1. Title and Approval Page

Watershed Monitoring Program for Rhode Island

Rhode Island Department of Environmental Management (DEM)

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3. Distribution List and Project Organization

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4. Background of Watershed Monitoring Program for Rhode Island

A. Problem Statement

In 1991/92, the Civil and Environmental Engineering Department (CVE) at the University of Rhode Island (URI) conducted research for the Rhode Island Department of Environmental Management (RI DEM) establishing a Baseline Monitoring Program for the rivers of Rhode Island. The main purpose of the program was to establish a long-term water quality database. The study conducted seasonal sampling of 25 river stations throughout the state of Rhode Island. The original project was extended and has successfully collected seasonal samples from the 25 rivers for a period of twelve years.

Recently, an outside consultant evaluated the various RIDEM programs in operation in order to develop a water quality monitoring program that would meet the needs of the state for the next several years. The result of this evaluation is a shift to a watershed wide water quality monitoring program that will enable the RIDEM to thoroughly evaluate watersheds within Rhode Island on a rotating basis.

The current proposal entails the evaluation of the Wood River Watershed, and is similar in scope to the previous program in that many of the same water quality constituents will be monitored at a select number of locations for the next year. At the end of this period, another watershed will be selected by the Rhode Island Department of Environmental Management to undergo the same monitoring program as was accomplished in the Wood River Watershed.

B. Intended Use of Data

The project is conducted to collect water quality data (physical and chemical) that represents baseline conditions of the wadeable rivers of the state. The data is used to assess the water quality status of the rivers for use in water quality management, 305(b) assessments, 303(d) listings, and refinement of certain water quality criteria.

5. Project Task Description

A. Objectives

1.To conduct a dry weather monitoring program, which includes the measurement of water quality and flow for a maximum of 60 river stations in Rhode Island. The station locations

will be established annually based on input from RIDEM with an intention of rotating around the state consistent with the forthcoming monitoring strategy.

2. To provide an interim draft data report to RIDEM that will include the data sets for the first (all stations) and second (Subset #1) dry surveys. The draft data report will be submitted in electronic format within 30 days after Subset #1 sampling survey is completed.

3. To provide an interpretation of the data in a comprehensive final report which will be submitted annually.

Each station will be flowgaged in order to establish a stage–flow relationship, and to determine the mass loads at the station for selected constituents. Each dry weather sample is to be analyzed for 23 constituents. Included in the 23 analyses are three field measurements (conductivity, temperature and dissolved oxygen), and 14 laboratory tests (unfiltered five-day biochemical oxygen demand (BOD_5), chloride, sodium, dissolved ammonia (NH_3-N), dissolved nitrate ($N0_3$-N), pH, dissolved orthophosphate (PO_4-P), total nitrogen, total phosphorous, total and volatile suspended solids, dissolved metals (Cd, Cu, Pb), total iron (Fe), hardness (Ca and Mg as $CaCO_3$), turbidity, fecal coliform, and enterococcus. The constituent table is given below:

Constituent	Total DW[a] Samples To Be Analyzed	Sample Volume	Sample Container	Maximum Holding Time	Preserve
Dissolved Cd, Cu, Pb	Maximum 150	500 ml	P (HDPE)	6 Months	Add HNO_3 to pH<2
Total Fe	Maximum 150	500 ml	P (HDPE)	6 Months	Add HNO_3 to pH<2
Unfiltered BOD_5	Maximum 150	1000 ml	P (HDPE)	1 day	Refrigerate
Hardness (Ca, Mg as $CACO_3$)	Maximum 150	100 ml	P (HDPE)	6 Months	Add HNO_3 to pH<2
Sodium	Maximum 150	100 ml	P (HDPE)	6 Months	None required
Chloride	Maximum 150	100 ml	P (HDPE)	28 days	None required
DO, Temperature, Conductivity	Maximum 150	-	-	Field	-
NH_3-N	Maximum 150	500 ml	P (HDPE)	7 days	Refrigerate
NO_3+NO_2-N	Maximum 150	200 ml	P (HDPE)	28 days	Refrigerate

Constituent	Total DW[a] Samples To Be Analyzed	Sample Volume	Sample Container	Maximum Holding Time	Preserve
pH	Maximum 150	50 ml	P (HDPE)	Immediately	-
PO_4-P	Maximum 150	100 ml	P (HDPE)	28 days	Freeze at -10 °C
TN	Maximum 150	100 ml	P (HDPE)	28 days	Freeze at -10 °C
TP	Maximum 150	100 ml	P (HDPE)	28 days	Freeze at -10 °C
TSS and VSS	Maximum 150	200 ml	P (HDPE)	3 days	Refrigerate
Turbidity	Maximum 150	100 ml	P (HDPE)	24 hours in dark	Refrigerate
Fecal Coliform	Maximum 150	250 ml	P (HDPE)	6 hours	Refrigerate 1-4 °C
Enterococci	Maximum 150	250 ml	P (HDPE)	6 hours	Refrigerate 1-4 °C

[a] - Does not include field duplicates, trip blanks or extra laboratory runs; Refrigerate = storage at 4° C, in dark; P = plastic, HDPE = High Density Polyethylene

The Civil and Environmental Engineering (CVE) Department will conduct this project with laboratory analyses being conducted at the Environmental Engineering Laboratories at URI-Kingston with the exception of the microbiological samples that will be analyzed at Biological Analytical Laboratories in Cranston, RI. (BAL has been used in all the previous surveys.)

B. Project Timetable

Activity	Projected Start Date	Anticipated Date of Completion
QAPP	June 2004	August 2004
Field Setup	July 2004	August 2004
Station Flow Gaging	July 2004	August 2005
Sampling	August 2004	August 2005
Laboratory Analysis	August 2004	August 2005
Data Interpretation	August 2004	August 2005
Draft Report	August 2005	October 2005
Final Report	August 2005	December 2005

6. Measurement Quality Objectives

Measurement performance criteria are quantitative statistics used to determine the degree of acceptability of the data by the user. These criteria are known as Data Quality Indicators (DQLs) and include the following.

Precision

Accuracy

Representativeness

Completeness

Comparability

Measurement performance criteria for the constituents of interest are presented below.

A. Data Precision, Accuracy, and Measurement Range

Matrix	Parameter	Measurement Range	Accuracy	Precision
Water	BOD_5	ppm	±1% of Full Scale	± 20%
Water	Chloride	ppm	±0.5 mg/L	± 20%
Water	Conductivity	1-1000 μmhos/cm	±2.5%	± 20%
Water	Sodium	ppm	±20%	±20%
Water	Hardness (Ca, Mg as $CaCO_3$)	ppm	±20%	±20%
Water	Dissolved Oxygen	1-20 ppm	±1% of Full Scale	± 20%
Water	Fecal Coliform	CFU/100 mL	±10%	± 20%
Water	Enterococcus	Enterococci /100 mL	±10%	± 20%
Water	NH_3-N	ppm	±10%	± 20%
Water	NO_3-N	ppm	±10%	± 20%
Water	pH	2-10	±0.1 pH units	± 20%
Water	PO_4-P	ppm	±10%	± 20%
Water	Temperature	1 – 30 ºC	±0.5ºC	± 20%
Water	TN	ppm	±10%	± 20%

Matrix	Parameter	Measurement Range	Accuracy	Precision
Water	TP	ppm	±10%	± 20%
Water	TSS	ppm	±10%	± 20%
Water	VSS	ppm	±10%	± 20%
Water	Dissolved Cd	ppb	±20%	± 20%
Water	Dissolved Cu	ppb	±20%	± 20%
Water	Dissolved Pb	ppb	±20%	± 20%
Water	Total Fe	ppb	±20%	± 20%
Water	Turbidity	0-1000 NTU	±3%	± 20%

B. Data Representativeness

All sample locations will be chosen such that the samples collected during each dry survey will be representative of the site conditions on the day and time of collection, and will reflect the general steady state conditions of the watershed.

C. Data Comparability

The data collected will not be sent out as split samples to other laboratories. However, the data may be compared against the range of values from those samples that were collected during the ten years of the Baseline Monitoring Program. While not all watersheds in Rhode Island are represented in the Baseline database, there is a significant possibility that a number of the Baseline stations will be within the boundaries of watersheds in this monitoring program. If so, the data is available for comparison and will be utilized.

D. Data Completeness

Parameter	Number of Valid Samples	Number of Valid Samples Collected and Analyzed	Percent Complete
BOD_5	Maximum of 150	90%	90%
Chloride	Maximum of 150	90%	90%
Conductivity	Maximum of 150	90%	90%
Sodium	Maximum of 150	90%	90%

Parameter	Number of Valid Samples	Number of Valid Samples Collected and Analyzed	Percent Complete
Hardness (Ca, Mg as $CaCO_3$)	Maximum of 150	90%	90%
Dissolved Oxygen	Maximum of 150	90%	90%
Fecal Coliform	Maximum of 150	90%	90%
Enterococcus	Maximum of 150	90%	90%
NH_3-N	Maximum of 150	90%	90%
NO_3-N	Maximum of 150	90%	90%
pH	Maximum of 150	90%	90%
PO_4-P	Maximum of 150	90%	90%
Temperature	Maximum of 150	90%	90%
TN	Maximum of 150	90%	90%
TP	Maximum of 150	90%	90%
TSS	Maximum of 150	90%	90%
VSS	Maximum of 150	90%	90%
Dissolved Cd	Maximum of 150	90%	90%
Dissolved Cu	Maximum of 150	90%	90%
Dissolved Pb	Maximum of 150	90%	90%
Total Fe	Maximum of 150	90%	90%
Turbidity	Maximum of 150	90%	90%

7. Training Requirements

A. Training Arrangements and Responsibilities

All field and laboratory work will be performed under the supervision of the URI Project Manager and the URI Laboratory Manager. Graduate students performing any field or laboratory work will be trained prior to any work being performed. The training is a hands-on

process that is supervised by one of the project managers. A qualification record will be kept on site to track the training and performance of those personnel assigned field or laboratory tasks.

8. Documentation and Records

The URI Project Manager and Project QA Officer will be responsible for the proper collection of all field and analyses data , and for transmission of the results to RIDEM. They will also collect, consolidate and forward to RIDEM all data received from BAL for the micro biological analysis. Original field logs, sample log-in forms, laboratory analysis sheets, and chain-of-custody forms will be maintained in the project files at URI by the QA officer. To reduce superfluous paperwork, copies of these documents will be forwarded to the DEM and URI Project managers only if requested.

9. Sampling Process and Design

A. Rationale for Selection of Sampling Sites

The sampling sites for the 2004 cycle have been chosen in accordance with the State's draft Monitoring Strategy. The State will be conducting a rotating basin monitoring strategy where the individual station locations are determined using a geometric approach. For 2004, the state is piloting this approach on the Upper and Lower Wood River sub basins. In addition to the geometrically determined stations, a number of targeted stations will be located within the basin/sub basin as determined by stakeholders.

B. Field Sampling Program Tasks

The water quality stations will vary by watershed and will be determined by RIDEM before the beginning of each sampling period. The frequency each station will be sampled will also be determined by RIDEM, in consultation with URI. A proposed schedule is given below, but it is understood that this remains flexible for each watershed. For each watershed there will be a maximum of 60 stations in any year. The total number of samples to be taken in a year would not exceed 150. The total number of flow measurements will be equal to the number of samples and will not exceed 150.

1. Each watershed will require the development of the draft sampling plan, participation in meetings, review of the draft, and time to finalize the sampling plan. This must be accomplished before the water quality program can be started each year.
2. Sampling station reconnaissance.
3. All stations would be sampled annually, typically during late summer/ early fall. The sampling would include one water quality sample and a flow measurement (maximum of 60 stations). (60 stations and 60 samples)
4. Subset #1 would include approximately 40 (2/3rds of the total) stations and would require a second set of water quality and flow measurements, potentially in the early spring of the following calendar year. (Approximately 40 stations and 40 samples)
5. Subset #2 would include approximately 25 (1/2 of the total) stations of subset #1 and would require two additional sampling periods for water quality and flow measurements in the spring/ early summer. (Approximately 25 stations and 50 samples)
6. Subset #3 would include approximately 10 of the stations in subset #2 and would require two consecutive low-flow summer days of sampling every four hours for field measurements. (Laboratory analysis will be added if deemed necessary by RIDEM.)
7. Each year a QAPP will be developed and approved to reflect the changes in the field sampling program.

C. Field and Laboratory Water Quality Analyses Tasks

A listing of 23 constituents is carried over from the Baseline Monitoring Program. Not all constituents will be determined for each water quality sample. This sampling list will remain flexible with the possibility of modifying this list at the discretion of RIDEM. It is expected that the maximum number of analyses will not exceed 3,450 for a year. If the maximum number of samples taken are monitored for all constituents, this would be a total of 150 x 23 = 3,450.

1. 3 field measurements: Temperature, Specific Conductance, and Dissolved Oxygen.
2. 18 URI laboratory measurements: pH, Turbidity, Total Suspended Solids, Volatile Suspended Solids, Dissolved Trace Metals (Cd, Cu, Pb), Total Iron (Fe), Hardness (Ca, Mg), Unfiltered Biological Oxygen Demand (BOD_5), Dissolved Nitrate, Dissolved Ortho-phosphate, Dissolved Ammonia, Total Nitrogen, Total Phosphorous, Chloride, and Sodium.
3. 2 contracted laboratory measurement: Fecal Coliform and Enterococcus.
4. Each year a QAPP will be developed and approved to reflect the changes in the field and laboratory water quality program.

All of these constituents with the exception of the microbiological parameters will be analyzed in the Civil and Environmental Engineering Laboratories. An outside laboratory specializing in microbiological analysis will perform the Coliform and Enterococcus analysis.

D. Interpretation and Final Report

The water quality interpretation will include all surveys. The results of the interpretation will be presented in a comprehensive final report. Specifically, the tasks to be completed include the following:

1. At the request of RIDEM, synthesize all data being taken in this watershed. This will require the interaction between all participants in the watershed.
2. Relationships between water quality and land use will be investigated. Land use information will be necessary for proper data interpretation. It is anticipated that land use delineation will be determined through a joint effort with RIDEM.
3. The stations will be compared and ranked for each constituent based on concentration and mass loading.
4. Trends in the data will be investigated. This will include seasonal trends and trends over the period of record.
5. Draft data and reports will be delivered by hardcopy and electronically.

10. Sampling Handling and Custody Procedures

The samples will be collected under the supervision of the QA officer who will be following guidelines approved by the EPA. Sample containers were prepared and washed in accordance with the procedures recommended in *Standard Methods* 1995.

All samples for NO_3 and NH_3 and PO_4 analysis will be filtered as soon as they are received with Gelman Type A/E glass micro fiber filters and placed under refrigeration until analysis (within 24 hours). Trace metal samples will be filtered upon arrival in the CVE laboratory and preserved with trace metal grade nitric acid to pH <2 and placed under refrigeration. For every survey, sampling crews will carry field blanks representing all constituents, and duplicate samples will be collected at two water quality stations for each survey. All field blanks and duplicate samples will be processed following the identical procedures used with the water quality samples.

A. Sample Custody Procedures

All samples will be collected and transported under the supervision of the QA officer. A cleaned and prepared Teflon bucket will be used to collect raw water samples from all locations. The bucket is rinsed three times with water from the particular sample station before the sample is collected and transferred into the prepared bottles. The samples will be placed into an iced

cooler for the remainder of the sampling run. All samples will be delivered to the URI-CVE laboratory at URI. As soon as the samples are received, they are logged in. The sequence of handling the samples once received will be as follows:

1. All samples will be logged in.
2. pH will be immediately run.
3. Nutrient samples will be filtered and placed under refrigeration until analyzed.
4. Trace metal samples will be filtered, preserved and placed under refrigeration until analyzed.
5. The fecal coliform samples will be transported in ice to the microbiological laboratory within 2 hours of receipt.
6. All other samples will be placed under refrigeration until analyzed.

11. Analytical Procedures

Dissolved oxygen and temperature will be determined in the field using a Yellow Springs Instrument (YSI Model 57) dissolved oxygen meter. The connected probe is a membrane covered Clark-type polarographic sensor with built-in thermistors for temperature measurements and compensation. The membrane isolates the sensors from the environment but allows gases, like oxygen, to migrate to the sensors, which are polarized by an applied voltage. The membrane passes oxygen at a rate proportional to the pressure difference between the dissolved oxygen in the water and the oxygen in the cathode chamber. The reaction of oxygen with the cathode produces a current, which is measured. The probe requires a steady supply of oxygen (the water around the probe has to be in motion), because the reaction consumes oxygen that passes through the membrane. The instrument will be calibrated prior to the first sample run using the water saturated air procedure supplied by YSI. Calibration was re-verified at the end and beginning of each sampling run for the dry surveys. A complete initial calibration will be performed if the instrument fails the continuing calibration check. Temperature accuracy will be verified in the laboratory prior to field deployment by comparing the instrument's temperature reading to a NIST certified thermometer.

Specific conductance is measured in the field using a Yellow Springs Instrument (YSI Model 33-T-C-S) specific conductance meter with a conductivity probe. This probe comprises two Platinized nickel electrodes and a thermistor encapsulated in a rigid PVC body. The meter is

calibrated prior to its use according to the instrument's guidelines. Calibration will be checked at the end of each run, and at the end of the field sampling. A complete initial calibration is performed if the instrument fails the continuing calibration check.

For pH measurements, an Orion Instrument Model 720A connected to a pH probe will be used. Calibration is accomplished following the manufacturer's procedure and the guidelines in *Standard Method 4500-H B* and *USEPA Method 150.1*. Measurements will be performed in the URI laboratory on water samples collected in 1L bottles for TSS/VSS analysis. These bottles are filled up to the top, avoiding trapped air spaces beneath the lid. Samples are uncovered and the pH is measured as soon as the samples reach room temperature. However, the Model 720A can compensate for sample temperature changes. The EPA in the 1991 Water Quality Study followed this procedure on the Blackstone River (Hartmann 1992). The instrument is calibrated at the beginning of all analyses with pH buffers of 4.00, and 7.00, and the initial calibration verification checked with a pH buffer of 6.00. A continuing calibration check will be performed for each set of samples.

Unfiltered five-day Biochemical Oxygen Demand (BOD_5) is measured according to *Standard Method 5210 B* and *USEPA Method 405.1*. A BOD-bottle will be filled with 300 ml of a sample. A pretreatment of the sample, like dilution or pH adjustment (6.5-7.5), will be done if it is required. The Dissolved Oxygen concentration will be measured with a similar probe as was described in the procedure for Dissolved Oxygen. Afterwards, the bottles are sealed and stored in an incubator at 20°C. After five days, the DO concentration in the bottle is measured again. Out of the difference between the two readings, the oxygen uptake is calculated as the 5-day biochemical oxygen demand for the unfiltered sample.

All nutrients (Ammonia, Nitrate, Ortho-phosphate, Total Nitrogen, and Total Phosphorous) analyses are run on the OI Analytical Flow Solution IV (FS-IV), a high-throughput, automated system for ion analysis employing segmented flow analysis (SFA). The FS-IV uses an advanced Expanded Range (ER) detector, allowing single calibration ranges of 3 to 4 orders of magnitude, significantly reducing sample reruns due to off-scale samples. The system's WinFLOW software package allows random access sampling, automatic recalibration, and real-time results. Calibration curves are run using a minimum of 5 standards, and a reagent blank. The correlation coefficient must be >0.999, otherwise, a new calibration is run. The curve

is checked with initial calibration verification (ICV) standards prior to the samples being analyzed, and continuing calibration verification (CCV) standards are run at 5% intervals throughout the course of the analysis to ensure the calibration is maintained. The curve is redone if the CCV is outside ±10% of the standard's value.

The analysis for ammonia follows *Standard Method 4500-NH_3-D* and *USEPA Method 350.1*. Ammonia reacts with alkaline phenol and hypochlorite to form indophenol blue in an amount that is proportional to the ammonia concentration. The blue color is intensified with sodium nitroferricyanide. The absorbency of this compound is measured in a flow cell at 660nm. The WinFLOW software displays the dissolved ammonia concentrations of the water samples as NH_3-N.

Dissolved nitrate is analyzed following *Standard Method 4500-NO_3-F* and *USEPA Method 353.2* (Colorimetric, Automated, Cadmium Reduction). Nitrate is reduced quantitatively to nitrite by cadmium metal in the form of an open tubular reactor. The nitrite thus formed plus any originally present in the sample is colorimetrically detected at 540 nm, following its diazotization with sulfanilamide, and subsequent coupling with N-1-naphthylethylenediamine dihydrochloride. The dissolved nitrate concentrations of the samples are calculated as NO_3-N.

Dissolved orthophosphate is analyzed following *Standard Method 4500-P F* and *USEPA 365.1* (Colorimetric, Automated Ascorbic Acid Reduction Method). A reagent composed of ammonium molybdate, ascorbic acid, potassium antimony tartar and sulfuric acid is produced. The water sample is mixed with the combined reagent and heated inside the FS-IV to 36°C. A blue phosphomolybdate complex is formed, which absorbency is measured at 660nm in a flow cell as PO_4-P.

Total Nitrogen (TN) is analyzed following *Standard Method 4500-NO_3-D*. Prior to analysis, samples are digested via persulfate digestion to convert organic and inorganic nitrogen to nitrate. Total Nitrogen is determined by analyzing the digested samples following *Standard Method 4500-NO_3-F* and *USEPA Method 353.2* (Colorimetric, Automated, Cadmium Reduction). Nitrate is reduced quantitatively to nitrite by cadmium metal in the form of an open tubular reactor. The nitrite thus formed plus any originally present in the sample is colorimetrically detected at 540 nm, following its diazotization with sulfanilamide, and

subsequent coupling with N-1-naphthylethylenediamine dihydrochloride. The dissolved nitrate concentrations of the samples are calculated as NO_3-N.

Total Phosphorus (TP) is determined following *Standard Method 4500-P F* and *USEPA Method 365.1*(Automated Ascorbic Acid Reduction). Prior to analysis, samples are digested via persulfate digestion to hydrolyze phosphorus to orthophosphate. Orthophosphate reacts with molybdenum (VI) and antimony (III) in an acidic solution to form an antimony-phosphomolybdate complex. This complex is reduced with ascorbic acid to form a blue color, and the absorbance is measured at 660 nm.

Total Suspended Solids (TSS) are analyzed following the *Standard Method 2540 D* and *USEPA Method 160.2* (Gravimetric, Dried at 103-105°C). Glass micro fiber filters are prepared by washing with three successive 20ml portions of reagent grade water, placed in an aluminum weighing dish, dried in an oven at 103-105°C, and weighed prior to use. This is subsequently used to filter a well-mixed sample volume of 250ml minimum. The filter is replaced in the weighing dish, again dried in a muffle furnace for one hour at 103-105°C, and then allowed to cool in a desiccator. The filter and dish is weighed again after the cooling process until a constant weight is obtained or until the weight change is 4% of the previous weighing or 0.5 mg, whichever is less. The difference in the results is the mass of solids in the sample.

Total Volatile Solids (VSS) are analyzed following the *Standard Method 2540 E*. and *USEPA Method 160.4* (Gravimetric, Ignition at 550°C). The filtered sample from the latter procedure (TSS) is now ignited to 550°C for 15 minutes. The weight loss between ignition at 550°C and the drying at 103°C is the mass of volatile solids in the water samples.

Chloride concentration is determined using an Orion Instrument Model 720A connected to an Orion chloride electrode, Model 96-17B. The procedure supplied by the manufacturer (Orion Laboratory Products Group) was followed for the analyses. Three standards are used to calibrate the instrument and then it is checked using an initial calibration verification (ICV) standard that was prepared separately from the calibration standards. The Orion 720A calculates the calibration curve internally, and displays the chloride concentration in mg/L. The calibration is checked every two hours and/or at the end of the analysis. For the analyses, 50ml of sample is measured into a beaker, and 1ml of ionic strength adjuster (ISA) solution (5M $NaNO_3$) is added.

The solution is mixed with a magnetic stirrer, and the electrode is placed in the sample for measurement. Reagent grade water is used to thoroughly rinse the electrode between samples, and then gently shaken to remove any excess water that may interfere with the measurements.

Turbidity is analyzed following *Standard Method 2130 B* and *USEPA Method 180.1* (Nephelometric). A DRT-15CE Turbidimeter from HF Scientific is used for the analysis. The instrument is calibrated following the manufacturer's procedure, and readings are in Nephelometric Turbidity Units (NTU). The analysis is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Standard suspensions of Formazin are used to calibrate the instrument, and the calibration is checked continuously during the sample analysis runs with a separate standard that was not used in the calibration. The calibration is checked again at the end of the analysis.

Trace metals (Cd, Cu, Pb, Fe, Na, Ca, Mg) will analyzed according to an outline of the EPA Narragansett Environmental Research Laboratory (NERL), which trained the URI-CVE laboratory personnel. The samples will be analyzed in a Perkin-Elmer 3100XL ICP-OES and on a Perkin-Elmer Model 5100 PC atomic absorption spectrophotometer, which is equipped with an HGA Graphite Furnace. For dissolved trace metals, the samples are filtered and the filtrate is preserved with HNO_3 to pH <2 for analysis. Spiked samples (mixing of samples with known concentrations) will be used for quality control.

Fecal Coliform samples are analyzed by BAL Laboratory following *Standard Method 9213 D* with mTEC media. Samples are stored in iced coolers at a temperature below 4 ºC and delivered to the laboratory within 6 hours of collection. Samples are filtered through a membrane filter and rinsed several times with sterile phosphate buffer. The membrane is removed aseptically from the filter holder and placed onto sterile petri plates that contain mTEC agar. The plates are incubated at 35 ± 0.5 ºC for 2 hours to rejuvenate injured or stressed bacteria, and then incubated at 44.5 ± 0.2 ºC for 22 hours. After this period, the filters are checked and yellow colonies are counted as fecal coliforms. The membrane filters are then transferred to a filter pad saturated with urea substrate. After 15 minutes, the yellow or yellow-brown colonies are considered to be *E. coli*. Prior to each use, the mTEC media undergoes a QC check, and ten percent of all samples received are analyzed in duplicate.

Enterococcus samples are analyzed by BAL Laboratory following *EPA M-1600 Method.* The MF method provides a direct count of bacteria in water based on the development of colonies on the surface of the membrane filter (Reference 18.5).A water sample is filtered through the membrane which retains the bacteria. Following filtration, the membrane containing the bacterial cells is placed on a selective medium, mEI agar, and incubated for 24 h at 41 °C. All colonies (regardless of color)with a blue halo are recorded as enterococci colonies. Magnification and a small fluorescent lamp are used for counting to give maximum visibility of colonies. Samples are stored in iced coolers at a temperature below 4 ºC and delivered to the laboratory within 6 hours of collection.

Summaries of the analytical methods used are provided below. The matrix for all analyses will be water.

Methodology for Analyzed Constituents

Constituent	Units	Methodology	Reference
BOD_5	mg/L	Membrane Electrode YSI Model 57	EPA 405.1 SM 5210 B
Chloride	mg/L	Electrode Orion Instrument Model 720A	Orion Instrument Manual Model 720A
Conductivity	µmhos/cm	Electrode YSI Model 33-T-C-S Meter	EPA 120.1 SM 2510-B
Sodium	mg/L	PE 3100XL ICP-OES	EPA 200.7
Hardness (Ca, Mg as $CaCO_3$)	mg/L	PE 3100XL ICP-OES	EPA 200.7
DO	mg/L	Membrane Electrode YSI Model 57 Meter	EPA 360.1 SM 4500-0 G.
Fecal Coliform	CFU/100ml	Membrane Filtration	SM 9213-D
Enterococcus	Enterococci /100ml	Membrane Filtration	EPA M-1600
NH_3-N	mg/L	Calorimetric Automated Phenate Alpkem Flow IV SFA Instrument	EPA 350.1 SM 4500-NH_3-G
NO_3-N	mg/L	Calorimetric Automated Cadmium Reduction Alpkem Flow IV SFA Instrument	EPA 353.2 SM 4500-NO_3-F
pH	pH units	Electrode Orion Instrument Model 720A	EPA 150.1 SM 4500-H B

Constituent	Units	Methodology	Reference
PO_4-P	mg/L	Calorimetric Automated Ascorbic Acid Alpkem Flow IV SFA Instrument	EPA 365.1 SM 4500-P-F
Temperature	°C	Electrode YSI Model 57 Meter	EPA 170.1 YSI Instrument Manual
TN	mg/L	Calorimetric Automated Ascorbic Acid Alpkem Flow IV SFA Instrument	SM 4500-N_{org} -D
TP	mg/L	Calorimetric Automated Ascorbic Acid Alpkem Flow IV SFA Instrument	EPA 365.1 SM 4500-P-F
TSS and VSS	mg/L	Gravimetric	EPA 160.2 and 160.4 SM 2540 D and 2540 E
Dissolved Metals Cd, Cu, Pb	µg/L	PE 3100XL ICP-OES and PE 5100PC Graphite Furnace	EPA 200.7 and 213.2
Total Fe	µg/L	PE 3100XL ICP-OES and PE 5100PC Graphite Furnace	EPA 200.7 and 213.2
Turbidity	NTU	Nephelometric DRT-15CE Turbidimeter	EPA 180.1 SM 2130 B

YSI = Yellow Springs Instrument Co., Inc.; PE = Perkin Elmer; SFA = Segmented Flow Analysis

12. Quality Control Requirements

The URI Environmental Engineering laboratories apply the following general rules for all analyses conducted with the exception of suspended solids (SS), BOD_5, turbidity, pH, and constituents measured in the field. Field instruments are checked throughout the sampling run as described in the procedures for each instrument.

1. Initial calibration with 3 to 5 standards and a reagent blank is run for all analytical methods.

2. Calibration curves are checked with an initial calibration verification standard (ICV), and continuing calibration standards (CCV) are conducted at intervals that are 5% of the sample number analyzed.

3. Reagent blanks are run with the samples, one per sample set.

4. Procedural or method blanks are run with all samples that require pretreatment prior to the analysis.

6. Spiked samples and matrix spikes are run for every set of samples analyzed, and all samples are sampled in duplicate to check the precision of the analyses.

Spiked samples will be prepared and measured for trace metals, chloride, and all nutrients. The samples are selected at random and will be spiked with a known standard concentration. Percent recovery of spiked standards is expected to be between 80 and 120%.

Duplicates sample analyses will be run for all nutrients and trace metal samples and the relative standard deviation (RSD) measured. Any RSD greater than 20% will require the sample to be re-run. An additional test of precision will be based on triplicate analyses carried out on two or more stations per survey.

The completeness of the study will be measured as the percentage of total samples collected that were completely analyzed.

All constituent concentrations will be corrected by using reagent and procedural blanks. The results of the trip and procedural blanks will be presented in the annual report.

13. Instrument/Equipment Testing, Inspection and Maintenance

All instrument and equipment calibration and inspection procedures can be found in the section covering analytical procedures. Maintenance logs for the field equipment, trace metal and nutrient analyzers will be maintained in the CVE laboratories.

14. Instrument Calibration and Frequency

The instrument calibration procedures and frequency can be found in the analytical procedures for the constituents of interest.

15. Inspection/Acceptance Requirements

All reagent chemicals and standards will be checked by the URI QA Project Officer. A master chemical list is maintained by the URI QA officer and a copy is on file with the URI Safety Department.

16. Data Acquisition Requirements

There will be no data acquired from external sources.

17. Data Management

The URI Project Manager and QA Officer will be responsible for the proper collection of analyzed data, preparation and transmission of results to RIDEM. Prior to transmission of results, both managers will review all analytical data for accuracy and will maintain file copies of the data in the project file at URI.

18. Assessment and Response Actions

Laboratory data will be periodically assessed to ensure that the collected data is usable for the purposes of this project. Laboratory results will be reviewed to verify that values are within the acceptable range of each parameter. Any discrepancies will be discussed with the project QA Officer to assess the need to re-test the sample. Outlier data will be reported in the final report and potential sources of error will be described.

19. Reports

The data sets for the first two dry surveys will be submitted to RIDEM within 30 days of the completion of the second (Subset #1) survey. The water quality interpretation will include all surveys. A draft report is to be submitted prior to the final comprehensive report, and will include all results and the data interpretation for all surveys. A comprehensive final report is to be delivered to RIDEM in hardcopy and in electronic format. The URI Project Manager will synthesize all data taken for this project and forward this to RIDEM.

20. Data Review, Validation, and Verification

All data will be reviewed by the URI Project and rechecked by the project QA Officer for completeness and accuracy. All data collected will be included in the Final draft Report. Once data is collected, it is entered into Microsoft Excel files. The project manager will review log

sheets and proofread the data entry for any errors, and correct any. Outliers and inconsistencies will be flagged for further review with the Project QA Officer. Problems will be discussed in the final report. Decisions to qualify or reject data will be made by the Project Managers and the QA Officer.

21. Reconciliation with Project Goals

If the data collected meet the criteria in Sections 5A, 6A, 11, 12, and the SOPs, then the project quality objectives have been met. If the criteria have not been met, the project team will determine if additional data needs to be collected.