyses. With the monitoring associated with this QAPP, CT DEEP and RIDEM hope to build on on-going efforts within the estuary by developing a water quality data set and model in the upland contributing watershed to develop a scientifically defensible framework to move from water quality analysis and evaluation through to planning and implementation efforts in both the upland and estuarine portions of the watershed. The development of innovative solutions must be used to address the nutrient-related impacts within these and other coastal estuaries located in Southeast New England. (Written communication, Traci Iott, 2018).

To better understand water quality within the freshwater portion of the Pawcatuck River watershed, the States of Connecticut and Rhode Island require information on water quality and stream flow in locations throughout the freshwater portion of the watershed. This will provide information to develop an HSPF watershed model calibrated for nutrients, total suspended solids, stream flow and related parameters to assist in the assessment and management of nutrients in the Pawcatuck River watershed consistent with Water Quality Standards established by the EPA. Information on diurnal dissolved oxygen, in addition to data on nitrogen and phosphorus concentrations, are critical components of these new approaches and will be required as input data sets in a planned watershed scale hydrology and water quality model.

The USGS's mission as the lead scientific federal agency in water resources is to provide data to help define and manage the Nation's water resources. The USGS has developed a streamflow and water-quality database as part of the USGS National Water Information System (NWIS) on the web (URL http://waterdata.usgs.gov/nwis). This database contains data that are reliable, unbiased, archived, and published. These data are widely used by Federal, State, and local agencies; by private industry; and by academia. All data collected for this project will be stored in the USGS NWIS database and be accessible to the public.

The USGS will conduct monthly nutrient (table 4) sampling at 14 locations and chlorophyll-*a* sampling at 1 location within the Pawcatuck Watershed (Figure 1, Figure 2 and table 1). A continuous water quality monitor will also be installed at the Pawcatuck River at Westerly RI to monitor for continuous dissolved oxygen, pH, water temperature, turbidity, specific conductance, and chlorophyll. In addition, discrete field parameters of dissolved oxygen, pH, specific conductance, barometric pressure, and water temperature will be taken in conjunction with each sample. The purpose of the study is to collect water-quality data and instantaneous streamflow data. These data will assist in calculating modelled nutrient loads from the watershed to be done as a separate phase of the project. The CTDEEP, the RIDEM, and the USEPA, and local town officials may use nutrient loads to develop a detailed watershed nutrient management plan for the Pawcatuck watershed.

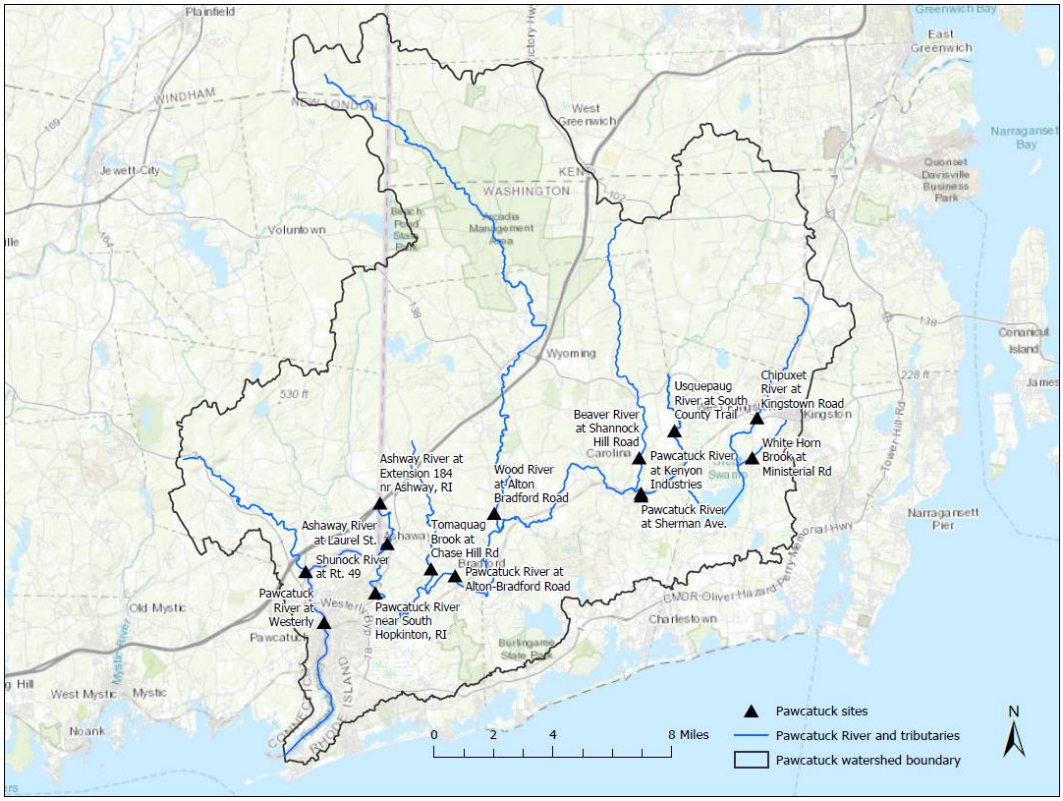


Figure 1 Pawcatuck Watershed Boundary with Site Locations

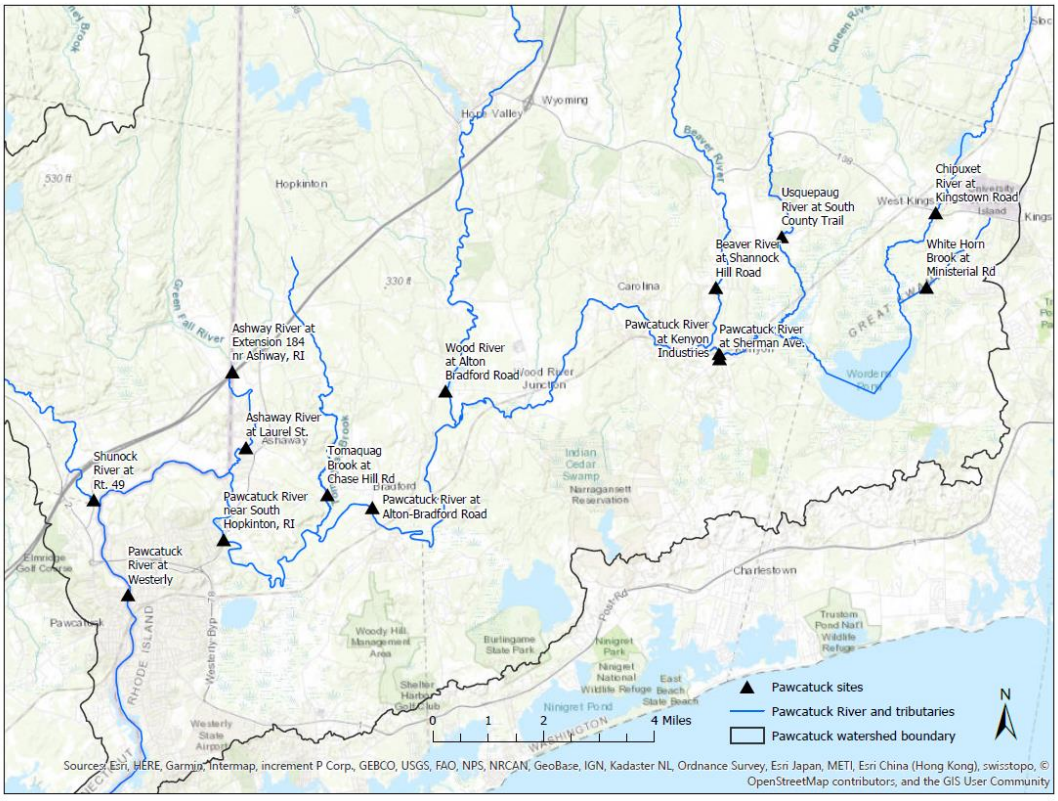


Figure 2 Pawcatuck Watershed Site Locations

Station number	Station Name	Lat/Long	Water Quality Parameters Sampled	Discrete Water Quality Field Parameters Measured (1)	Continuous Water Quality Field Parameters Measured
01117350	Chipuxet River AT West Kingston, RI	41.48253, -71.55113	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01117351	White Horn Brk at Ministerial Rd near West Kindgston, RI	41.463114 , -71.554651	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01117420	Usquepaug River near Usquepaug, RI	41.47681, -71.60479	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01117455	Pawcatuck River at Sherman Ave. at Kenyon, RI	41.445197 ,-71.626908	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Disharge	N/A
01117471	Beaver River Shannock Hill RD, near SHANNOCK, RI	41.46379, -71.62789	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118009	Wood River near Alton, RI	41.43762, -71.72228	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118030	Pawcatuck River at Alton-Bradford Road at Bradford, RI	41.40742, -71.74817	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118055	Tomaquag Brrok, At RT. 216, At Bradford, RI	41.410889 , -71.7637	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118100	PAWCATUCK River near South Hopkinton, RI	41.39945, -71.79990	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118356	Ashway River at Extension 184 near Ashway, RI	41.443264 , -71.796250	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118360	Ashway River at Ashway, RI	41.423447 , -71.791806	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118400	Shunock River near North Stonington, CT	41.410214 , -71.844883	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A
01118500	Pawcatuck River at Westerly, RI	41.385337 , -71.833309	Nutrients, total suspended solids and Chlorophyll	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	pH, Specific Conductance, Dissolved Oxygen (mg/L), Dissolved Oxygen (% saturation), Barometric Pressure Water Temperature, Turbidity, Chlorophyll
412647071373701	Pawcatuck River at Kenyon Industries at Kenyon, RI	41.446532 , 71.627027	Nutrients and total suspended solids	pH, Specific Conductance, Dissolved Oxygen, Water Temperature, Discharge	N/A

Table 1 Names, station numbers and measured parameters for the surface water quality monitoring stations.

(1) Table 1 Footnote: 18 discrete samples will be collected at each monitoring location. Samples will be collected monthly except during April – September, samples will be collected biweekly.

5.0 Project Description and Schedule

The primary task of this study:

Measure streamflow and collect water-quality nutrient, TSS and chlorophyll-a samples for whole water and filtered forms of phosphorus, nitrogen and chlorophyll-a from Pawcatuck Watershed:

Samples at the 14 locations chosen for this project were chosen by request from RIDEM and CT DEEP. Samples will be taken at existing USGS stream gage locations when able. In some cases, the USGS historically managed a stream gage at some locations but has since removed the gage. Where no stream gage exists, a unique USGS station ID (table 1) was created. The U.S. Geological Survey will utilize existing streamflow gages on the Pawcatuck watershed to collect continuous streamflow information when sampling is done at the same location as the streamflow gage. If selected sampling locations have a nearby streamflow gage a watershed drainage-area correction factor (calculated from USGS Stream Stats) will be applied (Table 2). This approach will be used if the watershed correction factor is less than ten percent of the sampling watershed area. At selected sampling locations where no streamflow gages exist, or streamflow gages exist that have correction factors greater than ten percent, instantaneous discharge measurements will be made at the time of sampling. The discharge data collected in conjunction with the nutrient samples will be used to calculate loads from the Pawcatuck Watershed for use in the HSPF model in a future study.

Discrete water quality sampling for nutrients, TSS and related parameters will be conducted at 14 sites in the Pawcatuck River Watershed (Table 1, Figure 1) starting after the Quality Assurance Project Plan is approved by EPA in the spring of 2019. All personnel involved with the project will be trained to collect water quality samples according to the procedures and methods spelled out in the USGS National Water Quality Field Manual (USGS, 2012). During the project 18 separate samples will be collected at each station over the course of one year. The sampling frequency will have one sample per month for the following months; January, February, March, October, November, and December and two sampling events per month from April through September. At station 01118500, the Pawcatuck River at Westerly, the USGS is already contracted by CTDEEP and RIDEM to collect monthly water quality samples. Therefore, the sample collection at this site will be monthly with an additional sample collected from April through September as part of this project. The sampling parameters and analysis method for the existing monitoring at the Pawcatuck River at Westerly RI station are the same as the monitoring being used by this project (Appendix 6: Rhode Island Surface Water Quality Monitoring Network Project Plan). In addition to the nutrient sampling at station 01118500 Pawcatuck River at Westerly, samples for chlorophyll-a will also be taken starting in April 2019 and ending September 2019.

All discrete water quality samples will be shipped to the USGS National Water Quality Laboratory (NFQL) for analysis. Specific laboratory method information can be found in table 4 and appendixes 3 and 8.

The streamflow and water-quality data for the 14 sites on the Pawcatuck watershed for the collection period will be collected and loaded into NWIS following the processes and procedures described in the USGS Generic QAPPs for streamflow and water quality data collection (Appendix 4: *Stream-Gaging and Streamflow Computation* and *Surface Water-Quality Sampling for Nutrients*).

The USGS will install, operate, and maintain a YSI EXO (appendix 10) multi parameter sonde on the Pawcatuck River at Westerly RI for the entire duration of the project. The monitor will be located near the USGS stream gage 01118500 at the bridge on Stillman Ave. Data will be collected at 15-minute intervals and will include: specific conductance, water temperature (°C), dissolved oxygen (mg/L and % saturation), turbidity, and chlorophyll-a. USGS personnel will visit the site on

a monthly to bimonthly basis for monitor maintenance including cleaning the sonde, checking the calibration and re-calibrating when necessary, and downloading data. During USGS site visits to the continuous monitor, a second independent set of measurements using a field Sonde will be collected to confirm the data being collected by the continuous monitoring equipment, and to track changing conditions while sonde maintenance is being conducted. Criteria for the maintenance and calibrations of continuous water quality monitors are spelled out in Wagner and others, 2006.Additionally, a water column profile, will be conducted to collect measurements from the within 1-2 feet of the surface and within 1-2 feet of the bottom (within 1-2 feet), as well as the same depth as the installed equipment. A recording barometric pressure (BP) sensor will be installed near the monitor at the Pawcatuck River at Westerly RI streamflow gage and log BP readings at 15-minute increments. The barometric data will be used to calculate precise dissolved oxygen percent saturation values.

The project schedule is as follows:

Activities	Anticipated date of Initiation	Anticipated Date of Completion	Deliverable	Deliverable Due Date
QAPP preparation	3/2019	4/2019	QAPP document	4/5/19
Data collection for stations	4/2019	3/2020	Data stored in USGS NWIS database	Within 1 week of data collection
Data Approval	5/2019	5/2020	Quality Assured data review of both discrete and continuous data	5/30/2020

6.0 Measurement/Data Acquisition

Several SOP's, generic QAPP's and project plans are used as references regarding the various data collection and processing involved with this project. A complete list of those documents can be viewed in table 2 below as well as in appendices 1-9.

Laboratory SOP's and Documentation	
Laboratory Method Codes for all Sampled Constituents	Appendix 8
Field SOP's and Documentation	
Generic QAPP for Surface Water Quality Nutrient Sampling	Appendix 4
Generic QAPP for Stream Gaging and Streamflow Computation	Appendix 4
Rhode Island Surface Water Quality Monitoring Project Plan	Appendix 5
Water Quality Sampling and Monitoring of the Pawcatuck River Watershed	Appendix 6
Preparations for Water Sampling	Appendix 7
Selection of Equipment for Water Sampling	Appendix 7
Cleaning of Equipment for Water Sampling	Appendix 7
Processing of Water Samples	Appendix 7
Field Measurements	Appendix 7
Algal Biomass Indicators	Appendix 7

Table 2 All SOP and QAPP material referenced in the body of this QAPP.

6.1 Discrete Water Quality Sampling

Samples for nutrients (whole-water and filtered forms of phosphorus and nitrogen) will be collected at a monthly sampling frequency at 14 sites in the Pawcatuck Watershed (see table 4) beginning April 2019 to April 2020 to examine the concentrations within the watershed. From April 2019 to September 2019, sites will be sampled twice a month. USGS stream gages will be used to provide continuous stream flow data when applicable. In the locations where no stream gaging equipment is established, a discharge measurement or drainage-area correction (calculated with USGS Stream Stats) will be applied (table 3). This discharge data will be used for in calculating loads from the watershed. The water-quality monitoring and streamflow calculations will be done in accordance

with the Generic QAPPs titled: *Surface Water-Quality Sampling for Nutrients* and *Stream Gaging and Streamflow Computation.*

Station number	Station Name	Proposed Discharge Method
01117350	CHIPUXET RIVER AT WEST KINGSTON, RI	Discharge from gage
01117351	White Horn Brk at Ministerial Rd near West Kindgston, RI	Discharge Measurement Required using Flowtracker or Aquacalc
01117420	USQUEPAUG RIVER NEAR USQUEPAUG, RI	Discharge from gage
01117455	Pawcatuck River at Sherman Ave. at Kenyon, RI	Basin Draining correction of 7.88% based on 01117430
01117471	BEAVER River Shannock Hill RD, NEAR SHANNOCK, RI	Discharge Measurement Required using Flowtracker or Aquacalc
01118009	WOOD River NEAR Alton, RI	Discharge Measurement Required using an ADCP
01118030	Pawcatuck River at Alton-Bradford Road at Bradford, RI	Discharge Measurement Required using an ADCP
01118055	TOMAQUAG BROOK, AT RT. 216, AT BRADFORD, RI	Discharge Measurement Required using Flowtracker or Aquacalc
01118100	PAWCATUCK River near South Hopkinton, RI	Basin correction of -8.48% based on 01118030
01118356	Ashway River at Extension 184 near Ashway, RI	Basin correction of -6.39% based on 01118360
01118360	ASHAWAY RIVER AT ASHAWAY, RI	Discharge Measurement Required using an ADCP, Flowtracker, or Aquacalc
01118400	SHUNOCK River NEAR NORTH STONINGTON, CT	Discharge Measurement Required using Flowtracker or Aquacalc
01118500	PAWCATUCK River at WESTERLY, RI	Discharge from gage
412647071373701	Pawcatuck River at Kenyon Industries at Kenyon, RI	Discharge provided by factory

Table 3. Proposed Discharge methods for Pawcatuck sites

The U.S. Geological Survey National Field Manual (NFM) for the Collection of Water-Quality Data (Techniques of Water-Resources Investigations, Book 9) provides extensive documentation for all aspects of water-quality sample collection. Chapters of the NFM that are applicable to this QAPP include Preparations for Water Sampling (Chapter A1), Selection of Equipment for Water Sampling (Chapter A2), Cleaning of Equipment for Water Sampling (Chapter A3), Processing of Water Samples (Chapter A5), Field Measurements (Chapter A6) (appendix 7).

Starting in April 2019 and continuing through Sept 2019, grab samples of chlorophyll will be taken at 1 site (01118500) in conjunction with the nutrient sampling. These samples will be taken twice a month according to the U.S. Geological Survey National Field Manual (NFM) for the Collection of Water-Quality Data (Chapter A7.4) Samples to be analyzed will include chlorophyll a, and pheophytin A. Samples for chlorophyll-a will be collected using a brown hdpe bottle directly from the stream at the sonde location and will be stored on wet ice until arrival at the office where they will be filtered and immediately frozen. The filters will then be shipped on dry ice to the USGS NWQL for analysis within one week of collection.

All the water-quality samples collected as part of this project will be collected as single point grab samples at the centroid of flow. Nutrients and ROE samples will be collected into a two-liter plastic jug that has been triple rinsed with DI water before use in the field. Jugs are single use only and will be recycled upon sample completion. Chlorophyll samples will be collected by a single point grab into a 250ml brown hdpe bottle. The samples will be collected according to a schedule, usually the second and fourth week of a month over a two-day period. The sampling stations will all be sampled for nutrients and suspended sediments and the Pawcatuck River at Westerly RI station will be sampled for nutrients, suspended sediments and chlorophyll-*a*.

Specific laboratory methods used for the processing of the various constituent can be found in table 4 and in appendix 8. Nutrients to be analyzed include; ammonia, dissolved; ammonia-plus-organic nitrogen (Kjeldahl), whole; ammonia-plus-organic nitrogen (Kjeldahl), dissolved; nitrogen, nitrite-plus-nitrate, dissolved; nitrogen, nitrite, dissolved; phosphorus, total; phosphorus, dissolved; phosphorus, phosphate, ortho, dissolved; total particulate nitrogen (TPN). All samples will be shipped to the USGS National Water Quality Laboratory (NWQL) in Lakewood Colorado. Samples will be shipped overnight on ice. Once samples are collected, field personnel will transfer water from the two liter sampling container to a series of three bottles and three 25mm filters. The tree bottles to be collected are: one 125ml brown polyethylene bottle, one 125ml clear polyethylene bottle and one 250ml clear polyethylene bottle. Three TPN filters are taken with each sample to act as a triplicate, and all three are sent to the lab for analysis. More information regarding bottle types and holding times can be viewed in table 5.

The chlorophyll-a laboratory analysis of chlorophyll-a samples will be completed by the U.S. Geological Survey National Water Quality Laboratory according to the laboratory SOPs for analysis schedule 1508: Chlorophyll A in Phytoplankton and Pheophytin a in Phytoplankton. (attachment in Appendix 3, EPA 445, "In Vitro Determination of Chlorophyll a and Pheophytin a"). Sample will be collected directly into 500ml brown hdpe. Bottle will then be chilled and filtered back at the lab within 6 hours of collection.

Analyte	Lab	Analysis method (1)	Parameter Codes	NWQL Detection Limit	NWQL Minimum Reporting Limit
Ammonia (Dissolved)	NWQL	***Method ID:*** *I-2522-90* (Fishman, 1993)	00608	0.01 mg/L	0.01 mg/L
Ammonia + Organic Nitrogen (Whole)	NWQL	***Method ID:*** *I-4515-91* (Patton and Truitt, 2000)	00625	0.07 mg/L	0.07 mg/L
Ammonia + Organic Nitrogen (Dissolved)	NWQL	***Method ID:*** *I-2515-91* (Patton and Truitt, 2000)	00623	0.07 mg/L	0.07 mg/L
Nitrite (Dissolved)	NWQL	***Method ID:*** *I-2540-90, I-2542-89* (Fishman, 1993)	00613	0.001 mg/L	0.001 mg/L
Nitrite + Nitrate (Dissolved)	NWQL	***Method ID:*** *I-2547-11* (Patton and Kryskalla, 2011)	00631	0.04 mg/L	0.04 mg/L
Phosphorus (Dissolved)	NWQL	**Method ID:** 365.1 (EPA 365.1, 1993)	00666	0.003 mg/L	0.003 mg/L
Orthophosphate (Dissolved)	NWQL	**Method ID:** I-2601-90, I-2606-89 (Fishman, 1993)	00671	0.004 mg/L	0.004 mg/L
Phosphorus (Total)	NWQL	**Method ID:** 365.1 (EPA 365.1, 1993)	00665	0.004 mg/L	0.004 mg/L
Total nitrogen (NH3+NO2+NO3+Organic)	NWQL	***Method ID:*** *I-2650-03* (Patton and Kryskalla, 2003)	62854	0.05 mg/L	0.05 mg/L
Total Particulate Nitrogen (TPN)	NWQL	***Method ID:*** *365.1* (Zimmerman and others, 1997)	49570	0.03 mg/L	0.03 mg/L
Chlorophyll-a, phytoplankton	NWQL	***Method ID:*** *445.0* (Arar and Collins, 1997)	70953	0.1 ug/L	0.1 ug/L
Pheophytin, phytoplankton	NWQL	***Method ID:*** *445.0* (Arar and Collins, 1997)	62360	0.1 ug/L	0.1 ug/L
Total Suspended Solids, Residue on Evaporation (ROE)	NWQL	***Method ID:*** *I-3765-85* (Fishman and Friedman, 1989). Page 443	00530	15 mg/L	15 mg/L
Chlorophyll	Field	Bennett and others (2014), YSI EXO user Manual (appendix 10)	N/A	N/A	N/A
Dissolved Oxygen	Field	Wagner and others (2006)	00300	N/A	N/A
Specific conductance	Field	Wagner and others (2006)	00095	N/A	N/A
pH	Field	Wagner and others (2006)	00400	N/A	N/A
Water Temperature ℃	Field	Wagner and others (2006)	00010	N/A	N/A
Turbidity	Field	Wagner and others (2006)	63680	N/A	N/A

Table 4 List of analytes, Analysis Methods parameter codes and reporting levels. Appendix 8.

Table 4 Footnote: EPA method number is provided when available. Otherwise, the method number from NWQL is indicated.

Laboratory Analyte	**Sample Container Volume**	**Container Name**	**Preservation and Shipping Requirements**	**Hold Time** (appendix 9)	**Filtered (0.45 µm)**
Ammonia	125ml brown polyethylene bottle	FCC	No preservation	30 days	Y
Ammonia + Organic Nitrogen (Whole)	125ml clear polyethylene bottle	WCA	Acidify to pH <2 with H_2SO_4	30 days	N
Nitrogen, Ammonia + Organic Nitrogen (Dissolved)	125ml brown polyethylene bottle	FCC	No preservation	30 days	Y
Nitrite	125ml brown polyethylene bottle	FCC	No preservation	30 days	Y
Nitrite + Nitrate	125ml brown polyethylene bottle	FCC	No preservation	30 days	Y
Phosphorus (Dissolved)	125ml brown polyethylene bottle	FCC	No preservation	30 days	Y
Phosphate, Orthophosphate	125ml brown polyethylene bottle	FCC	No preservation	30 days	Y
Phosphorus (Whole)	125ml clear polyethylene bottle	WCA	Acidify to pH <2 with H_2SO_4	30 days	N
Total nitrogen (NH3+NO2+NO3+Organic)	125ml brown polyethylene bottle	FCC	No preservation	30 days	Y
Total Particulate Nitrogen (TPCN)	25 mm baked glass fiber filter	TPCN	No preservation	100 days	N
Chlorophyll-a, phytoplankton	47mm Glass fiber filter	Chl	No preservation shipped frozen on dry ice	25 days	N
Pheophytin, phytoplankton	47mm Glass fiber filter	Chl	No preservation shipped frozen on dry ice	25 days	N
Total Suspended Solids, Residue on Evaporation (ROE)	250ml clear polyethylene bottle	SUSO	No preservation	180 days	N

Table 5 Data quality requirements, preservation, and hold time for laboratory samples. [All samples will be chilled to < 4℃and shipped overnight on ice to NWQL. RPD, relative percent difference]

Discrete water quality field parameter measurements of DO, SC, water temperature and pH will be taken with each sample at all sites using a muti probe YSI monitor. pH and SC probes will be calibrated each day before field work is conducted and all calibration logs will be kept in a dedicated bound notebook located with the meters. DO will be calibrated at the site location and DO calibration information will be stored in field form documents (appendix 2) and archived with other site visit documentation. Water temperature probes are periodically temperature tested against an NIST certified probe in the lab approximately every 3 months for accuracy. These temperature checks are logged in a bound notebook and kept in the CT USGS laboratory. All field parameters will be taken in situ at the location that the sample was taken. Specific methodologies for meter calibration standards and criteria can be found in table 6 below.

Discrete water quality field data will be initially recorded on water proof paper field forms (appendix 1). All paper field forms will be scanned in and electronically archived within one week of sample completion. At the end of each sampling round field technicians will enter in all sampling data into the USGS program Personal Computer Field Forms (PCFF). PCFF will then be used as a conduit to enter all site information into the USGS NWIS database. PCFF files will be archived electronically with all site visit related information. Site visit information will be entered into USGS NWIS database within one week of sample completion. Analytical Service Request (ASR) forms to the U.S. Geological Survey NWQL laboratory will be filled out in the field immediately after each

sample collection and kept with the samples until shipping. ASR forms will be scanned in and electronically filed with all site visit information (appendix 1).

6.2 Continuous Water Quality Monitoring

USGS personnel will visit the site at Pawcatuck river at Westerly RI on a monthly to bimonthly basis for continuous monitor maintenance that includes cleaning the sonde, checking the calibration and re-calibrating when necessary, and downloading data. Sonde maintenance and calibration will follow the protocols and standards laid out in Wagner and others, 2006.

Typically, sonde maintenance site visits will follow the following steps:

1. Conduct site inspection
    a. Record* monitor readings, time, and monitor conditions
    b. With an independent field meter, observe and record readings and time near the sensor(s)
2. Remove sonde from the monitoring location
3. Clean sensors
4. Return sonde to the monitoring location
    a. Record* monitor readings and time
    b. Using an independent field meter, observe and record* reading and time near the sensor(s)
5. Remove sonde, rinse thoroughly, and check calibration of all parameters
    a. Record* calibration-check values
    b. Recalibrate if necessary
6. Return sonde to monitoring location
    a. Record* monitor readings and time
    b. B. Using an independent field meter, observe and record* readings near the sensor(s)

    *To assist with the USGS process of eliminating use of paper forms in the field, values stored in Site Visit Mobile Aquarius (SVMAQ), a USGS program. Data are then uploaded into the USGS Aquarius database via SVMAQ upon return from the field.

All the continuous data will be uploaded to the USGS time-series database for storage and processing, and to the USGS National Water Information System (NWIS) for display. Processing of data will include (1) the download of data from the sensors, (2) Analysis of sensor data and application of data corrections due to sensor fouling and calibration drift (all analysis will be documented using the USGS Records Management System, copies of analysis and electronic field notes will be provided to CT and RI, (3) approval of the data following Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting (Wagner and others, 2006) and Wilde, F.D., ed., (variously dated), Continuous monitor servicing and data processing for chlorophyll-a sensor will follow the guidelines outlined in U.S. Geological Survey Quality-Assurance Plan for Continuous Water-Quality Monitoring in Kansas, 2014 (Bennett and others, 2014) as well as the EXO user manual in appendix 10 and (4) uploading data to the publicly accessible USGS website. All parameters will be made publicly assessable through the NWIS database. USGS will provide CTDEEP and RIDEM additional calibration or maintenance data upon request.

6.3 Quality Assurance/ Quality Control

Every sampling trip will have at least 1 replicate and 1 blank sample collected. The replicate and blank samples will be scheduled so that every station will be have at least 1 blank and 1 replicate sample collected over the course of the project as per USGS protocols. Field replicate data quality requirements when comparing replicate to environmental samples is either a 20% relative percent difference or twice the laboratory minimum reporting limit. Field blank data quality requirements is less than the minimum laboratory reporting limit (table 4). Samples that exceed these data quality criteria will be qualified in the NWIS database and additional QA/QC actions will be reviewed. QA/QC sampling will be conducted on a scheduled basis and occur regardless of weather or sampling conditions.

Before any sampling is conducted USGS personnel will conduct a laboratory equipment blank on the two-liter plastic jugs used for collecting the samples, verifying equipment cleanliness. Equipment blank will be analyzed for nutrients, TPN and ROE. Equipment blank data quality requirement is less than the minimum laboratory reporting limit for each of the analyzed constituents. Accuracy requirements for discrete measurements are spelled out in table 6.

Analyte	**Data Quality Indicators**	**Measurement Performance Criteria**	**QC Sample or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling(S) or Laboratory Analysis (A)**
All Analytes (table 4)	Precision-overall	Relative Percent Difference < 20 percent	Field replicates	SA
All Analytes (table 4)	Accuracy/bias	No target compounds > laboratory reporting level	Field blanks	SA
Temperature (field)	Accuracy -- Stabilization criterion for measurements	Thermistor thermometer: ± 0.2 ° C Liquid-in-glass thermometer: ± 0.5 ° C	Field QA procedures and field replicate	S
Specific Conductance (field)	Accuracy -- Stabilization criterion for measurements	± 5 percent, when ≤ 100 µS/cm ± 3 percent, when > 100 µS/cm	Field QA procedures and field replicate	S
pH (field)	Accuracy -- Stabilization criterion for measurements	Meter displays to 0.01: ± 0.1 unit	Field QA procedures and field replicate	S
Dissolved Oxygen (field)	Accuracy -- Stabilization criterion for measurements	Amperometric method: ± 0.3 mg/L	Field QA procedures and field replicate	S
Turbidity (field)	Accuracy -- Stabilization criterion for measurements	Turbidimetric method, in NTU: ± 10 percent	Field QA procedures and field replicate	S

Table 6 Measurement Performance Criteria [<, less than value shown; >, greater than value shown; ≤, less than or equal to value shown; ±, plus or minus value shown; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; NTU, nephelometric turbidity unit].

6.4 Data Analysis

Sample collection, processing, analysis, and archival are discussed in more detail in this section as well as within the Generic QAPP Surface Water-Quality Sampling for Nutrients (Appendixes 4). All nutrient, chlorophyll, water quality and streamflow data for the Pawcatuck watershed will be compiled and reviewed for completeness and entered in to the NWIS database at the end of each sampling trip by field staff. Analysis of field data will be done by the project manager at the completion of each sampling event. Laboratory data review will be done by the project manager on

a weekly basis. Field replicates and blanks as well as NWQL internal QA/QC will be used when reviewing laboratory data and determining data quality. Field parameter data and continuous data is typically available to the public within one week of sample collection. Laboratory data is typically available within 30 days of sample collection. All discrete data collected for the project will be reviewed for accuracy and completion and approved within 120 days of collection. All discrete data collected as part of the project will be stored in the USGS NWIS database and be publicly accessible. Data collected as QA/QC (field blanks and replicates) will be stored in USGS NWIS database but will not be publicly accessible. All QA/QC data will be provided to CTDEEP and RIDEM upon request. Supporting documentation such as field sheets and calibration logs are scanned in and are stored internally on a USGS platform. All supporting documents will be made available upon request. All data analysis and approval will occur internally by USGS.

Continuous data collected as well as the SVMAQ files for this project will be stored in the USGS database Aquarius and can be accessed through the USGS NWIS data portal. Continuous data will be accessible to the public within one week of data collection. USGS will provide data files upon request, as well as any additional site visit information needed. Calibration and fouling correction are applied directly to data sets in Aquarius and are reflected directly in NWIS. Corrections are applied according to the guidance spelled out in Wagner and others, 2006. Continuous water quality data will be analyzed, and correction applied within 60 days of a site visit completion. Continuous data will be approved within 120 days of the data analysis.

The data collected through this project is intended to be used to support HSPF modeling for the Pawcatuck River watershed and to inform development of management activities to address nutrient-related water quality impacts. The development of the HSPF model however is not in the scope of this project.

7.0 Assessment/Oversite

Quarterly reports are the standard format for documenting an ongoing project in the USGS New England Water Science Center. These quarterly reports summarize USGS project activities, report problems and corrective actions, outline the status of planned products, and summarize plans for the following quarter. These quarterly reports will be provided to the DEEP and RIDEM project managers. The project manager will contact CTDEEP or RIDEM by phone or email regarding any issues or concerns that occur between these scheduled quarterly reports. For urgent or time sensative matters, USGS will contact Traci Iott directly by phone or email. Informal status reports and updates are also provided to the cooperator upon request. The final report of the project will present the findings and provide a sumary statement for CT DEEP and RI DEM. In addition, the final report will include discussions of project quality objectives, major problems encountered and their resolution, quality-assurance and quality-control procedures for the project, and the reconciliation of project data with project quality objectives.

Upon data completion, a USGS data release report will document the results of the study and document all discrete and continuous data collected.

In addition, a series of technical project reviews will be conducted internally by USGS Discipline Specialist (USGS – New England Water Science Center) in the field of investigations. The technical reviews ensure that appropriate analytical techniques are being used and resolves any problems in achieving the project objectives. The technical reviews are also a thorough review of data analysis and interpretations. Three reviews are scoped out for all projects, and occur at 10% of project completion, 40% and 70%. This ensures oversite of projects from start to finish.

The USGS technical review schedule is as follows:

Tentatively Scheduled for:	**Technical review comments due on:**
5/30/19	6/30/19
10/1/19	11/30/19
1/1/20	1/30/20

Project assessments will be performed periodically throughout the project to ensure that usable data are generated. Written documentation will be developed for the following project assessments as applicable. Written documentation for all assessments will be maintained in the project file as a permanent record.

Assessment	**Frequency**	**Internal**	**Organization**	**Person(s) responsible**
Data management systems review	Periodically throughout the project	Internal	USGS	Kaitlin Laabs
Project status assessment (quarterly reviews)	Quarterly	External/Internal	USGS/CTDEEP	Jon Morrison, Kaitlin Laabs (USGS) Traci Iott (CTDEEP)
Project technical reviews	Three time during the project	Internal	USGS	Jon Morrison, Kaitlin Laabs

8.0 Data Validation and Usability

Quality-assurance procedures and quality-control requirements established by the USGS for streamflow and water-quality data collection, computation of streamflow and water quality, and statistical analyses of streamflow and water quality provide a high level of confidence that the data generated by the project will be both valid and usable. Internal and external assessments and technical review ensure that required procedures are followed correctly and consistently. The USGS project manager is responsible for validating that the data are scientifically defensible and meet the data quality objectives of the project. When issues with data quality arise or are identifued, the project manager will investigate and determine the cause of the problem and implement any appropriate corrective actions. Any affected data will be qualified in the NWIS database, and the project manager will verify that the issue has not persisited. Analytical accuracy at the NWQL will be evaluated by using the performance evaluation samples provided by the project (USGS Branch of Quality Systems LEP). Any results that are found to be outside these established QC limits will be qualified.

Data (surface-water and water-quality data) for USGS stations can be obtained by downloading the data from NWIS as RDB files; these data can be imported into statistical software for analyses.

As described in the Generic QAPP titled: *Surface Water-Quality Sampling for Nutrients*, the U.S. Geological Survey TWRI Book 9 National Field Manual for the Collection of Water-Quality Data provides extensive documentation for all aspects of surface water-quality data collection. It is a comprehensive description of standardized procedures for collection and processing of water-quality samples.

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Appendices

Appendix 1. U.S. Geological Survey, Analytical Services Request (ASR) form. **See attached documents>**

Pawcatuck Nutrient and TSS ASR	Pawcatuck_NWQL_ ASR.pdf
Pawcatuck Chlorophyll a and Pheophytin a ASR	Pawcatuck_NWQL_ ASR_Chloro.pdf

Appendix 2. U.S. Geological Survey, Field Forms. **See attached documents>**

Pawcatuck Field Form Template	Pawcatuck Field Forms.pdf

Appendix 3. U.S. Geological Survey National Water Qulality Laboratory SOPs for chlorophyll analysis **See attached documents>**

In Vitro Determination of Chlorophyll a and Pheophytin a	In Vitro Determination of Ch

Appendix 4. Generic QAPPs **See attached documents>**

Generic QAPP for Surface Water Quality Nutrient Sampling	Generic QAPP for Surface Water Quali
Generic QAPP for Stream Gaging and Streamflow Computation	Generic QAPP for Stream Gaging and

Appendix 5. Rhode Island Surface Water Quality Monitoring Project Plan **See attached documents>**

Rhode Island Surface Water Quality Monitoring Project Plan	 RIQW_Rhode Island Surface Water Quali

Appendix 6. Water Quality Sampling and Monitoring of the Pawcatuck River Watershed **See attached documents>**

Water Quality Sampling and Monitoring of the Pawcatuck River Watershed	 Water Quality Sampling and Monit

Appendix 7. U.S. Geological Survey National Water Quality Field Maunal SOP's for the Collection of Water Quality Samples

Preparations for Water Sampling	Chapter A1
Selection of Equipment for Water Sampling	Chapter A2
Cleaning of Equipment for Water Sampling	Chapter A3
Processing of Water Samples	Chapter A5
Field Measurements	Chapter A6
Algal Biomass Indicators	Chapter A7.4

Appendix 8. U.S. Geological Survey National Water Quality Laboratory Method ID's for all sampeld Constituents

Analyte	Analysis method
Nitrogen, Ammonia	***Method ID:*** *I-2522-90* (Fishman, 1993)
Nitrogen, Ammonia + Organic Nitrogen (Whole)	***Method ID:*** *I-4515-91* (Patton and Truitt, 2000)
Nitrogen, Ammonia + Organic Nitrogen (Filtered)	***Method ID:*** *I-2515-91* (Patton and Truitt, 2000)
Nitrogen, Nitrite	***Method ID:*** *I-2540-90, I-2542-89* (Fishman, 1993)
Nitrogen, Nitrite + Nitrate	***Method ID:*** *I-2547-11* (Patton and Kryskalla, 2011)
Phosphorus (Filtered)	**Method ID:** 365.1 (EPA 365.1, 1993)
Phosphorus, Phosphate, Orthophosphate	**Method ID:** I-2601-90, I-2606-89 (Fishman, 1993)
Phosphorus (Whole)	**Method ID:** 365.1 (EPA 365.1, 1993)
Total nitrogen (NH3+NO2+NO3+Organic)	***Method ID:*** *I-2650-03* (Patton and Kryskalla, 2003)
Total Particulate Nitrogen (TPN)	***Method ID:*** *365.1* (Zimmerman and others, 1997)
Chlorophyll-a, phytoplankton	***Method ID:*** *445.0* (Arar and Collins, 1997)
Pheophytin, phytoplankton	***Method ID:*** *445.0* (Arar and Collins, 1997)
Total Suspended Solids, Residue on Evaporation (ROE)	***Method ID: I-3765-85*** (Fishman and Friedman, 1989)

Appendix 9. U.S. Geological Survey National Water Quality Laboratory Method Holding Times

Method holding times used by the National Water Quality Laboratory	NWQLMethodHoldtimes.pdf

Appendix 10. YSI EXO User Manual

YSI EXO User Manual	EXO User Manual.pdf