Sands Pond Quality Assurance Project Plan

Lead Organization: Rhode Island Department of Environmental Management
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A3.0 Distribution List (EPA-NE QAPP Worksheet #3)

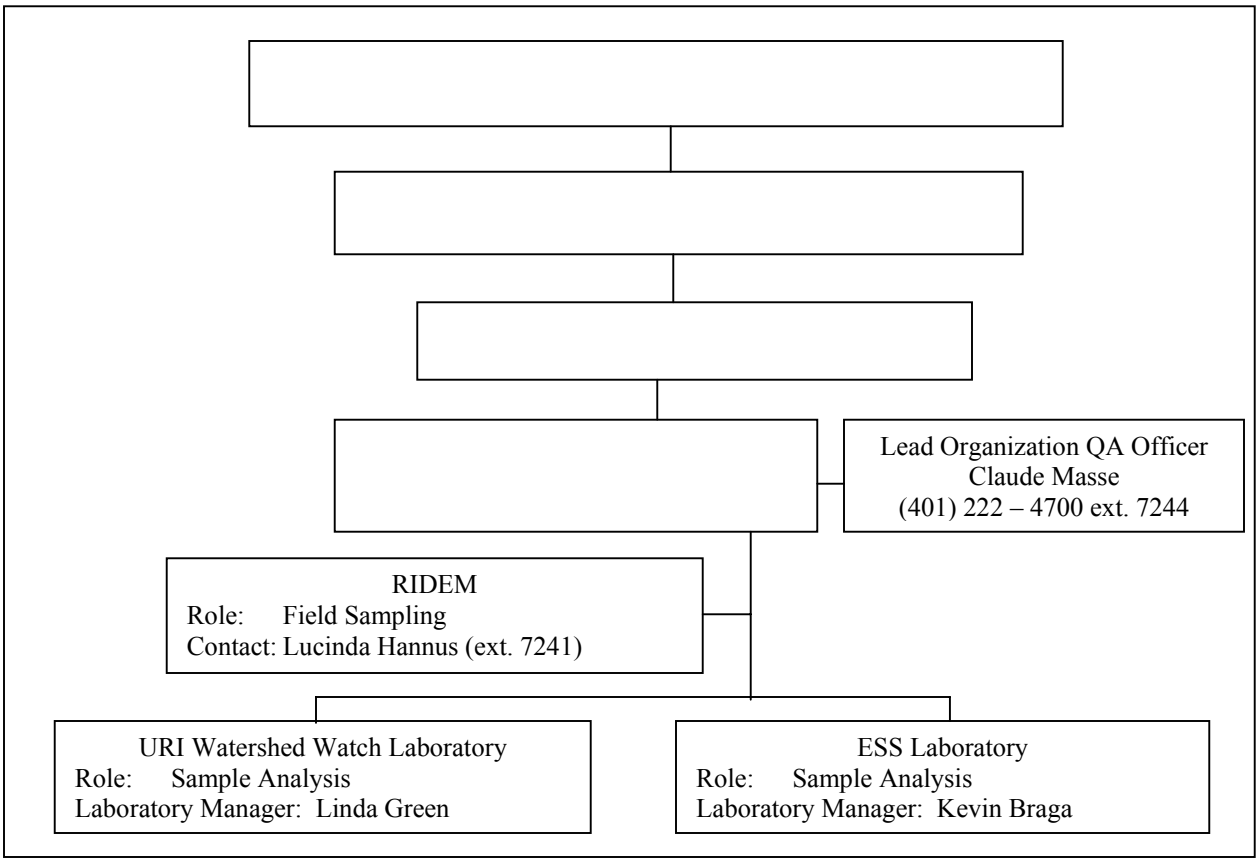
Table A3. 1 Distribution List Worksheet #3

QAPP Recipients	Title	Organization	Telephone Number
Wayne Jenkins	Supervisor	RIDEM	(401) 222-4700 ext. 7272
Lucinda Hannus	Project Manager	RIDEM	(401) 222-4700 ext. 7241
Claude Masse	QA Officer	RIDEM	(401) 222-4700 ext. 7244
Steve DiMattei	EPA QA Quality Assurance Chemist	Lexington Laboratory New England EPA	(781) 860-4369
Al Basile	EPA Project Officer	USEPA	(617) 918-1599
Linda Green	Laboratory Manager	URI Watershed Watch Laboratory	(401) 874-2905
Kelly DeSousa	Laboratory QA/QC Manager	ESS Laboratory	(401) 461-7181

A4.0 Project Organization

A4.1 Project Organizational Chart

Figure A4. 1 Project Organizational Chart



A4.2 Communication Pathways

This sampling will occur primarily during dry weather, but will include an initial wet weather survey. Storm criteria is discussed in Section B8.0. Rhode Island Department of Environmental Management (RIDEM) personnel will conduct sampling from a boat. University of Rhode Island Watershed Watch (URIWW) and ESS Laboratories will analyses the samples. Two RIDEM staff will perform each sampling event, which includes the Project Manager and an additional RIDEM Total Maximum Daily Load (TMDL) group staff person. This additional staff person may vary from sampling event to sampling event depending upon individual schedules and availability. All staff within the TMDL group are equally qualified to conduct this routine sampling, and are trained in acceptable procedures.

The Project Manager will monitor the weather and will contact RIDEM staff to schedule surveys. Prior to the beginning of the sampling season, the Project Manager will contact URIWW and ESS Laboratories to obtain sample bottles. These bottles will be kept at RIDEM and used during all sampling events.

A4.2.1 Modifications to Approved QAPP

It may be necessary to make changes to the sampling plan due to the results of the dry and wet weather shoreline surveys. The Project Manager shall record all modifications to the sampling plan and the decision to add, drop or relocate stations will be made jointly by the QA Officer and the Project Manager. All changes to the QA Plan will be reported in the sampling Status Report and the Final Report.

A4.3 Personnel Responsibilities and Qualifications

Each sampling event shall be performed by the Project Manager and an additional RIDEM, Office of Water Resource (OWR) staff person. This person will have been trained and is qualified to conduct this routine sampling. A copy of the Quality Assurance Project Plan (QAPP) will be provided to the staff person for review, prior to conducting sampling. The Project Manager shall record on the field sheet the name and title of the additional staff person who accompanied the Project Manager on the sampling run.

A5.0 Project Planning / Problem Definition

Sands Pond is identified on the State of Rhode Island's 303(d) lists of 1998 and 2000 as being impaired for Excess Algae Growth, Taste and Odor and Turbidity. The goal of this sampling program is to document water quality and to quantify inputs into the pond in both wet and dry conditions. During this sampling program, RIDEM will collect and organize all existing information and obtain additional information as required to develop a TMDL for this watershed.

TMDLs are required under Section 303(d) of the Clean Water Act and USEPA's Water Quality Planning and Management Regulations (40 CFR Part 130). The goal of this TMDL study is to quantify the existing loadings from nonpoint and point sources into Sands Pond and to establish the impact that these loadings have on water quality. At the completion of the study, the necessary load reductions needed to achieve water quality standards will be established.

A5.1 Project Planning Meetings

The Project Manager and Project Supervisor have had several informal meetings to formulate and define the purpose and expected results of this project. In addition, a site visit was completed on April 6, 2001 to allow the project team to become familiar with the watershed and to make initial contact with Block Island Water Company (BIWC) personnel and town land use officials.

Table A5. 1 Project Scoping Meeting Attendance Sheet

Program: TMDL			Site Name: Sands Pond	
Project Manager: Lucinda Hannus, RIDEM			Site Location: New Shoreham, RI	
Date of Meeting: April 6, 2001 Meeting Location: Sands Pond, New Shoreham, RI Town Hall, New Shoreham				
Name	**Project Role**	**Affiliation**	**Phone #**	**e-mail address**
Lucinda Hannus	Project Manager	RIDEM	401-222-4700 ext. 7241	Lhannus@dem.state.ri.us
Wayne Jenkins	Project Supervisor	RIDEM	401-222-4700 ext. 7272	Wjenkins@dem.state.ri.us
Joseph Shea	Acting Water Official	Town of New Shoreham	401-466-3232	
Marc Tillson	Building/Zoning Official	Town of New Shoreham	401-466-3206	
Meeting Purpose: Obtain available background information on watershed, water quality data and town zoning and land use information. Obtained copies of misc. data sheets, zoning maps, and plat maps. Toured area to obtain general site conditions.				
Comments and action items:				

A5.2 Sands Pond Watershed

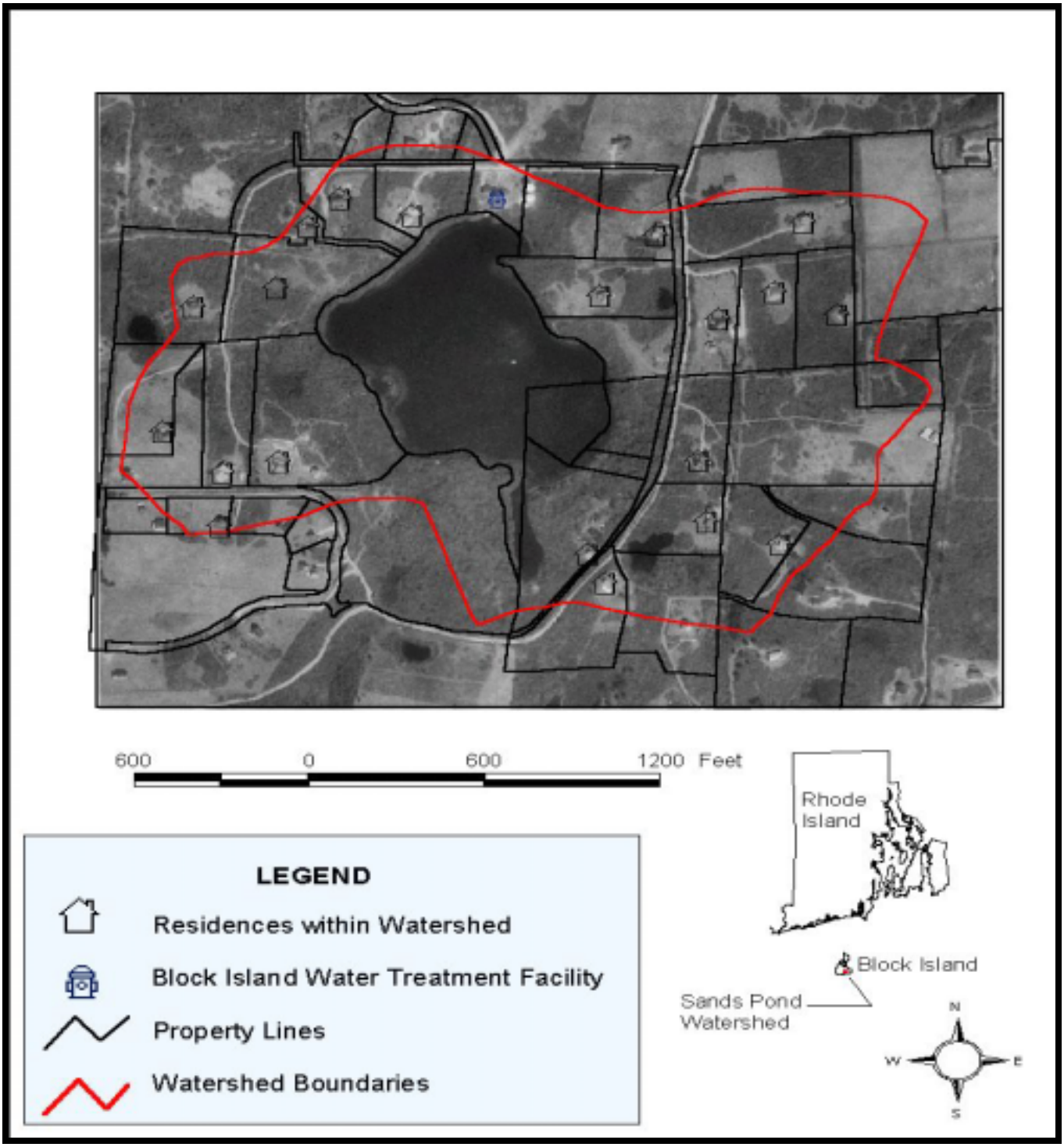
Sands Pond is a Class A waterbody, included in Group 2 on RI's 303(d) lists (High priority for TMDL development). Sands Pond is a 14-acre, relatively shallow public water supply reservoir located in the town of New Shoreham. New Shoreham is the only town located on the island of Block Island. Block Island is located approximately twelve miles south of the Rhode Island mainland. The Block Island Water Company (BIWC) is currently drawing water from a system of six adjacent wells and not the pond. The BIWC has stated (personal discussion Joseph Shea, BIWC) that the pond would only be used during high demand periods as a backup to the existing system of wells.

In addition to being Class A waters, Sands Pond is also identified by the RIDEM as a Special Resource Protection Water (SRPW). RIDEM's Water Quality Regulations define SRPW as those waters that are high quality surface waters having significant ecological or recreational uses. All public drinking water supplies are designated SRPW

Currently, there are twenty (20) residences and the BI Water Treatment facility located within the Sands Pond watershed. All of these homes rely upon on-site septic systems for the treatment of septic waste. The watershed for the pond includes approximately 88 acres of residentially developed, open space, and the BI Water Treatment facility. The zoning for the entire watershed is RA (Town of New Shoreham Zoning Ordinance, Eff. June 17, 1994), which requires a minimum lot size of 120,000 sq. ft. (2.75 acres) of developable land per homesite. The average lot size currently platted within the watershed is approximately three acres. There are no major agricultural sites developed within the watershed. Farming is allowed within an RA zone and the stabling of horses is only allowed by Special Use Permit.

Rhode Island General Law (R.I.G.L.) 46-14-1 prohibits bathing, swimming, discharge of sewage or drainage or refuse or polluting matter which may corrupt or pollute or impair the purity or quality of a public drinking water supply. State law further prohibits such use or any other activity in, on or in the immediate vicinity in which the director of health deems to render the water supply injurious to public health. Figure A5.1 is an aerial map of the Sands Pond watershed.

Figure A5. 1 Sands Pond Watershed



A6.0 Project Description and Schedule

A TMDL report is required for all waterbodies that do not meet their designated uses. Sands Pond is impaired by excess algae growth, taste, odor and turbidity. The requirements of the TMDL process have determined the scope of the Sands Pond study. The Sands Pond TMDL will be developed for total phosphorous, as phosphorous has been determined to be the limiting nutrient to algal growth in this system. RIDEM will quantify the phosphorous, chlorophyll a and turbidity loads within the waterbody in order to determine the impacts of these loads to water quality.

Table A6. 1 Contaminants of Concern

Contaminant	Analytical Method	Achievable Laboratory Limits	Project Limits	Laboratory
Total Phosphorous	URIWW SOP SP-1	0.01 (mg/l)	25 ppb (ug/l)	URIWW
Ortho-phosphate Phosphorous	URIWW SOP SP-2	0.005 (mg/l)	25 ppb (ug/l)	URIWW
Chlorophyll a	URIWW SOP SP-3	1.0 ppb (ug/l)	<10 ppb (ug/l)	URIWW
Turbidity	ESS SOP SP-4	0.02 NTU	5 NTU over background	ESS
Dissolved Oxygen	YSI – Model 85	0.01 (mg/l)	5.0 mg/l	YSI Model 85
Temperature	YSI – Model 85	+/- 2^0 C Field Measurement	Profile stratification	Field Sample

A6.1 Project Overview

Historically, Sands Pond has displayed non-attainment of turbidity standards. There has also been a history as reported by the Rhode Island Department of Heath (RIDOH) of taste and odor problems. Turbidity as measured in Nephelometric Turbidity Units (NTU) has exceeded the standard of 5 NTU over background. For this project a background level of 5 NTU will be used, resulting in a project limit of 10 NTU. BIWC sampling results ranged from a low of 2.19 NTU in March, 2000 to a high of 28.20 NTU in September, 2000. Average monthly ranges vary from a low of 2.49 NTU to a high of 16.30 NTU for the same time period.

Odors vary with the source and concentration. Most odors reported by public water users, besides chlorine, is a result of decaying organic material, decaying distribution lines or from home water heaters. Odor problems were indicated by the RIDOH in 1988 through 1992. Odors are a judgement call by the laboratory ranging in values of 1 – weak to 5 – strong. Sands Pond samples were rated from a musty 1 to a swampy –3 during this time period. Chlorine was also noted at a level 2 on two occasions.

Taste is a subjective parameter and varies widely between people. The sources of most complaints come from high levels of chlorine or high mineral content. Dissolved inorganic salts of potassium, sodium, zinc, copper, manganese and iron can be detected by taste and produce bitter or sour tastes. There is no data available to indicate the specific tastes that are objectionable with this water. As the Preliminary Data Report is developed

for this TMDL, all available data will be detailed for all impairments. Taste will not be reported as a sampling result but will be implicitly addressed by reducing nuisance algal species.

This watershed has no known point sources following the initial site survey. During the initial dry weather sampling, a shoreline survey will be conducted to determine the accuracy of this statement. Non-point sources include groundwater infiltration, surface runoff, and wildlife impacts. Likely sources include groundwater containing high levels of nutrients from improperly or under-treated septic waste, nitrates and phosphates from the use of fertilizers on residential lawns or agricultural uses and waterfowl/ wildlife droppings. Silt and clay sediments, inorganic and organic matter, algae and other microscopic organisms such as bacteria influence turbidity levels. The likely sources of these contaminates are from stormwater and wind erosion, untreated runoff from gravel roads, fluctuating water levels influencing organic growth within the pond and possibly improperly treated septic waste.

The monitoring program for this TMDL will be used to establish the existing water quality in Sands Pond. Sampling results for total phosphorous (TP), ortho-phosphate phosphorous (OP), chlorophyll a, dissolved oxygen and temperature will all be used to assess this waterbody's trophic condition. Turbidity levels will be monitored to determine reduction requirements. Odors will be considered by the sampler and noted during each sampling period. Seasonal fluctuations and critical conditions will be analyzed by monitoring through the spring to fall season, since winter conditions typically do not exceed standards. Wet and dry conditions will also be sampled. A review by New Shoreham wastewater facilities officials of existing septic systems within the watershed will be used to determine loadings associated with their use. Information gathered from this monitoring program will be used to establish reductions in concentrations of contaminants in order to achieve compliance with the state's water quality standards for this waterbody.

Table A6. 2 Analytical Services Table

Medium/ Matrix	Analytical Parameter	Analytical Method / SOP	No. Of Sampling Locations	No. of Field Duplicates	Total No. Samples to Laboratory	Data Package Turnaround	Laboratory
Surface Water	Total Phosphorous	SOP -1	6[1]	2	8	10 Days	URIWW
Surface Water	Ortho-phosphate Phosphorous	SOP -2	6[1]	2	8	10 Days	URIWW
Surface Water	Chlorophyll a	SOP -3	6[1]	2	8	10 Days	URIWW
Surface Water	Turbidity	SOP -4	6[1]	2	8	10 Days	ESS
Surface Water	Dissolved Oxygen	Field SOP FSOP-7	6[1]	N/A	N/A	N/A	Field Measurement
Surface Water	Temperature	Field SOP FSOP-7	6[1]	N/A	N/A	N/A	Field Measurement
Surface Water	Odor	Field SOP FSOP-5	3[1]	N/A	N/A	N/A	N/A

[1] Samples for TP, OP, Chlorophyll a, T, DO and Temp. will be taken at two water levels, one at the surface and the other at full depth.

The following tasks outline the steps needed to accomplish the objectives of the sampling program.

Task 1 Review Existing Data

As part of the development of the Preliminary Data Report, review and analysis of all existing data will be completed. Sources of data include but are not limited to, previous studies of pond water quality, and sampling performed by BIWC, sampling preformed by RIDOH and studies of surrounding land use and septic system status by the town of New Shoreham. Other available data will be used if, during the data collection phase, it is determined to be of suitable quality and relevance.

Task 2 Depth Measurement

The Project Manager shall conduct a limited bathymetric survey of the pond bottom with the assistance of an additional staff person. A transect grid pattern will be established to locate depth measurements. The transect shall be established on a 200' x 200' grid. Visual observations of transect lines shall be noted in the field notebook and drawn on the aerial map of the pond. Depth measurements shall be take at 200 foot intervals along the transect line. These depth measurements shall be recorded on the field sheet in which a copy is provided in Appendix A.

Task 3 Monitoring Program

Beginning in the spring of 2001, a sampling program consisting of three in pond sampling stations will initially be commenced. Additional stations may be added if wet weather conditions within the watershed warrant additional sampling locations. The three locations are:

1. Station SP1 Located offshore, adjacent to the BIWC treatment facility intake pipe;
2. Station SP2 Located along the shoreline, in fairly shallow water and;
3. Station SP3 Located centrally in the pond at the point of greatest depth.

These locations were chosen to compare historic sampling data at the BIWC intake pipe at site 1, site 2 (which is the most critical zone of the pond) and site 3, which is in the deepest water. A map depicting the locations chosen will be included upon completion of the bathymetric survey. Sampling weather criteria is outlined in section B8.0 of this report.

Task 3 Shoreline Surveys

Due to the limited accessibility to the shorelines of Sands Pond, little is currently known about runoff flow paths within the watershed. During the first dry-weather sampling run, a shoreline survey shall be completed by the sampling team. Observations of the shoreline edge and detailed descriptions, which include type and locations of any discharge pipes or areas of concentrated runoff shall be noted in the field notebook. A copy of a map of the pond and surrounding watershed shall also be provided, and any discharge of note shall be located

on this map. The information from the field notebook and location map will then be incorporated into the GIS database for further analysis. If any "point" discharges are located the sampling locations and number of samples collected may be modified to address these discharges.

In addition to the dry weather shoreline survey, during the first wet weather sampling event an additional shoreline survey will also be conducted to locate any additional points of discharge into the pond, or to verify the observations made during the dry weather reconnaissance. Any observations warranting a change in sampling locations shall be indicated in the field notebook by the sampling team. Modifications to the wet weather monitoring program may be made if so warranted.

Task 5 Map Production

Using Rhode Island GIS data, Block Island GIS data and other available internet mapping resources, maps and diagrams depicting land use, soils, hydrologic conditions, septic system locations, buildings and other essential evaluation parameters, will be produced for this TMDL. Additional data from New Shoreham wastewater officials regarding the status of individual septic systems (ISDS) within the watershed will also be evaluated and incorporated into the TMDL. A margin of safety will be developed to ensure compliance with water quality standards regardless of the imperfections inherent to environmental studies and natural conditions. Seasonal variations will be taken into account and consideration of future changes within the watershed will also be addressed. An implementation plan is an integral part of a TMDL and the implementation plan will be made based on observations, data, analysis and interpretation of all information collected during the monitoring period.

A6.2 Project Schedule

Table A6. 3 Project Schedule.

Task	Deliverable	2000								2001
		M	J	J	A	S	O	N	D	J
Review Existing Data[1]	Monitoring Plan									
QAPP Preparation	QAPP Document									
Site Preparation	NA									
Sample Collection	NA									
Laboratory Analysis	Laboratory Report									
Final Data Report	Final Data Report									

A7.0 Project Quality Objectives and Measurement Performance Criteria

Collecting high quality data is one of the most important goals of this project. Specific data quality objectives include method detection limits, precision, accuracy, representativeness, comparability, and completeness. All the data quality objectives will be met if the data collected is sufficient to complete the TMDL.

A7.1 Measurement Performance Criteria

Representativeness

The selected stations and sampling frequency were chosen for their representativeness of conditions in the waterbody. The sampling targets dry weather because this is when Sands Pond would have the greatest exceedance of its water quality standards.

Comparability

To maximize the quality of the data collected, and to collect data that is comparable with other studies, accepted sampling procedures will be used during this study. All samples collected will be sent to laboratories that use Standard Methods.

Sensitivity

Analytical methods were selected such that detection limits will not limit the usefulness of the data set.

Completeness

If the data collected is sufficient to complete the TMDL report, than the data is considered to be complete. Measurement performance criteria help determine the completeness of a data set. Tables, A7.1 through A7.4 document the measurement performance criteria for this project.

Table A7. 1 Total Phosphorous Measurement Performance Criteria

Sampling SOP	SOP-1
Medium/Matrix	Surface Water
Analytical Parameter	Total Phosphorous
Concentration Level	2 ppb (ug/l)

Data Quality Indicator	Analytical Method/ SOP Reference/ Laboratory	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S/A)
Precision	SM 4500-P F/ URIWW- SOP-1	<20%RPD	Lab Duplicates	A
Accuracy/bias Contamination	SM 4500-P F/ URIWW- SOP-1	< 2 ppb (ug/l)	Method Blank	A
Accuracy/bias Contamination	SM 4500-P F/ URIWW- SOP-1	Quantitation within limits	Performance Evaluation Standards - PES	A
Data - Completeness	SM 4500-P F/ URIWW- SOP-1	Data collected are determined to be useable	Anticipate 100%	A
Accuracy	SM 4500-P F/ URIWW- SOP-1	< 20 % RPD	Field Duplicates	S/A

Table A7. 2 Ortho-phosphate Phosphorous Measurement Performance Criteria

Sampling SOP	SOP-2
Medium/Matrix	Surface Water
Analytical Parameter	Ortho-phosphate Phosphorous
Concentration Level	2 ppb (ug/l)

Data Quality Indicator	Analytical Method/ SOP Reference/ Laboratory	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S/A)
Precision	SM 4500-P F/ URIWW- SOP-1	<20%RPD	Lab Duplicates	A
Accuracy/bias Contamination	SM 4500-P F/ URIWW- SOP-1	< 2 ppb (ug/l)	Method Blank	A
Accuracy/bias Contamination	SM 4500-P F/ URIWW- SOP-1	Quantitation within limits	Performance Evaluation Standards - PES	A
Data - Completeness	SM 4500-P F/ URIWW- SOP-1	Data collected are determined to be useable	Anticipate 100%	A
Accuracy	SM 4500-P F/ URIWW- SOP-1	< 20 % RPD	Field Duplicates	S/A

Table A7. 3 Chlorophyll a Measurement Performance Criteria

Sampling SOP	SOP-3
Medium/Matrix	Surface Water
Analytical Parameter	Chlorophyll a
Concentration Level	0.1 ug/l

Data Quality Indicator	Analytical Method/ SOP Reference/ Laboratory	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S/A)
Precision	SOP -3	20% RPD	Replicates	S/A
Accuracy/bias Contamination	SOP -3	< MDL	Method Blank	A
Accuracy/bias Contamination	SOP -3	<20% RPD	Pure Chl-a standards Turner Design	A
Data - Completeness	SOP -3	Data collected are determined to be useable	Anticipate 100%	A
Accuracy	SOP -3	<20% RPD	Lab Duplicates	A

Table A7. 4 Turbidity Measurement Performance Criteria

Sampling SOP	SOP-4
Medium/Matrix	Surface Water
Analytical Parameter	Turbidity
Concentration Level	0.02 NTU

Data Quality Indicator	Analytical Method/ SOP Reference/ Laboratory	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S/A)
Precision	SOP -4	+/- 20% RPD	Field Duplicates	S/A
Accuracy/bias Contamination	SOP -4	< MDL	Method Blank	A
Data - Completeness	SOP -4	Data collected are determined to be useable	Anticipate 100%	A
Accuracy	SOP -4	+/- 20% RPD	Field Duplicates	S/A

B8.0 Sampling Process Design

Weather Criteria

Dry Weather sampling shall be performed every two weeks during the months of June 2001 through September 2001. Sampling shall take place during dry conditions once during the months of May and October 2001. Dry weather is when there has been an antecedent dry period (ADP) of a minimum of three days prior to sampling.

Wet weather sampling shall take place during a storm event in June 2001. During this initial sampling run, a shoreline survey will also be conducted to observe runoff conditions during a storm event within the watershed. Particular attention shall be given for any collection and discharge points of overland flow, sedimentation plumes into the pond or any point discharges not observed during the initial dry weather shoreline survey. Additional sampling will be required if such discharges are observed and an adjustment in the sampling monitoring plan will be made. To be considered a storm event, the following characteristics must apply.

- Minimum rainfall of 0.5 inches in a 24-hr period;
- Minimum duration of 5 hours; and
- Minimum of three pre-storm dry days

B8.1 Sampling Design Rationale

Task 1A Source Sampling

Task 1 outlined in Section A6.1 describes the process for deciding sampling stations. Stations were chosen based on existing knowledge of the waterbody and watershed. Upon completion of the first shoreline survey and after the depths of the pond have been established, the three stations shall be further defined and located in the field notebook. Bearings for establishing the actual locations of the sampling station shall be thoroughly detailed in the field notebook such that sampling station locations can be duplicated upon subsequent sampling runs. The number, location and frequency of sampling may be modified following the initial dry and wet weather surveys. The Project Manager and QA Officer shall document any amendment to the monitoring plan or any changes to sampling locations that have been made and the rational for these changes will be documented in the Preliminary Data Report.

B9.0 Sampling Procedures and Requirements

B9.1 Sampling Procedures

Standard Operating Procedures (SOPs) for field sampling are located in Appendix B of this report.

Table B9. 1 Project Sampling SOP Reference Table

Reference Number/Title	Originating Organization	Equipment Identification	Modified for Work Project
Field Sampling SOP FSOP-1 Total Phosphorous Sampling	RIDEM	Not applicable	No
Field Sampling SOP FSOP-2 Ortho-phosphate Phosphorous Sampling	REDEM	Not applicable	No
Field Sampling SOP FSOP-3 Chlorophyll a Sampling	RIDEM	Not applicable	No
Field Sampling SOP FSOP-4 Turbidity Sampling	RIDEM	Not applicable	No
Field Sampling SOP FSOP-5 Odor Sampling	RIDEM	Not applicable	No
Field Sampling SOP FSOP-6 Depth Measurement	RIDEM	Calibrated weighted Line	No
Field Sampling SOP FSOP-7 Dissolved Oxygen and Temperature	RIDEM	YSI Model 85	No

B9.2 Equipment Cleaning

The laboratory that completes the sample analysis will provide the appropriate sterile bottles for sample collection.

B9.3 Field Equipment Calibration and Maintenance

The project manager shall ensure that all field equipment is accurate.

Table B9. 2 Field Sampling Equipment Calibration Table

Equipment	Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	SOP Reference
YSI Model 85	See Owners Manual	Before Sampling Season	+/- 0.3 mg/l	Re-calibrate	E-1
Calibrated weighted line	Check accuracy	Prior to first sampling run, and throughout monitoring	$\pm$ 1.0 inches	Repair or replace	FSOP - 6

B9.4 Inspection and Acceptance Requirements for Sample Containers

The Project Manager shall ensure that all sample containers are acceptable for use. Each respective laboratory shall provide sampling bottles as required. The Project Manager shall appropriately maintain this bottle supply. A log shall be kept in the project notebook documenting receipt and labeling of each sample bottle. All certificates of cleanliness shall be retained in the project file. Reference is also made to the appropriate SOP' attached to this document for each constituent and respective laboratory.

B10.0 Sample Handling, Tracking and Custody Requirements

B10.1 Field Notes

The Project Manager shall maintain a three ring binder containing field sheets. During the first dry weather survey, the depth measurements and general pond configuration shall be used to determine the station locations based on the criteria described in Task 3, Monitoring Program. It shall also include any indications of any areas of the shoreline that has the potential or is a point source for runoff. The Project Manager shall also record any changes to the sampling locations or number of stations and the reason thereof. The field binder shall also contain the information gathered from the depth measurements taken during the initial dry weather survey. The Project Manager shall transfer all data obtained and recorded on the field sheets to the project notebook and shall retain the field sheets in the project file.

B10.2 Sample Tracking

The Sample ID contains the Station Number followed by a letter noting the contaminant to analyze, followed by the notation indicating surface (S) or deep-water (D) sample. For example, the Station SP-1 sample for total phosphorous at the surface would be labeled SP-1-TP-S. The following is a list of the contaminants and their nomenclature.

Total Phosphorous	"TP"
Ortho-phosphate Phosphorous	"OP"
Chloropyll a	"C'
Turbidity	"T"
Odor	"O"

All sample bottles shall be labeled prior to the sampling run by the Project Manager. The station number, including sample type and depth, date, time and initials shall be filled in prior to sampling using a permanent marker.

B10.3 Sample Handling, Tracking , and Custody

All samples will be taken according to the requirements outlined in the field sampling SOP for each contaminant. The Project Manager or a designee shall deliver the samples to the appropriate laboratory for analysis. Copies of the chain of custody forms for each laboratory are included in APPENDIX C.

Table B10. 1 Sample Handling System

	Responsible Party	Samples
Sample Collection	RIDEM	In pond
Sample Delivery	RIDEM	In pond
Sample Analysis	URIWW ESS Laboratory	In pond
Sample Archival	None	N/A
Sample Disposal	URIWW ESS Laboratory	In pond

B11.0 Field Analytical Method Requirements

During sampling the dissolved oxygen, temperature and odor will be analyzed in the field. The Project Manager shall record in the field notebook the sample location and all results of field measurements. Any indication of any particular odor such as musty, swampy, none, or a description of any indication of any offensive odor that is believed to be exclusive of natural background or may be due to excess algae influence shall be indicated in the field notebook. Field Sampling SOPs are provided in APPENDIX B.

B11.1 Field Analytical Methods and Standard Operating Procedures

Table B11. 1 Field Analytical Method/SOP Reference Table

Reference Number	Title, Revision Date and/or Number	Definitive or Screening Data	Originating Organization	Analytical Parameter	Instrument	Organization Performing Field Analysis	Modified for Project Work Plan Y or N
FSOP – 5	RIDEM – Procedure for field sampling Odor	Screening	RIDEM	Odor	N/A	RIDEM	N
FSOP – 6	RIDEM – Procedure for field sampling Depth	Screening	RIDEM	Depth Measurement	Calibrated Line	RIDEM	N
FSOP – 7	RIDEM – Procedure for field sampling Dissolved Oxygen and Temperature	Definitive	RIDEM	Dissolved Oxygen	YSI Model 85	RIDEM	N
				Temperature	YSI Model 85	RIDEM	N

B12.0 Fixed Laboratory Analytical Method Requirements

All samples shall be taken to the appropriate laboratory for analysis. These samples will be analyzed according to the attached Standard Operating Procedures (SOP) from each of the laboratories(See Appendix D).

B12.1 Fixed Laboratory Analytical Methods and Standard Operating Procedures

Table B12. 1 Fixed Laboratory Analytical Method/SOP Reference Table

Reference Number	Fixed Laboratory Performing Analysis	Title, Revision Date and/or Number	Definitive or Screening	Analytical Parameter	Instrument	Modified for Work Project Y or N
SOP – 1	URIWW	SOP-1 Total Phosphorous & Total Nitrogen	Definitive	Total Phosphorous	Alpkem Corp. Model –300 Autoanalyzer	N
SOP – 2	URIWW	SOP – 2 Ortho-phosphate phosphorous	Definitive	Ortho-phosphate phosphorous	Alpkem Corp. Model –300 Autoanalyzer	N
SOP – 3	URIWW	SOP – 3 URI Watershed Watch Chlorophyll – A Analysis Procedure	Definitive	Chlorophyll –a	Turner Designs Digital Flurometer Model TD-700	N
SOP – 4	ESS Laboratory	SOP –4 Method # 180.1 , Turbidity (Nephelometric) Storet No. 00076	Definitive	Turbidity	Hatch Turbidimeter, Model 2100 and 2100 A	N

B13.0 Quality Control Requirements

Table B13. 1 Field Sampling QC: Total Phosphorous

Sampling SOP	FSOP-1
Medium / Matrix	Surface Water
Analytical Parameter	Total Phosphorous
Concentration Level	2 ppb (ug/l)
Analytical Method/ SOP Reference	SOP-1

QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person Responsible for Corrective Action
Field Duplicates	Minimum 1 per 5 samples	FSOP-1	Discuss any problems with Project Quality Control Officer	Project Manager
Cooler Temperature Blank	1 Per Cooler	4^0 C or less	Add Ice / Re- sample	Project Manager

Table B13. 2 Field Sampling QC: Ortho-phosphate Phosphorous

Sampling SOP	FSOP-2
Medium / Matrix	Surface Water
Analytical Parameter	Ortho-phosphate Phosphorous
Concentration Level	2 ppb (ug/l)
Analytical Method/ SOP Reference	SOP-2

QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person Responsible for Corrective Action
Field Duplicates	Minimum 1 per 5 samples	FSOP-2	Discuss any problems with Project Quality Control Officer	Project Manager
Cooler Temperature Blank	1 Per Cooler	4^0 C or less	Add Ice / Re- sample	Project Manager

Table B13. 3 Field Sampling QC: Chlorophyll – a

Sampling SOP	FSOP-1
Medium / Matrix	Surface Water
Analytical Parameter	Chlorophyll –a
Concentration Level	0.1 ug/l
Analytical Method/ SOP Reference	SOP-3

QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person Responsible for Corrective Action
Field Duplicates	Minimum 1 per 5 samples	FSOP-3	Discuss any problems with Project Quality Control Officer	Project Manager
Cooler Temperature Blank	1 Per Cooler	4^0 C or less	Add Ice / Re- sample	Project Manager

Table B13. 4 Field Sampling QC: Turbidity

Sampling SOP	FSOP-4
Medium / Matrix	Surface Water
Analytical Parameter	Turbidity
Concentration Level	0.5 NTU
Analytical Method/ SOP Reference	SOP-4

QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person Responsible for Corrective Action
Field Duplicates	Minimum 1 per 5 samples	FSOP-4	Discuss any problems with Project Quality Control Officer	Project Manager
Cooler Temperature Blank	1 Per Cooler	4^0 C or less	Add Ice / Re- sample	Project Manager

Table B13. 5 Fixed Laboratory Analytical QC: Total Phosphorous

Sampling SOP	SOP-1
Medium / Matrix	Surface Water
Analytical Parameter	Total Phosphorous
Concentration Level	Ug/l
Laboratory	URI Watershed Watch

Laboratory QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action (CA)	Person (s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	2 per set of 90 samples	<QL	Re-run	Linda Green	Accuracy/contamination	<Ql
Reagent Blank	2 per set of 90 samples	<QL	Re-run	Linda Green	Accuracy/contamination	<Ql
Storage Blank	N/A					
Instrument Blank	N/A					
Laboratory Duplicate	All samples are analyzed in duplicate or triplicate	<20%RPD	Re-run	Linda Green	Precision	<20%RPD
Laboratory Matrix Spike	N/A					
Matrix Duplicate Spikes	N/A					
LCS	Purchase external standard 2 per set of 90 samples	15%cv	Re-run	Linda Green	Accuracy/precision	15% cv
LFB	N/A					
Surrogates	N/A					
Internal Standards (ISs)	N/A					

Table B13. 6 Fixed Laboratory Analytical QC: Ortho-phosphate phosphorous

Sampling SOP	SOP-2
Medium / Matrix	Surface Water
Analytical Parameter	Ortho-phosphate phosphorous
Concentration Level	Ug/l
Laboratory	URI Watershed Watch

Laboratory QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action (CA)	Person (s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	2 per set of 90 samples	<QL	Re-run	Linda Green	Accuracy/contamination	<Ql
Reagent Blank	2 per set of 90 samples	<QL	Re-run	Linda Green	Accuracy/contamination	<Ql
Storage Blank	N/A					
Instrument Blank	N/A					
Laboratory Duplicate	All samples are analyzed in duplicate or triplicate	<20%RPD	Re-run	Linda Green	Precision	<20%RPD
Laboratory Matrix Spike	N/A					
Matrix Duplicate Spikes	N/A					
LCS	Purchase external standard 2 per set of 90 samples	15%cv	Re-run	Linda Green	Accuracy/precision	15% cv
LFB	N/A					
Surrogates	N/A					
Internal Standards (ISs)	N/A					

Table B13. 7 Fixed Laboratory Analytical QC: Chlorophyll - a

Sampling SOP	SOP-3
Medium / Matrix	Surface Water
Analytical Parameter	Chlorophyll – a
Concentration Level	Ug/l
Laboratory	URI Watershed Watch

Laboratory QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action (CA)	Person (s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per set of 40	<QL	Re-clean, re-run	Linda Green	Contamination	<Ql
Reagent Blank	1 per set of 40	<QL	Re-cleam, re-run	Linda Green	Contamination	<Ql
Storage Blank	N/A					
Instrument Blank	1 per set of 40	<QL	Re-clean, re-run	Linda Green	<QC	<QL
Laboratory Duplicate	All samples	<20%RPD	Qualify	Linda Green	Precision-lab	<20%RPD
Laboratory Matrix Spike	N/A					
Matrix Duplicate Spikes	N/A					
LCS	N/A	15%cv	Re-run	Linda Green	Accuracy/precision	15% cv
LFB	N/A					
Surrogates	2 per set of 40	<20%RPD	Qualify	Linda Green	Precision-lab	<20%RPD
Internal Standards (ISs)	N/A					
Other: external standards	2 per set of 40	<20%RPD	Qualify	Linda Green	<20%RPD	<20%RPD

Table B13. 8 Fixed Laboratory Analytical QC: Turbidity

Sampling SOP	SOP-4
Medium / Matrix	Surface Water
Analytical Parameter	Turbidity
Concentration Level	NTU
Laboratory	ESS Laboratory

QC	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person Responsible for Corrective Action	Measurement Performance Criteria
Method Blank	1 per batch	<MDL	Re-run batch	ESS Laboratory Manager	<MDL
Constant	Beginning, every 10 samples, end	+/- 10% true value	Check instrument calibration	ESS Laboratory Manager	+/- 10% true value
Laboratory Calibration Replicate	1 every 10 samples	+/- 20%	Re-run batch	ESS Laboratory Manager	+/- 20%

B14.0 Data Acquisition Requirements

Sands Pond is a public drinking water supply, and the Block Island Water Company and the Rhode Island Department of Health have previously monitored water quality. Historic data is limited and is not of sufficient quality or scope to adequately address the impairments to this waterbody. The information on water quality gathered from non-direct measurements will be used only as a reference, and will not impact the decision making process of the current project. Information obtained from secondary sources as tools for analyzing the watershed are listed below.

Table B14. 1 Non-Direct Measurements Criteria and Limitations

Non-Direct Measurement (Secondary Data)	Data Source	Data Generator	How Data Will Be Used	Limitations on Data Use
Rainfall	http://www.instaweather.com/wjar/blockisland	WJAR Channel 10 Weather Station, BI School	Quantify amount of rainfall received within watershed	
Watershed ISDS Status	Block Island Geographic Information System (BIGIS)	New Shoreham Waste Water Officer	Loading allocations for septic systems within watershed	Estimated quantities, seasonal variations
Land Use	BIGIS	BIGIS	Loading allocations for runoff characteristics	Assumed loadings based on reference information
Wildlife Populations	Observations, interviews, personnel discussions	Misc. sources	Loading allocations	Assumed loadings based on reference information

B15.0 Documentation, Records, and Data Management

The Project Manager shall maintain a field notebook, including field log sheets. The monitoring plan as detailed within this report shall be adhered to while sampling. The Project Manager shall review and consult with the Project Quality Control Officer following each sampling event in order to identify any possible errors or omissions.

The Project Manager shall collect all samples and complete the chain of custody forms for each sampling event. The samples and chain of custody forms shall also be rechecked upon delivery of the samples to the laboratory. A copy of the chain of custody form will be given to the Project Manager when the samples are dropped off at the laboratory. This copy will be retained in the project file. After analysis is complete, sample results from the laboratory will be mailed to the Project Manager at RIDEM.

Upon completion of the initial dry weather and wet weather survey, a brief status report will be written in order to document any changes made to the monitoring plan. All information collected throughout the project will be summarized in the Final Data Report. Information included in the Final Data Report is summarized in section B17.0. Table B15.1 summarizes the records that will be generated throughout this project.

The Project Manager is responsible for maintaining a project file, and storage of all sampling data. A central file is located in the Providence Office of RIDEM. All original documents, including the field notebook shall be maintained in this central file.

Table B15. 1 Project Documentation and Records

Sample Collection Records	Field Analysis Records	Fixed Laboratory Records	Data Assessment Records
Field Notes / Log Sheets	Field Notes / Log Sheets	Chain of Custody Records	Status Reports
Chain of Custody Records		Tabulated Data Summary Forms: Draft and Final	Final Data Report
Monitoring Plan			

C16.0 Assessments and Response Actions

The Project Manager shall be responsible for each of the project tasks and their associated quality assurance and quality control procedures. The Project Manager will provide consistency between sampling events. Continuous reports to the Project Quality Assurance Officer concerning the status of the project, sampling, quality assurance and quality control will highlight any problems that are encountered during sampling. If needed, the QA Officer and the Project Manager will halt sampling until problems are remedied.

Table C16. 1 Project Assessment Table

Assessment Type	Frequency	Internal or External	Person Responsible for Performing Assessment and Implementing Corrective Actions	Person Responsible for Monitoring the Effectiveness of the Corrective Action
Field Sampling Technical System Audit	Start of Sampling	I	Lucinda Hannus RIDEM	Wayne Jenkins RIDEM
URIWW Laboratory Technical System Audit	Prior to Sample Receipt	E	Linda Green URI Watershed Watch	Lucinda Hannus RIDEM
ESS Laboratory Technical System Audit	Prior to Sample Receipt	E	Kathy DeSousa ESS Laboratory	Lucinda Hannus RIDEM

C17.0 QA Management Reports

Table C17.1 lists the QA Management Reports that will be generated throughout this study.

As needed during the project, the Project Manager and the QA Officer will meet to discuss any issues related to sampling. These meetings will be verbal status reports. Problems encountered in the field will be discussed and any appropriate actions determined and implemented. Any changes and/or problems will be included in the final report.

After the shoreline surveys (dry and wet) the Project Manager will generate a Status Report. This Status Report will be the written record of any changes to the QA Plan. If stations are changed it will be documented here. Issues discussed during the Verbal Status Report can also be included.

Upon completion of the sampling the Project Manager will write a final report summarizing the sampling events. Information in this final report will include the following information:

- Brief description of each sampling event;
- Data tables of all data collected during each sampling event; and
- Attachments
  - Status Reports
  - Sampling Logs
  - Chain of Custody Forms
  - Laboratory data sheets provided by the labs

Table C17. 1 QA Management Reports

Type of Report	Frequency	Person(s) Responsible for Report Preparation	Report Recipient
Verbal Status Report	As needed	Lucinda Hannus RIDEM	Wayne Jenkins RIDEM
Written Status Report	After dry and wet weather shoreline surveys	Lucinda Hannus RIDEM	Wayne Jenkins RIDEM
Final Report	Completion of Sampling	Lucinda Hannus RIDEM	Wayne Jenkins RIDEM

C18.0 Verification and Validation Requirements

Both the Project Manager and the Project QA Officer will review data collected during this study to determine if the data meets QAPP Objectives. Decisions to qualify or reject data will be made by the Project Manager and QA Officer. All data collected will be included in the Final Report. To ensure correct interpretation of the data, all problems encountered in the field will be included in the Appendix to the report and discussed in the general text of the report. Problems will also be documented in each survey's written Status Report or included in the Field Notebook. To assist in data interpretation, statistical information on sampling events, including sampling

size, sample mean, and sample variance, will be reported, where applicable. A discussion on duplicate precision and accuracy criteria and results will also be discussed in the Final Report.

C19.0 Verification and Validation Procedures

All data collected during the sampling events will be included in the appendix of the report. Once the data has been collected, it will be entered into Microsoft Excel or similar spreadsheet reporting software. The Project Manager will proofread the data entry for errors, and will correct any discrepancies. Outliers and inconsistencies will be flagged for further review with the QA Officer. The decision to discard data will be made by the Project
Manager and the Project QA Officer. Problems will be discussed in the Final Report. Table C19.1 discusses the data verification process.

Table C19. 1 Data Verification Process

Verification Task	Description	Internal / External	Responsible for Verification
Field Notes	Field notes will be collected at the end of each sampling event and the dry and wet weather shore- line surveys. Any required corrective actions will be addressed and implemented prior to the next sampling session. Field notes will be transcribed into the final project report and copies will be maintained with the project file.	I	Lucinda Hannus RIDEM
Chain of Custody Forms	Chain of Custody forms will be reviewed when samples are collected for delivery to the laboratory in the field and at the laboratory. The forms will be maintained in the project file.	I/E	Lucinda Hannus RIDEM Linda Green URI Watershed Watch Kelly DeSousa ESS Laboratory
Laboratory Data	All laboratory data packages will be verified internally by the laboratory performing the work for completeness prior to submittal. The data packages will also be reviewed by the Project Manager.	I/E	Lucinda Hannus RIDEM Linda Green URI Watershed Watch Kelly DeSousa ESS Laboratory

Data validation will utilize the measurement performance criteria documented in Tables B13.5 through B13.8 of this report.

C20.0 Data Usability / Reconciliation with Project Quality Objectives

As soon as possible after each sampling event, calculations and determination for precision, completeness, and accuracy will be made and corrective action implemented if needed. If data quality indicators meet those measurement performance criteria documented throughout this QA plan, the project will be considered a success. If there are data that do not meet the measurement performance criteria established in this QA Plan, the data may be discarded and sampled again or the data may be used with stipulations written about its accuracy in the Final Report. The cause of the error will be evaluated. If the cause is sampling error, additional training will be provided. Any limitations with the data will be documented in the Status Reports and the Final Report.

APPENDIX A

DEPTH MEASUREMENT – TASK 3

SAMPLING STATION LOCATION SHEET – TASK 3

FIELD SAMPLING LOG SHEET

DEPTH MEASUREMENTS FIELD SHEET

TASK 2

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Insert 11 X 17 Depth Measurement Field Sheet

SAMPLING STATION LOCATION SHEET

TASK 3

Sands Pond
New Shoreham, Rhode Island
Sampling Station Location Sheet
Task 3

Date: _____

Survey Number: _____

Station Number: _____

Sampling Team Names: _____**Project Manager**

_____**Title:** _____

Station Location Description: _____

First Bearing: _____

_____

_____

Second Bearing: _____

_____

_____

Depth: _____

FIELD SAMPLING LOG SHEET

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Insert Field Sampling Log sheet

APPENDIX B

GENERAL FIELD PROCEDURES
FIELD SAMPLING PROCEDURES – FSOP - 1 THROUGH FSOP – 7

GENERAL FIELD PROCEDURES

Sampling shall be conducted on a bi-monthly schedule starting in early spring, and continue till fall.

For all sampling

- Confirm sampling date and schedule with RIDEM personnel
- Check current and forecasted weather
- Obtain proper safety equipment, and personnel floatation device.
- Obtain sampling equipment and supply checklist

All dry weather sampling should take place during the hours of 10:00 am and 3:00 pm.

Equipment checklist:

- Anchor with calibrated line to check depth
- Secchi disk with calibrated line and 2 clothespins
- Horizontal water sampler (Cleaned and prepared for sampling)
- Ice cooler with ice or freezer packs
- Clipboard, pencils
- Field notebook containing map and sampling log sheets
- Sampling Field Procedures

Load and launch boat.

Samplers shall locate the station by using the appropriate landmarks visible on the shore that are described in the field notebook, and shown on the map of the pond.

Locate the first bearing using the described landmarks, turn 90^0 , and locate the second bearing to confirm sampling location. Drop the anchor to maintain position. Care should be taken to not reposition the anchor and disturb sediments on the bottom.

Measure the depth to further verify the sampling location.

Two sampling depths will be used for Total and Ortho-phosphate Phosphorous, Chlorophyll a and Turbidity. The first sample shall be taken at a depth of approximately 1- 1 1/2 feet by carefully reaching from the side of the boat. The second sample shall be taken using the horizontal water sampler at a depth just above the bottom.

Complete observation portion of log sheet for each sample location.

Measure Secchi depth as per FSOP # 5, record depth on appropriate log sheet.

Collect two point samples for each constitute following appropriate FSOPs.

Using YSI Model *85 Handheld Oxygen, Conductivity, Salinity and Temperature gage, measure the Dissolved Oxygen and Temperature for each sampling site as per FSOP – 7 and record values in the field log book.

Complete sampling for all locations indicated in the field notebook.

Return to shore and unload boat. Add ice or freezer packs to cooler as necessary to maintain proper temperature. Clean equipment as required. The Secchi disk and water sampler should be rinsed off with fresh tap water.

Complete appropriate Chain of Custody form according to constituent and laboratory.

Deliver all samples to appropriate laboratory ASAP or within six (6) hours.

Reference:		Field Standard Operating Procedure
Total Phosphorous	(TP)	FSOP – 1
Ortho-phosphate Phosphorous	(OP)	FSOP – 2
Chlorophyll a	(C)	FSOP – 3
Turbidity	(T)	FSOP – 4
Odor	(O)	FSOP – 5
Depth Measurement		FSOP – 6
Dissolved Oxygen & Temperature		FSOP - 7

FSOP – 1
TOTAL PHOSPHOROUS (TP)

The following field procedures shall be followed.

The laboratory shall provide clean sample bottles of the appropriate size and type.

Ensure all bottles are labeled properly prior to sampling.

Surface (Maximum depth of 1 – 1 ½ ft)

Remove cap from appropriate sample container, taking care not to touch the container mouth.

Rinse the container with pond water by holding it by the bottom and plunging it mouth-first into the pond to about elbow depth. Your hand should always move in a forward motion to avoid water from sliding over your arm and into the container. Fill the container, turn the mouth upwards, bring it above the surface, empty the container.

Rinse the cap at the same depth, holding the outside of the cap when plunging.

Using the same motion, collect the sample of water in the container. Tip out some of the water to leave an air space and cap the container.

Store container in cooler.

Deep Sample Using Horizontal Water Sampler

Using the self-closing horizontal water sampler, prepare the sampler for sampling and lower to the appropriate depth. Record depth on field notesheet.

Move the sampler from side to side through the water to ensure that it is flushed with ambient water, then release the messenger to isolate the sample.

Bring the sampler up on deck, then draw off the water into the appropriate container.

Fill the appropriate container for Total Phosphate taking care not to contaminate container or cap.

Store sample in cooler.

During each run a blind duplicate sample will be taken from the surface at one station and at full depth at another station. Duplicates will be collected as separate samples and are not splits of routine samples.

Upon completion of all sampling, return to shore and unload equipment

Add ice or freezer packs to cooler to maintain proper temperature. Transport all samples to the appropriate laboratory as soon as possible or within 6 hours.

FSOP – 2
Ortho-phosphate Phosphorous (OP)

The following field procedures shall be followed.

The laboratory shall provide clean sample bottles of the appropriate size and type.

Label all sample bottles prior to sampling

Surface (Maximum depth of 1 – 1 ½ ft)

Remove cap from appropriate sample container, taking care not to touch the container mouth.

Rinse the container with pond water by holding it by the bottom and plunging it mouth-first into the pond to about elbow depth. Your hand should always move in a forward motion to avoid water from sliding over your arm and into the container. Fill the container, turn the mouth upwards, bring it above the surface, empty the container.

Rinse the cap at the same depth, holding the outside of the cap when plunging.

Using the same motion, collect the sample of water in the container. Tip out some of the water to leave an air space and cap the container.

Store container in cooler.

Deep Sample Using Horizontal Water Sampler

Using the self-closing horizontal water sampler, prepare the sampler for sampling and lower to the appropriate depth. Record depth in field logbook.

Move the sampler from side to side through the water to ensure that it is flushed with ambient water, then release the messenger to isolate the sample.

Bring the sampler up on deck, then draw off the water into the appropriate container.

Fill the appropriate container for Ortho-phophate Phosphate taking care not to contaminate container or cap.

Store sample in cooler.

During each run a blind duplicate sample will be taken from the surface at one station and at full depth at another station. Duplicates will be collected as separate samples and are not splits of routine samples.

Upon completion of all sampling, return to shore and unload equipment.

Add ice or freezer packs to cooler to maintain proper temperature. Transport all samples to the appropriate laboratory as soon as possible or within 6 hours.

FSOP – 3
Chlorophyll a (C)

The following field procedures shall be followed.

The laboratory shall provide clean sample bottles of the appropriate size and type.

Label all sample bottles prior to sampling

Surface (Maximum depth of 1 – 1 ½ ft)

Remove cap from appropriate sample container, taking care not to touch the container mouth.

Rinse the container with pond water by holding it by the bottom and plunging it mouth-first into the pond to about elbow depth. Your hand should always move in a forward motion to avoid water from sliding over your arm and into the container. Fill the container, turn the mouth upwards, bring it above the surface, empty the container.

Rinse the cap at the same depth, holding the outside of the cap when plunging.

Using the same motion, collect the sample of water in the container. Tip out some of the water to leave an air space and cap the container.

Store container in cooler.

Deep Sample Using Horizontal Water Sampler

Using the self-closing horizontal water sampler, prepare the sampler for sampling and lower to the appropriate depth. Record depth in field logbook.

Move the sampler from side to side through the water to ensure that it is flushed with ambient water, then release the messenger to isolate the sample.

Bring the sampler up on deck, then draw off the water into the appropriate container.

Fill the appropriate container for Chlorophyll a taking care not to contaminate container or cap.

Store sample in cooler.

During each run a blind duplicate sample will be taken from the surface at one station and at full depth at another station. Duplicates will be collected as separate samples and are not splits of routine samples.

It is very important to put all chlorophyll sample bottles into the cooler and out of the sunlight as soon as possible.

Upon completion of all sampling, return to shore and unload equipment

Add ice or freezer packs to cooler to maintain proper temperature. Transport all samples to the appropriate laboratory as soon as possible or within 6 hours.

Keep the lid on the cooler closed to keep sample out of sunlight.

FSOP – 4
Turbidity (T)

The following field procedures shall be followed.

The laboratory shall provide clean sample bottles of the appropriate size and type.

Label all sample bottles prior to sampling.

Surface (Maximum depth of 1 – 1 ½ ft)

Remove cap from appropriate sample container, taking care not to touch the container mouth.

Rinse the container with pond water by holding it by the bottom and plunging it mouth-first into the pond to about elbow depth. Your hand should always move in a forward motion to avoid water from sliding over your arm and into the container. Fill the container, turn the mouth upwards, bring it above the surface, empty the container.

Rinse the cap at the same depth, holding the outside of the cap when plunging.

Using the same motion, collect the sample of water in the container. Tip out some of the water to leave an air space and cap the container.

Store sample in cooler.

Deep Sample Using Horizontal Water Sampler

Using the self-closing horizontal water sampler, prepare the sampler for sampling and lower to the appropriate depth. Record depth in field logbook.

Move the sampler from side to side through the water to ensure that it is flushed with ambient water, then release the messenger to isolate the sample.

Bring the sampler up on deck, then draw off the water into the appropriate container.

Fill the appropriate container for Chlorophyll a taking care not to contaminate container or cap.

Store sample in cooler.

During each run a blind duplicate sample will be taken from the surface at one station and at full depth at another station. Duplicates will be collected as separate samples and are not splits of routine samples.

Deliver sample to laboratory as soon as possible.

Preservatives are not practical, analysis should begin as soon as possible. Refrigeration or icing to 4^0 C, to minimize microbiological decomposition of solids, is recommended.

FSOP – 5
Odor

Odors are a very subjective parameter to sample, and individual samplers may have a strong or weak sense of smell. Therefore, the project manager shall make the odor observations so as to remain consistent throughout the project. The project manager will discuss with the additional staff person assisting with the sampling for confirmation of the noted odors. Discrepancies between samplers shall be noted on the field sample log sheet.

Upon arriving at the sample site, the project manager shall record in the sample log sheet any indication of any odors detected at the sample site. Refer to the sample log sheet for descriptions and intensity values.

Each sample site shall be sampled.

FSOP – 6
Depth Measurement

For confirmation of the correct sampling location, the depth of the pond shall be measured and recorded on the field sample log sheet.

Using a calibrated anchor line, the project manager shall lower the anchor line slowly to the bottom of the pond. Avoid disturbing the bottom sediments with excess relocation of the anchor.

While holding the line taut read the depth measurement from the calibrated line and record measurement on the field sample log sheet.

The depth measurement should be within +/- 0.5 feet of desired depth.

If depth measurement exceeds the tolerance, relocate boat by repositioning along described bearings from sample log sheet.

Repeat anchoring procedure as necessary to obtain proper position, again being careful not to disturb bottom sediments.

FSOP – 7
Dissolved Oxygen (DO) and Temperature (Temp)

Sampling for Dissolved Oxygen and Temperature shall take place at all sample locations and at the two depths, the first at the surface and the second one – two feet above the bottom.

A YSI Model # 85 Handheld Oxygen, Conductivity, Salinity, and Temperature System field meter shall be used.

The meter shall be calibrated prior to field sampling according to manufacturer's instructions. Field calibration is not necessary.

A spare set of fresh batteries should be required equipment.

The probe cable shall be calibrated using pieces of duct tape at one foot intervals in order to measure the depth of the probe at each sample station.

Turn the meter on, allow the meter to run through it's self-test procedure until completed and no internal problem is detected. Follow troubleshooting instructions provided by the manufacturer to correct any errors.

Temperature is always displayed.

Press and release the mode button on the meter until the legend on the far right side of the LCD reads Dissolved Oxygen in mg/l with ^{0}C. If the instrument is reading Dissolved Oxygen the large numbers on the display will be followed by mg/l. It is important to remember that the dissolved oxygen probe is stirring dependent. This is due to the consumption of oxygen at the sensor tip during measurement. When taking dissolved oxygen measurements the probe must be moved through the sample at a rate of one foot per second to provide adequate stirring.

The meter thermistor and oxygen probe is lowered into the water to the appropriate depth as required by the project manager and as indicated on the sample log sheet. **The oxygen probe must not be allowed to come in contact with the lake bottom.**

Lower the probe into the water just below the surface, let the probe aclimate according to manufacturer's instructions, take a temperature and oxygen reading, and record it on the sample log sheet.

Lower the probe to the required depth and repeat the above step.

Turn meter off and place electrode into storage chamber. Note: If sampling sites are relatively close together, it is acceptable to leave the meter on until all measurements are recorded.

APPENDIX C

UNIVERSITY OF RHODE ISLAND WATERSHED WATCH CHAIN OF CUSTODY FORM

ESS LABORATORY CHAIN OF CUSTODY FORM

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Insert URI Chain of Custody Form

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Insert ESS laboratory chain of custody form

APPENDIX D

LABORATORY STANDARD OPERATING PROCEDURES SOP –1 THROUGH SOP – 4

FIELD STANDARD OPERATING PROCEDURE SOP - 5

SOP -1

TOTAL PHOSPHORUS & TOTAL NITROGEN

I. References

Alpkem Corporation. 1986. *Operator's Manual and Methodologies for the RFA-300*. PO Box 648, 9445 SW Ridder Rd., Wilsonville, OR 97070.

Ameel, JJ, RP Axler, and CJ Owen. 1993. Persulfate Digestion for Determination of Total Nitrogen and Total Phosphorus in Low-Nutrient Waters. American Laboratory.

American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*. 1995 edition. Section 4500-N_{org}. D. Persulfate Method (with automated cadmium reduction)

American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*. 1995 edition. Section 4500-P F. Phosphorus - Automated Ascorbic Acid Reduction Method.

Labtronics Inc. 1992. Labtronics DP-1000 Program. Labtronics Inc. 95 Crimea St, Guelph, Ontario NIH 2Y6, Canada.

Oviatt, CA and KM Hindle. 1994. Manual of Biological and Geochemical Techniques in Coastal Areas. MERL Series, Report #1, Third Edition. Section 1.6, pp. 88-91, " Total Dissolved and Total Particulate Nitrogen and Phosphorus." The University of Rhode Island, Kingston, Rhode Island.

U S. Environmental Protection Agency. EPA Method 365 Series, EPA 600/4-79, rev. March 1983. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Valderrama, J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Marine Chemistry* 10:109-122.

II. Summary of Method:

This procedure is a simultaneous digestion for total nitrogen and total phosphorus. All glassware must be thoroughly cleaned and pre-digested to avoid phosphorus contamination. Nutrient samples are collected in acid-washed brown glass bottles, stored on ice. After logging in at laboratory, 20 ml aliquots are pipetted into pre-treated glass vials. A suite of standards are similarly set up as are QC samples. A neutral potassium persulfate digesting reagent is added to samples, standards and blanks. Samples and standards are digested in a water bath - raised from room temperature to boiling, boiled for 15 minutes, and then allowed to cool to room temperature in the water bath. Vials are refrigerated until analysis. Analysis is performed using an Alpkem Model 300 Autoanalyzer.

All equipment and supplies are listed at the end of this document.

III. Procedure for Sample Preparation and Processing

A. Before Sample Collection

- **1. Re-crystallize Potassium Persulfate. This procedure takes two days. It should be done at least a week before the potassium persulfate is to be used.** This procedure was developed because of nitrogen contamination in commercially available low-N potassium persulfate.
  1. Weigh out about 75 g potassium persulfate into 600 ml beaker.

2. Add about 500 ml Millipore water, magnetic stir bar, cover with Al Foil or cover glass.
3. Place beaker on magnetic stirrer. Heat, with stirring to dissolve crystals.
4. Put beaker in pan packed with ice, also cool squeeze bottle of MQ water. Put pan and squeeze bottle in refrigerator overnight.
5. Attach Buchner funnel to filter flask, attach to vacuum manifold.
6. Turn on vacuum suction.
7. Decant (pour) supernatant (liquid) from cold beaker through funnel, then pour and scrape crystals into funnel.
8. Rinse beaker and crystals repeatedly with cold MQ water, continuing vacuuming.
9. Continue vacuuming until crystals are dry, occasionally scraping crystals away from side of funnel and "fluffing" them up.
10. Remove from vacuum, scrape crystals into beaker. Store crystals in dessicator.

- **2. Prepare Glassware - this takes 3 days to complete.**

(note: MQ refers to Millipore water, which is de-ionized water that has been further purified.)

1. Empty contents of vials, if they have been previously used.

2. Place vials and their tops in a bucket of (non-phosphate) soapy water. The labels of the samples are easier to remove after the vials have soaked.

3. Scrub out the vials using a brush and the soapy water.

4. Rinse the vials with tap water 3-5X.

5. Rinse the vials and caps with MQ water 3-5X.

6. Acid wash vials (not caps) by filling vials with 10% HCl. Let soak overnight.

7. Empty out acid from vials, rinse 3X with MQ water inside and out.

8. Fill vials with MQ water. Let soak overnight.

7. If the vials cannot be pre-digested that day fill them with MQ water cap and store, labeled "ready for pre-digestion."

8. If digesting reagent is available, add 5 ml to each vial, using the "old digesting reagent" re-pipette. (Directions for making the digesting reagent can be found below.) Cap the vials tightly. If the vials cannot be digested that day it is ok. Just remember to label them as to their contents.

9. Place capped vials in a rack and in a water bath. If needed add DI water to the water bath to approximately 1/3 of vial height. Put the cover on the water bath. It will not reach 100 deg C if the cover is off. Turn on water bath and bring to boiling. This takes 45-60 min. Boil for 15 minutes. Turn off the water bath.

10. Let the vials cool to room temperature in the water bath overnight.

11. Remove cooled vials and empty out digesting reagent.

12. Rinse 3-5X with MQ water.

13. Fill the vials completely with MQ water and cap them. The vials are stored filled with MQ until the day they are to be used.

14. On the day they are to be used, empty the MQ water from the vials. Rinse the vials 3X with MQ water. Shake out excess water. Stand the vials upright in their rack. Do not cap the vials.

15. Dry vials in 105 deg C oven (in room 018). This takes about 15-20 minutes. Put the caps face down on a paper towel stacking them like this //////. They do not need to be completely dry before they are used. Do not put the caps in the oven or they will melt.

3. Prepare Standards for Total and Dissolved Inorganic Phosphorus.
This takes two days to complete.

NOTE: All glassware should have been soapy water washed, Millipore water rinsed, 10% HCl soaked and then soaked in Millipore water overnight. Never use glassware that has just come from acid soaking. It must equilibrate in deionized water first. Use non-phosphate detergent. All phosphorus glassware should be dedicated to phosphorus analysis only and not used for any other analyses.

1. Dry **KH_2PO_4 at 105 deg. C for 1 hour**; store in dessicator. This is potassium dihydrogen phosphate, molecular weight KH_2PO_4 = 136.1. molecular weight P = 30.97.
2. **Calibrate balance**. Use a balance that weighs to at least 0.0001 g. Use the set of calibration weights (in drawer under the balance) to check the calibration of the balance. Use forceps to lift calibration weights, not your fingers.
3. Make **phosphorus stock solution**.

To calculate amount of KH_2PO_4 needed to make a 100 mg/l solution (=0.1g/l):

0.1 g X 136.1/30.97 = 0.4394 g KH2PO4) per liter

- For this **stock solution**, weigh out 0.4394 g, dilute to 1000 ml with MQ water.
  0.2127 g to 500 ml
  0.1099 g to 250 ml
- After making to volume, preserve with **2 ml chloroform per liter**. This solution is stable for at least 6 months, stored in a refrigerator.
- **This solution is 100 mg P04-P per liter, or 100 ug P04-P per ml, or 100 ppm.**

4. Make **intermediate stock solution**. Dilute 100 ml of 100 ppm stock solution to 1000 ml, or **25 ml to 250 ml. This solution is 10 ppm** (or ug/ml or mg/l) or **10,000 ppb P**.
5. **Calibrate pipette**. Use Eppendorf micropipettes, room temperature deionized water and the Mettler balance to calibrate pipettes. The nominal volume on the pipettes is not always accurate. Calibrate by dispensing a chosen volume of room temperature water into a tared beaker on the balance. 1.000 ml = 1.0000 gram. Adjust pipette as needed, recheck with each change in pipette delivery volume.
6. Fill selected volumetric flasks part way with MQ water. **Use appropriate sized Eppendorf micropipette to add intermediate stock solution, according to chart below.** Be aware of the volumetric flask size. Bring to volume with MQ water. Cover with parafilm, shake. Allow to sit at least 1/2 hour before using.

7. To make working standards for Phosphorus:

Use these Standardsf or "clean" water	Use these standards for ISDS (sewage) samples	Final Concentration (ug/l, or ppb)	ul (ml) of 10 mg/l intermediate stock solution to use	ul (ml) of 10 mg/l intermediate stock solution to use	dilution factor
			Using 200 ml volumetric flasks	**Using 250 ml volumetric flasks**	
X		**5 ppb (ug/l)**	100 ul	125 ul	2000
X		**10**	200 ul	250 ul	1000
X		**15**	300 ul	375 ul	666.6
X		**20**	400 ul	500 ul	500
X		**25**	500 ul	625 ul	400
X		**50**	1000, (1.0 ml)	1250, (1.25 ml)	200
X	**X**	**100**	2000, (2.0)	2500, (2.5)	100
X	**X**	**200**	4000, (4.0)	5000, (5.0)	50
	X	**400**	8000, (8.0)	10,000, (10.0)	25
	X	**500**	10000 ul, (10.0 ml)	12,500 ul, (12.5 ml)	20
	x	**1000**	20,000, (20.0)	25,000, (25.0)	10

- **4. Prepare Standards for Total and Nitrate Nitrogen**

Dry **KNO3 at 105 deg. C for 24 hours**; store in dessicator.

1. 4. For **stock solution**, weigh out 0.7218 g, dilute to 1000 ml with MQ water.

0.3609g	**to**	**500 ml**
0.1805g	to	250 ml
0. 0722g	to	100 ml.

2. Preserve with **2 ml chloroform per liter**. This solution is stable for at least 6 months.
3. This solution is 100 mg NO3-N per liter, or 100 ug NO3-N per ml, or **100 ppm**.

This stock solution requires no intermediate stock solution.

4. Fill volumetric flasks part way with water. Use appropriate sized Eppendorf micropipette to add stock solution, according to chart below. Bring to volume with MQ water. Cover with parafilm, shake. Allow to sit at least 1/2 hour before using.
5. To make up **working standards for Nitrogen**:

Use these standards for "clean" water	Use these standards for ISDS (sewage samples)	Final Concentration (ug/l, or ppb)	ul (ml) of 100 mg/l stock	ul (ml)of 100 mg/l stock	dilution factor
			200 ml vol. flask	**250** ml vol. flask	
X		50	100 ul	125 ul	2000
X		75	150	188	1333
X		100	200	250	1000
X		250	500	625	400
X	**X**	500	1000 ul, (1 ml)	1250, (1.25 ml)	200
X	**X**	1000	2000, (2 ml)	2500, (2.5 ml)	100
X	**X**	1500	3000, (3 ml)	3750, (3.75 ml)	66.67
X	**X**	2000	4000, (4 ml)	5000, (5 ml)	50
	X	3000	6000, (6 ml)	7500, (7.5 ml)	33.3
	X	4000	8000, (8 ml)	10000, (10 ml)	25
	X	5000	10000 ul, (10ml)	12500, (12.5 ml)	20

B. Day of sample collection

Information about Sample Replicates, Standards, and Blanks

- Generally we prepare one replicate for every 5-10 samples.
- QC samples are from two sources, purchased QC standards and QC samples remaining from EPA blind water pollution QC testing. All of these QC samples are stored in the refrigerator near the TP/TN standards, some have been diluted. We typically run 1-2 of each QC sample, at each dilution, with each digestion batch.
- Standards: We typically run two sets of standards with each digestion batch if there are >50 samples. The standards used are indicated in the charts (above).
- Lab Blanks: Set up at least 2 vials of MQ water per digestion batch.

- **1. Prepare liquid digesting reagent**

The liquid digesting reagent should be made fresh for the day of use.
Use re-crystallized potassium persulfate (see end of document)

Digesting Reagent for Total Phosphorus and Total Nitrogen

to make	**1 liter**	**500 ml**	**250 ml**	**200 ml**
1. Potassium Persulfate, recrystallized (see instructions at end)	50 g	25 g	12.50 g	10 g
2. Boric Acid	30 g	15 g	7.50 g	5 g
3. 1N NaOH solution	350 ml	175 ml	87.50 ml	70 ml
Dilute reagents with MQ H2O to	900 ml	450 ml	200 ml	150 ml
Fills ~ # vials	350	175	80	70

Use a beaker with a magnetic stir bar that has been specifically reserved for TP digestions.
Weigh the dry reagents into the beaker.
Add the sodium hydroxide solution.
Using MQ water, dilute to the appropriate volume according to the chart above.
Cover beaker with aluminum foil.
Place beaker onto a heating magnetic stirrer.
Stir with low heat until all crystals are dissolved. This takes 5-10 minutes.
When crystals are dissolved, pour solution into appropriate sized volumetric flask specifically reserved for "TP only".
Let digesting reagent cool. Make to volume with MQ water.
Transfer to an amber Repipet, labeled "new digesting reagent." Label with current date.
2.5 ml of digesting reagent are used for each 20 ml "clean water" sample. 5.0 ml of digesting reagent are used for each diluted ISDS sample.
Any leftover reagent can poured into the "old TP digest" Repipet and used for "pre-digesting" vials.

- **2. Prepare the Clean Vials**

1. Use vials that have been cleaned and pre-digested as described in previous section. These vials should have been filled with MQ water and capped.
2. Pour out MQ water and rinse with 3 aliquots MQ. Shake out as much excess water as possible.
3. Stand vials upright in rack.
4. Put rack in 105 deg. C. drying oven until vials are dried (about 15-20 minutes.) Do not put caps in the oven. Stack them face down /////// on a clean paper towel.

- **3. Fill the Vials**

1. Prepare labels for samples and standards.
2. Remove samples and standards from refrigerator, bring to room temperature.
3. Just prior to sampling. shake the samples/standards well.
4. Use a 20 ml glass pipette to transfer 20 ml "clean" water into a labeled vial. "Clean water" refers to samples from non septic system source (lakes, ponds, rivers, etc.)
5. For ISDS/sewage samples: Pipette 1.0 ml sample and 19.0 ml MQ water into vial.
6. Replicate each 5 to 10 samples.
7. Rinse pipette well (with MQ water) between samples.
8. Fill all vials.
9. ***At this point samples in vials can be capped and stored in refrigerator until you are ready to add digesting reagent..***

- **4. Add Digesting Reagent**

10. Pump Repipet containing digesting reagent several times to make sure that there are no air bubbles in the delivery tube.
11. Check calibration to make sure that repipet is dispensing desired volume by dispensing "one shot" into a tared beaker on a balance: 2.5 ml =2.5 grams.
12. Dispense **2.5 ml** of digesting reagent into each vial for **lake, river, pond water**.
13. Dispense **5.0 ml** of digesting reagent into each vial for **ISDS/sewage samples**.
14. Cap each vial tightly and shake vigorously. Place in rack.

- **5. Digest Samples and Standards**

15. Put rack of vials into room temperature water bath. Add DI water to water bath to level of liquid in vials.
16. Put lid on water bath and turn it on. It will take 45 – 60 minutes to reach boiling temperature.
17. Boil gently for 15 minutes. Turn off water bath. Cool to room temperature (overnight) in water bath. Keep cover on water bath.

- **6. After digestion**

18. The next day, remove racks of vials from water bath. Store racks in refrigerator until day of analysis. TN should be analyzed <= 1 week, TP <= 1 month.

IV. Analytical Procedure

Background: URI watershed Watch uses an Alpkem Model 300 automated spectrometer (known as an autoanalyzer) with a 880 nm filter for phosphorus and an 540 nm filter for nitrogen. Detailed instructions will not be repeated here, and can be found in the various manuals that came with the autoanalyzer. The autoanalyzer was purchased in 1988 (cost approximately $40,000). NO ONE IS ALLOWED TO USE THE AUTOANALYZER WITHOUT PERMISSION OF LINDA GREEN.

A. Summary of Analytical Procedure:

1. All digested samples, standards, blanks are allowed to warm to room temperature. This takes place while the autoanalyzer is being set up.
2. For **total phosphorus we use Standard Methods #4500-P F, Automated Ascorbic Acid Reduction Method**. We follow the detailed instructions from Alpkem for reagent preparation. Since the digesting reagent is neutral we do not need to neutralize the digested samples.
3. For **total nitrogen we use Standard Methods #4500- N_{org} D, automated cadmium reduction**, as modified above.
4. Summary of Autoanalyzer Operation: A calibrated volume of sample is introduced into the RFA system by the sampler. The sample is delivered to the analytical cartridge by a peristaltic pump that compresses the pump tubing. It is then combined with reagents and air bubbles in a continuously moving stream. As the sample moves through the cartridge it passes through mixing coils, a heating bath, as specified by test conditions. A color is produced by the specific analyte in the sample. The intensity of the color is determined by the amount of analyte present. This colored stream then flows to the photometer where the color intensity is measured and converted to an electronic signal. A recorder displays these signals on calibrated chart paper. (from RFA Operator's Manual, Alpkem Corp.) The electronic signal is also sent to a computer where the Labtronics DP-1000 program processes the signal to create a standard curve and numerical results for the standards and samples. (Labtronics Operators Manual, Labtronics Inc.)
5. Each autoanalyzer tray has ninety places. A set of standards is run at the beginning and at the end of each run. Approximately 4 blanks are analyzed each run and also 1-2 sets of QC standards. This leaves about 50 spots for actual water samples. We replicate every 5-10 water samples in a run.
6. The autoanalyzer can be set for replicate sampling of each sample cup in the tray. We typically run duplicate or triplicate analyses of each sample cup.
7. There are two outputs from the autoanalyzer. The first is a **chart paper recording**. Analytes are recorded as peaks. This chart paper record provides a tangible hard copy record of each run. It is used to verify the baseline at beginning and end, baseline drift, the shape of the peaks, the separation of the peaks, the height of the peaks, and whether there are any offscale samples that need to be diluted and re-run. If the computer does not function, peak heights can be manually measured and sample concentrations determined using a regression equation of the standards.
8. **The autoanalyzer is also connected to an IBM PC computer**. We use Labtronics Corporation's program to analyze the data. This program was developed specifically for this autoanalyzer. It performs a linear regression on the standards and determines sample concentrations. A graph of concentration vs peak height of standards is displayed and can be manipulated to remove obvious outliers. The standard curve is rejected if r^2 is less than 0.95. Quite often the regression is 0.9999.
9. After the computer results are printed, they are carefully compared to the recorder printout. This is a critically important comparison because the computer prints out only a number and the recorder shows peak

shape. The samples with poor peak shape can be re-analyzed. If all the samples are of low concentration, they can be re-analyzed with less concentrated standards.

10. QC results are compared to previous results as well as "true values". If the results of the run meet original EPA requirements for "acceptable" the results of the run are also deemed acceptable.
11. After the printout has been approved, the data is entered into appropriate Excel spreadsheet files, where it is subsequently re-checked for data entry errors.

B. Range, Precision, Accuracy, Blanks, Percent Recovery

Phosphorus

Limit of detection: 2 ug/l phosphorus
Limit of quantitation: 4 ug/l phosphorus
Upper Limit: 1 mg/l without sample dilution
Precision: 15% coefficient of variation
Accuracy: +/- 10% of EPA WP sample true values
Average blank: 0-2 ug/l phosphorus

Nitrogen

Limit of Detection: 20 ug/l nitrogen
Limit of Quantitation: 25 ug/l nitrogen
Upper Limit: 5 mg/l without sample dilution
Precision: 15% coefficient of variation
Accuracy: +/- 10% of EPA EP sample true values
Average Blank: 0-5 ug/l nitrogen

V. Equipment and supplies

A. Major Laboratory Equipment:

105 C° Glassware drying oven
Vacuum source
Alpkem RFA 300 Rapid Flow Analyzer
Strip chart recorder
Personal computer
Refrigerator
Balance capable of weighing to 0.0001 g
Source of Millipore water
dessicator
Water bath capable of heating to 100 C°

B. Other Laboratory Equipment

Heated magnetic stirrer and stir bars
Pipette dispenser, preferably electronic
600 - 1000 ml acid-washed beaker, reserved for P use
Cover glass, or AL foil
Metal tray
Squeeze bottle containing Millipore water
Ice
60 ml Buchner funnel with rubber stopper
250 - 1000 ml side arm flask, or Mason jar set up for filtering
Spatula for scraping
Beaker to store re-crystallized potassium persulfate in
10-15 200-250 ml volumetric flasks
2-4 1000 ml volumetric Flasks

C. Consumable Supplies

Vials (for phosphorus digestion)

Fisher Chemical Company Co #03-339-5D
Borosilicate glass, Type 1, class B
Capacity 45 ml (or 11 drams)
28 mm O.D. X 108 mm high
Thread 24-400
Sold in case of 144
Price: $47.00 (7/95)

Caps for vials

Fisher Chemical Company #02-923-14B
Nalgene polypropylene #5150-0240
24 mm I.D.
24-400 thread
Sold in pack of 12
Price: $3.00 (7/95)

20 ml Volumetric pipettes, class B accuracy +/- 0.06 ml
Fisher Chemical Company #13-650N
Calibrated "to deliver"
Sold singly
price: $6.00 (7/95)

Blue coated-wire Rack (capacity 72 TP vials)
This rack is cataloged as a "Whirl-pak Bag Rack".
It is found in the "bag" section of the catalog, not in the rack section.
Fisher Chemical Company #01-812-5G
It is NASCO # B1048, with a capacity of 12, 710 ml samples (NASCO #B1020)
Sold singly
Price: $29.00 (list 7/95)

White Plastic racks (capacity 24 TP vials)
For tubes 30 mm
There are a variety of racks, be sure they can go in oven (to dry vials) and will not float in water bath.
Fisher Chemical Company: 14-809D, list $20 singly, or $74 for case of 4 (7/95)
or # 14-810-12D List $22.50

Repipet low profile dispenser (for dispensing digesting reagent)
There are a variety, make sure the one you order can withstand most reagents, has two openings and has a capacity for dispensing up to 10 ml.
Fisher Chemical Company # 13-687-35
Price: $225.00 (list, 7/95)

Brown Glass Bottles, Qorpak, with TFE-lined closures
Fisher Chemical Company:

#03-320-8D, 240 ml, case of 24	$ 54.00 (7/95)
#03-320-8C, 120 ml, case of 24	$64 (list 7/95)

D. Chemical Reagents for Processing Samples

Potassium Persulfate, 500 g, certified, ACS, low nitrogen (<0.001%)
for digesting reagent ($K_2S_2O_8$)
Fisher Chemical Company
#P282-500, low nitrogen, this still needs to be re-crystallized before use
Price: $90.00 (list 7/95)

Boric Acid powder, certified ACS, 500 g
for digesting reagent (H_3BO_3)
Phosphate <= 0.001%
Fisher Chemical Company #A74-500
Price: $37 (list 7/95)

Sodium Hydroxide pellets, certified ACS, 500 g
for digesting reagent (NaOH)
Nitrogen compounds <= 0.001%
Phosphate compounds <= 0.001%
Fisher Chemical Company #S318-500
Price: $26.00 (list 7/95)

Potassium Dihydrogen Phosphate, also known as potassium phosphate monobasic (KH_2PO_4), primary standard, crystalline, 500 g
Fisher Chemical Company #P382-500
Price: $38.00 (list 7/95)

Potassium Nitrate KNO_3, primary standard
Fisher Chemical Company #P383-100

E. Reagents for Rapid Flow Analyzer

- **Phosphorus**

Antimony Potassium Tartarate
Fisher #A 867-500

Ammonium Molybdate
Fisher #A674-500

Ascorbic Acid,
Fisher #A61-100

DowFax
Surfactant for P analysis
Available from Alpkem

Sulfuric Acid, concentrated
Fisher #A300-212

- **Nitrogen Reagents**

Imidizole
Fisher#03196-500

Cupric Sulfate
Sigma#c7631

Sulfanilimide
Fisher#04525-100

N-1-Napthylethylenediamine (NED)
Sigma #N-9125

Brij-35% solution surfactant
Available from Alpkem

SOP - 2
Ortho-phosphate phosphorus

I. References

Alpkem Corporation. 1986. *Operator's Manual and Methodologies for the RFA-300*. PO Box 648, 9445 SW Ridder Rd., Wilsonville, OR 97070.

American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*. 1995 edition. Section 4500-P F. Phosphorus - Automated Ascorbic Acid Reduction Method.

Labtronics Inc. 1992. Labtronics DP-1000 Program. Labtronics Inc. 95 Crimea St, Guelph, Ontario NIH 2Y6, Canada.

U S. Environmental Protection Agency. EPA Method 365 Series, EPA 600/4-79, rev. March 1983. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

I. Summary of Method:

This method is for the simultaneaous analysis of ortho-phosphate phosphorus and nitrate-nitrogen. All glassware must be thoroughly cleaned and pre-digested to avoid phosphorus contamination. Nutrient samples are collected in acid-washed brown glass bottles, and stored on ice. Water samples are filtered through 0.45 um glass fiber filters (Gelman Type A/E) either in the field (if filtering samples for subsequent chlorophyll analyses) or in the laboratory. Filtered samples are logged in at the laboratory, and refrigerated until analysis. Analysis is performed using an Alpkem Model 300 Autoanalyzer.

All equipment and supplies are listed at the end of this document.

II. Procedure for Sample Preparation and Processing

A. Before Sample Collection

Prepare Standards for Total and Dissolved Inorganic Phosphorus: this takes two days to complete.
NOTE: MQ refers to Millipore water, which is de-ionized water that has been further purified. All glassware should have been soapy water washed, Millipore water rinsed, 10% HCl soaked and then soaked in Millipore water overnight. Never use glassware that has just come from acid soaking. It must equilibrate in deionized water first. Use non-phosphate detergent. All phosphorus glassware should be dedicated to phosphorus analysis only and not used for any other analyses.

1. Dry **KH_2PO_4 at 105 deg. C for 1 hour**; store in dessicator. This is potassium dihydrogen phosphate, molecular weight KH_2PO_4 = 136.1. molecular weight P = 30.97.
4. **Calibrate balance**. Use a balance that weighs to at least 0.0001 g. Use the set of calibration weights (in drawer under the balance) to check the calibration of the balance. Use forceps to lift calibration weights, not your fingers.
5. Make **phosphorus stock solution**.

To calculate amount of KH_2PO_4 needed to make a 100 mg/l solution (=0.1g/l):

0.1 g X 136.1/30.97 = 0.4394 g KH2PO4) per liter

- For this **stock solution**, weigh out 0.4394 g, dilute to 1000 ml with MQ water.
  0.2127 g to 500 ml
  0.1099 g to 250 ml
- After making to volume, preserve with **2 ml chloroform per liter**. This solution is stable for at least 6 months.
- **This solution is 100 mg P04-P per liter, or 100 ug P04-P per ml, or 100 ppm.**

8. Make **intermediate stock solution**. Dilute 100 ml of 100 ppm stock solution to 1000 ml, or **25 ml to 250 ml. This solution is 10 ppm** (or ug/ml or mg/l) or **10,000 ppb P**.
9. **Calibrate pipette**. Use Eppendorf micropipettes, room temperature deionized water and the Mettler balance to calibrate pipettes. The nominal volume on the pipettes is not always accurate. Calibrate by dispensing a chosen volume of room temperature water into a tared beaker on the balance. 1.000 ml = 1.0000 gram. Adjust pipette as needed, recheck with each change in pipette delivery volume.
10. 7. Fill selected volumetric flasks part way with MQ water. **Use appropriate sized Eppendorf micropipette to add intermediate stock solution, according to chart below.** Be aware of the volumetric flask size. Bring to volume with MQ water. Cover with parafilm, shake. Allow to sit at least 1/2 hour before using.

11. To make working standards:

Standardsf or **"clean" water**	**Standardsf or ISDS (sewage) samples**	**Final Concentration (ug/l, or ppb)**	**ul (ml) of 10 mg/l intermediate stock solution to use**	**ul (ml) of 10 mg/l intermediate stock solution to use**	**dilution factor**
			Using 200 ml volumetric flasks	**Using 250 ml volumetric flasks**	
X		**5 ppb (ug/l)**	100 ul	125 ul	2000
X		**10**	200 ul	250 ul	1000
X		**15**	300 ul	375 ul	666.6
X		**20**	400 ul	500 ul	500
X		**25**	500 ul	625 ul	400
X		**50**	1000, (1.0 ml)	1250, (1.25 ml)	200
X	**X**	**100**	2000, (2.0)	2500, (2.5)	100
X	**X**	**200**	4000, (4.0)	5000, (5.0)	50
	X	**400**	8000, (8.0)	10,000, (10.0)	25
	X	**500**	10000 ul, (10.0 ml)	12,500 ul, (12.5 ml)	20
	x	**1000**	20,000, (20.0)	25,000, (25.0)	10

Prepare Standards for Total and Nitrate Nitrogen

Dry **KNO3 at 105 deg. C for 24 hours**; store in dessicator.

4. 4. For **stock solution**, weigh out 0.7218 g, dilute to 1000 ml with MQ water.

0.3609g	**to**	**500 ml**
0.1805g	to	250 ml
0. 0722g	to	100 ml.

5. Preserve with **2 ml chloroform per liter**. This solution is stable for at least 6 months.
6. This solution is 100 mg NO3-N per liter, or 100 ug NO3-N per ml, or **100 ppm**.

This stock solution requires no intermediate stock solution.

6. Fill volumetric flasks part way with water. Use appropriate sized Eppendorf micropipette to add stock solution, according to chart below. Bring to volume with MQ water. Cover with parafilm, shake. Allow to sit at least 1/2 hour before using.
7. To make up **working standards**:

Standards for "clean" water	Standards for ISDS (sewage samples)	Final Concentration (ug/l, or ppb)	ul (ml) of 100 mg/l stock	ul (ml)of 100 mg/l stock	dilution factor
			200 ml vol. flask	**250** ml vol. flask	
X		50	100 ul	125 ul	2000
X		75	150	188	1333
X		100	200	250	1000
X		250	500	625	400
X	**X**	500	1000 ul, (1 ml)	1250, (1.25 ml)	200
X	**X**	1000	2000, (2 ml)	2500, (2.5 ml)	100
X	**X**	1500	3000, (3 ml)	3750, (3.75 ml)	66.67
X	**X**	2000	4000, (4 ml)	5000, (5 ml)	50
	X	3000	6000, (6 ml)	7500, (7.5 ml)	33.3
	X	4000	8000, (8 ml)	10000, (10 ml)	25
	X	5000	10000 ul, (10ml)	12500, (12.5 ml)	20

III. Analytical Procedure

Background: We use an Alpkem Model 300 automated spectrometer (known as an autoanalyzer) with a 880 nm filter for phosphorus and an 540 nm filter for nitrogen. Detailed instructions will not be repeated here, and can be found in the various manuals that came with the autoanalyzer. The autoanalyzer was purchased in 1988 (cost approximately $40,000). NO ONE IS ALLOWED TO USE THE AUTOANALYZER WITHOUT PERMISSION OF LINDA GREEN.

A. Summary of Analytical Procedure:

12. All filtered samples, standards, and blanks are allowed to warm to room temperature. This takes place while the autoanalyzer is being set up.
13. For ortho-phosphate phosphorus we use Standard Methods #4500-P F, Automated Ascorbic Acid Reduction Method. We follow the detailed instructions from Alpkem for reagent preparation. Since the digesting reagent is neutral we do not need to neutralize the filtered samples.
14. For nitrate-nitrogen we use Standard Methods #4500-NO_3^- F, automated cadmium reduction, as modified above.
15. Summary of Autoanalyzer Operation: A calibrated volume of sample is introduced into the RFA system by the sampler. The sample is delivered to the analytical cartridge by a peristaltic pump. It is then combined with reagents and air bubbles in a continuously moving stream. As the sample moves through the cartridge it passes through mixing coils, a heating bath, as specified by test conditions. A color is produced by the specific analyte in the sample. The intensity of the color is determined by the amount of analyte present. This colored stream then flows to the photometer where the color intensity is measured and converted to an electronic signal. A recorder displays these signals on calibrated chart paper. (from RFA Operator's Manual, Alpkem Corp.) The electronic signal is also sent to a computer where the Labtronics DP-1000 program processes the signal to create a standard curve and numerical results for the standards and samples. (Labtronics Operators Manual, Labtronics Inc.)
16. Each autoanalyzer tray has ninety places. A set of standards is run at the beginning and at the end of each run. Approximately 4 blanks are analyzed each run and also one set of QC standards. This leaves about 50 spots for actual water samples. We replicate every 5-10 water samples in a run.
17. The autoanalyzer can be set for replicate sampling of each sample cup in the tray. We typically run duplicate or triplicate analyses of each sample cup.
18. There are two outputs from the autoanalyzer. The first is a **chart paper recording**. Analytes are recorded as peaks. This chart paper record provides a tangible record of each run. It is used to verify the baseline at beginning and end, baseline drift, the shape of the peaks, the separation of the peaks, the height of the peaks, and whether there are any offscale samples that need to be diluted and re-run. If the computer does not function, peak heights can be manually measured and sample concentrations determined using a regression equation of the standards.
19. **The autoanalyzer is also connected to an IBM PC computer**. We use Labtronics Corporation's program to analyze the data. This program was developed specifically for this autoanalyzer. It performs a linear regression on the standards and determines sample concentrations. A graph of concentration vs peak height of standards is displayed and can be manipulated to remove obvious outliers. The standard curve is rejected if r^2 is less than 0.99. Quite often the regression is 0.9999.
20. After the computer results are printed, they are carefully compared to the recorder printout. This is a critically important comparison because the computer prints out only a number and the recorder shows peak

shape. The samples with poor peak shape can be re-analyzed. If all the samples are of low concentration, they can be re-analyzed with less concentrated standards.

21. QC results are compared to previous results as well as "true values". If the results of the run meet original EPA requirements for "acceptable" the results of the run are also deemed acceptable.
22. After the printout has been approved, the data is entered into appropriate Excel spreadsheet files, where it is subsequently re-checked for data entry errors.

Information about Sample Replicates, Standards, and Blanks

- Generally we use one replicate for every 5-10 samples.
- QC samples are from two sources, purchased QC standards and QC samples remaining from EPA blind water pollution QC testing. All of these QC samples are stored in the refrigerator near the TP/TN standards, some have been diluted. We typically run 1-2 of each QC sample, at each dilution, with each digestion batch.
- Standards: We typically run two sets of standards with each digestion batch if there are >50 samples. The standards used are indicated in the chart (above).

Blanks: Set up at least 2 vials of MQ water per digestion batch.

B. Range, Precision, Accuracy, Blanks, Percent Recovery

Phosphorus

Limit of detection: 2 ug/l phosphorus
Limit of quantitation: 4 ug/l phosphorus
Upper Limit: 1 mg/l without sample dilution
Precision: 15% coefficient of variation
Accuracy: +/- 10% of EPA WP sample true values
Average blank: 0-2 ug/l phosphorus

Nitrogen

Limit of Detection: 20 ug/l nitrogen
Limit of Quantitation: 25 ug/l nitrogen
Upper Limit: 5 mg/l without sample dilution
Precision: 15% coefficient of variation
Accuracy: +/- 10% of EPA EP sample true values
Average Blank: 0-5 ug/l nitrogen

IV. Equipment and supplies

- **Major Laboratory Equipment:**
  Alpkem RFA 300 Rapid Flow Analyzer
  Strip chart recorder
  Personal computer
  Refrigerator
  Balance capable of weighing to 0.0001 g
  Source of Millipore water

- **Other Laboratory Equipment**
  Heated magnetic stirrer and stir bars
  Pipette dispenser
  600 - 1000 ml acid-washed beaker, reserved for P use
  Cover glass, or AL foil
  Metal tray
  Squeeze bottle containing Millipore water
  10-15 200-250 ml volumetric flasks
  2-4 1000 ml volumetric Flasks

Brown Glass Bottles, Qorpak, with TFE-lined closures
Fisher Chemical Company:

#03-320-8D, 240 ml, case of 24	$ 54.00 (7/95)
#03-320-8C, 120 ml, case of 24	$64 (list 7/95)

- **Chemical Reagents**

Potassium Dihydrogen Phosphate, also known as potassium phosphate monobasic (KH_2PO_4), primary standard, crystalline, 500 g
Fisher Chemical Company
#P382-500
Price: $38.00 (list 7/95)

Potassium Nitrate
KNO3, primary standard
Fisher Chemical Company
#P383-100

Reagents for Rapid Flow Analyzer

- **Phosphorus**

Antimony Potassium Tartarate
Fisher #A 867-500

Ammonium Molybdate
Fisher #A674-500

Ascorbic Acid,
Fisher #A61-100

DowFax
Surfactant for P analysis
Available from Alpkem

Sulfuric Acid, concentrated

- **Nitrogen Reagents**

Imidizole
Fisher#03196-500

Cupric Sulfate
Sigma#c7631

Sulfanilimide
Fisher#04525-100

N-1-Napthylethylenediamine (NED)
Sigma #N-9125

Brij-35% solution surfactant
Available from Alpkem

SOP - 3

URI WATERSHED WATCH CHLOROPHYLL-A ANALYSIS PROCEDURE

Fluorometric Analysis of Extracted chlorophyll

Summary of Analytical Methodology

References:

- Standard Methods for the Examination of Water and Wastewater, 1995 edition "Chlorophyll" #10200 H.
- Arar, AJ and GB Collins, 1997, "*In Vitro* Determination of Chlorophyll *a* and Phaeophytin *a* in Marine and Freshwater Algae by Fluorescence." EPA Method 445.0, National Exposure Research Laboratory, Office of Research and Development , US EPA, Cincinnati OH.
- Welschmeyer, NA, 1994. "Fluorometric Analysis of Chlorophyll a in the Presence of Chlorophyll b and Phaeophytins." *Limnology and Oceanography* 39:1985-1992.
- Turner Designs webpage, www.turnerdesigns.com, address: 845 West Maude St. Sunnyvale, CA 94086. "Measuring Extracted Chlorophyll a Free from the Errors Associated with Chlorophyll b and Phaeopigments."

Note: This procedure covers laboratory analysis of chlorophyll a in collected samples. It does not fully address sample collection and field processing procedures.

Summary of Field Sample Filtration: Generally two replicate samples are filtered from each water sample within two hours of sample colelciton. If filtration cannot take place immediately after sample collection, water samples must be refrigeratred. In subdued light water samples are filtered through 0.45 um glass fiber filters (Gelman Type A/E). Individual filters are folded in half, wrapped first in blotting filters (for example a piece of white paper towel or white coffee filter), and then in squares of aluminum foil. A (pre-printed) label is attached and the following information is recorded: location, date, amount of water filtered, sample depth, number of filters in the foil square. The filter packets are placed in a plastic ziplock bag containing desiccant chips and then frozen. The filters are kept frozen until just prior to extraction and analysis.

Summary of Extraction Procedure: A glass fiber filter, through which has been filtered a known aliquot of water, is placed in the bottom of a sample vial. 5 ml of 90% acetone is added to the vial. The vial is capped, shaken vigorously and allowed to steep 18 – 24 hours at 4 deg. C. Prior to analysis the rack of vials is brought to room temperature. The chlorophyll filter is removed from the vial just prior to analysis.

Summary of Analysis: A Turner Designs digital fluorometer (model TD-700) is used for this analysis, using the Welschmeyer non-acidification procedure. It is equipped with a blue mercury vapor lamp, a 436 nm excitation filter and a 680nm emission filter. The fluorometer is calibrated at the start of each season, typically in May, with two liquid chlorophyll a standards, with replicate daily confirmation of calibration made using a secondary standard. Blanks of 90% acetone, and an unused filter extracted with 90% acetone are set up with each rack of 38 samples. Samples are read twice on the fluorometer. The readout is in the direct concentration mode.

Summary of Calibration and Calculation: The fluorometer is calibrated at the beginning of each monitoring season with 2 liquid pure chlorophyll-a standards and reagent blanks. At the time of calibration a solid secondary standard is also analyzed and the formula for calculating chlorophyll-a in samples is determined. That solid standard is analyzed with each batch of samples. When sample concentration is calculated an allowance for instrument drift is made using the daily batch readings of the solid standard.

Limit of Detection and Limit of Quantitation.

Limit of Detection is 1 ug/l chl-a as read on the fluorometer, which is equivalent to 0.1 ug/l chl-a in a 50 ml aliquot of water.

Limit of Quanititation is 2 ug/l chl-a as read on the fluorometer, which is equivalent to 0.2 ug/l in a 50 ml aliquot of water.

Precision: 20% relative percent difference ((A-B/A)X100) <=20. typically each measurement is replicated twice, four aliquots of water are typically filtered, yielding 8 measurements for each water sample.

Standard Operating Procedure:

Basic Instrument Operation

Chlorophyll a procedures must be done in a darkened room. Keep overhead lights off, and shades drawn to limit the light entering the room. The fluorometer is kept on except if use is not planned for >1 month.

1. Fill a vial with the sample to be analyzed.
2. Wipe the outside dry with a Kimwipe.
3. Insert the sample into the sample holder and close the lid.
4. Immediately press <*>. This initiates the following sequence: a 7 second delay for signal stabilization(DLY on display), a 12 second averaging period (AVG on display), then a 5 second display of readout (END on display.
5. Record the reading on the data sheet.

Calibration Procedure

The calibration procedure sets the instrument's sample concentration range and sensitivity based on the chosen fluorescent standards. In addition, the direct calibration mode assigns a digital value to the known standard so that subsequent standards or samples can be referenced to the original standards. Two purchased (from Turner Designs) standards and a blank are used. Additionally, a secondary standard is read immediately after the calibration procedure. The secondary standard is read at the beginning and end of each rack of 40 samples, and compared to its original reading in the calculation of amount of chlorophyll a in the extracted samples to account for instrument drift.

Initial Standardization with liquid primary standards

Note: A sufficient quantity of pure chlorophyll-a in 90% acetone is received with each order to fill 2 vials, so that analysis of each (of two) standards can be done in duplicate.

1. Remove standards from refrigerator and bring to room temperature. Prepare a blank of 90% acetone.
2. Press <ENT> on Home screen, press <1> for set-up, press <1> for Mode. Toggle to choose Multi-optional Mode.
3. Press <ESC> to return to previous screen, press <2> to choose calibration procedure. Toggle to the "Direct Concentration" choice.
4. Press <ESC> to return to previous screen, press <3> to choose the units. Toggle to "ug/l". Press <ESC> twice to return to set-up/Cal screen.
5. Press <2>. The Direct Concentration calibration sequence will appear.
6. When the fluorometer calls for the maximum range press <9> and then enter 250. This is the maximum linear range of the fluorometer.
7. Key in the number of standards, press <ENT>.
8. When the fluorometer asks for the "HiStd Conc", press <9> then enter the concentration and press <ENT>.
9. Fill a vial with that standard, wipe it dry, insert into cuvette holder, and press<*>.
10. Repeat step 8&9 for the next standard, entering its concentration. Press <ENT> when finished.
11. Prepare a vial with the blank (90% acetone) insert it when prompted, and press <ENT>. When the blank has stabilized press <0>. The instrument will read the blank and then return to the Home screen.

Initial Standardization with the Solid Secondary Standard

(after above calibration is completed)

1. Place the solid standard in the cuvette holder with "L" on your left side. Press <*> to read the value. Record this number as the low standard.
2. Remove the standard from the holder, rotate it 180 degrees and place in the holder again, so that "H" is on your left.
3. Press <*> to read the value. Record as the high concentration.
4. Remove the standard and replace cuvette holder.
5. Repeat these measurements at the beginning and end of each rack of 40 samples.

Sample Preparation (day before analysis)

Gather Supplies:
in the fluorometer room (Coastal Institute in Kingston, room 019) except where noted.

- white test tube racks
- 13x100 mm disposable glass vials (test tubes)
- vial caps
- Repipet containing a buffered 90% acetone solution, in fume hood in fluorometer room
- forceps
- Chlorophyll Analysis Data Sheets
- Frozen filters in freezer in room 002.

Organize Data Sheets:
Blank data sheets are kept next to the fluorometer in the inner room of 19A Coastal Institute-Kingston (CIK), URI, referred to as "the fluorometer room." The data sheets are set up to correspond to the sample rack. A maximum of forty samples and blanks can be accommodated in each rack (and on each data sheet.) *It is recommended that no more than 4 racks be analyzed in one sitting.*

Begin Sample Extraction Procedure (day before analysis):

1. Turn on fan for fume hood if it is not already on.
2. Gather supplies for preparation and analysis days.
3. Fill in top of data sheet. Sheets are numbered in consecutive order, 2000-1, 2000-2, etc..
4. If needed, make up buffered 90% acetone solution, store in Repipet. (instructions at end of section.)
5. Check calibration of Repipet. Pump several times to remove air bubbles, then dispense into tared beaker on balance. Check to see that weight is 5.0 g. If not, adjust dispensing volume and re-check.
6. Filters are stored in ziplock bags in the walk-in freezer in room 002.
7. Bring ziplock bag(s) to darkened fluorometer lab when ready to set up for extraction.
8. Remove foil filter packs from the ziplock bags and sort by date. Set foil packets in chronological order.
9. Enter information from sample label onto the chl-a analysis data sheets. Be sure to read and enter the information *carefully*. While most foil packets will contain only one filter per packet, some may contain more, and should have been labeled as such. Location, date, volume filtered and sample depth must be entered for each filter. Rack ID number and setup date must be indicated on the data sheet.
10. Turn on fan for fume hood if it is not already on.
11. Gather supplies for preparation and analysis days.
12. Fill in top of data sheet. Sheets are numbered in consecutive order, 2000-1, 2000-2, etc..
13. If needed, make up buffered 90% acetone solution, store in Repipet. (instructions at end of section.)
14. Check calibration of Repipet. Pump several times to remove air bubbles, then dispense into tared beaker on balance. Check to see that weight is 5.0 g. If not, adjust dispensing volume and re-check.
15. Filters are stored in ziplock bags in the walk-in freezer in room 002.
16. Bring ziplock bag(s) to darkened fluorometer lab when ready to set up for extraction.
17. Remove foil filter packs from the ziplock bags and sort by date. Set foil packets in chronological order.

18. Enter information from sample label onto the chl-a analysis data sheets. Be sure to read and enter the information *carefully*. While most foil packets will contain only one filter per packet, some may contain more, and should have been labeled as such. Location, date, volume filtered and sample depth must be entered for each filter. Rack ID number and setup date must be indicated on the data sheet.
19. Once the data sheet has been completed for a row of 10 samples, using the forceps, remove the filter(s) from the aluminum foil (remember to keep the room dark for this part) and place a filter in the bottom of glass vial. Do not touch the filter with your fingers! The vial containing the filter should then be placed in the test tube rack matching the position identified on the data sheet.
20. Dispense 5ml buffered 90% acetone into each vial using the Repipet, and snap fulcon cap onto top of vial. Vigorously shake each vial, making sure that the filter remains completely submerged in acetone at end of shaking.
21. Continue until the rack has been filled. The second to last spot should be contain an unused filter, for a filter blank, the last spot on the rack should be have a vial containing just 90% acetone (no filter).
22. Cover the rack completely with aluminum foil. Tape the data sheet to its corresponding rack.
23. Place the completed racks in labeled aluminum foil covered cardboard boxes. Tape lids shut.
24. Place the box in the 4 degree walk-in refrigerated room in the CIK. Allow 18-24 hours for complete extraction of chlorophyll from the filter.

Analysis Day:

Gather Supplies: (kept in fluorometer room, except where noted)

- Turner Fluorometer, model TD-700.
- racks of chlorophyll samples (from walk-in cooler)
- Filter remover (6" piece aluminum wire, with bent tip)
- 90% acetone blank, in aluminum covered box in refrigerator in room 19A CIK.
- Turner Designs liquid chlorophyll standards, in refrigerator in room 19A CIK.
- Turner Designs solid secondary standard, in drawer under fluorometer.
- Repipet containing 90% acetone for dilution, in fume hood in fluorometer room.

Remember to keep the lights off during analysis.

Procedure:

1. The fluorometer should already be on.
2. Remove the chlorophyll racks from the walk-in cooler, keep them covered. Bring everything to fluorometer room and allow the samples and any liquid standards to warm to room temperature. All samples/standards *must* be at room temperature before analysis.
3. (This step can be done while the samples are warming to room temp) Shake the first sample vigorously. Remove the cap, and using the filter remover, remove the filter.
4. Replace the cap, and wipe outside of tube with a Kimwipe (removes fingerprints/moisture which interfere with readings). Replace tube in the rack.
5. Repeat step 3 & 4 for the remaining samples on the rack.
6. By the time step 5 has been completed, the samples should be warmed up.
7. **Load sample vial into fluorometer:**
   - wipe off fingerprints,
   - uncap *fluorometer* sample holder (the cap is on a chain so you can't lose it),
   - hold sample vial by its cap and
   - gently put it into the fluorometer sample holder, and
   - recap sample holder.
7. Immediately press <*>. This initiates the following sequence: a 7 second delay for signal stabilization(DLY on display), a 12 second averaging period (AVG on display), then a 5 second display of readout (END on display.)
8. Record the reading on the data sheet.
9. Analyze all the samples & blanks on the rack and then repeat to obtain a second (replicate) value.

Clean-up

1.Empty out tubes into waste acetone receptacle in fume hood in fluorometer room.
2.Leave tubes in racks in fume hood until ready to wash.
3.Clean off work surface.
4.Return Turner Designs standards, and acetone blank to their aluminum-foil box and back into refrigerator.
5.Dump desiccant chips from ziplock bags into bottle in fume hood (to be regenerated later).
6.Put empty ziplock bags in box for later re-use.
7.Make a copy of completed data sheets. Put the original in the chlorophyll file in room 002 CIK and the copy in the *Chl to be entered* file in the in-basket next to computer in room 002.

Washing Vials:
Although the test tubes are disposable, we wash and re-use them.
1.Allow acetone to evaporate from vials in fume hood.
2.Soak vials and caps in soapy water.
3.Use brush to gently scrub (vials break easily).
4.Rinse with tap water, then 3X with de-ionized water.
5.Store vials inverted in test tube rack to dry.
6.Dry caps inverted on paper towel.

Calculation: the equation to calculate chlorophyll concentration is:

Chl-a (ug/l) = (Fo)(Fs)(xtn vol/filt vol)(high solid calib/high solid analysis)
Chl(ug/l) = (Fo)(1)(5/filt vol)(75.0/high solid analysis day)
Chl(ug/l) =375 (Fo)/[(filt vol)(high solid on analysis day)]

- **Fo** = sample reading from fluorometer
- **Fs** = concentration of the liquid standard divided by the mean fluorometric reading. Since the fluorometer reading is set to the value of the liquid standard, Fs = 1 by definition.
- **xtn vol** = volume (ml) of 90% acetone used to extract Chl from frozen filters, assumed to be **5 ml**.
- **filt vol** = volume (ml) of sample water filtered through the filter, variable but usually 50 ml, entered on spreadsheet for each sample.
- **High solid calib** = fluorometric reading of the high solid secondary standard on day of instrument calibration, for 2000 it equals 75. This is recalculated with annual re-calibration with liquid standards. It has not been determined for 2001.
- **High solid analysis** = fluorometric reading of the high solid secondary standard on day that samples are analyzed. This has not been measured for 2001.

The equation above is for a single measurement of chl-a, using high solid calibration standard. Two replicate analyses are made and then averaged. Typically 4 aliquots of water are filtered, yielding 8 measurements of chlorophyll-a for each water sample.

Equipment

- Fluorometer: Turner Designs model TD-700. Excitation filter 436nm, emission filter 680 nm, Property of URI Natural Resources Science Department. Turner Designs, 845 W Maude St, Sunnyvale, CA 94086, 408-749-0998.
- Freezer, -80 deg. C, property of URI Natural Resources Science Department
- Walk -in cool room or refrigerator, maintained at 4 deg. C
- Balance capable of weighing 0.1g
- Repipet, Barnstead/Thermolyne brand, volume range to 20 ml, set to dispense 5ml

Magnetic stirrer and stir bar

Supplies:

- 13x100 mm disposable glass test tubes (Fisher # 14-958-10C, case of 1000)
- vial caps (Fisher "Tainer Tops"#02-706-28)
- 40 place test tube racks
- deionized water
- 10, 100 ml graduated cylinders
- dedicated 500 ml graduated cylinder
- 250 ml beaker
- forceps

Standards:

- **Primary standards.** Liquid chlorophyll-a standards (part # 10-850) are purchased annually from Turner Designs. The two standards are approximately 155 ug/l (high standard) and 15.5 ug/l (low standard). Actual concentration is listed on the certificate of analysis shipped with each set of standards. They are stored in aluminum foil-covered chlorophyll vials in a 4 deg C refrigerator. They are used to calibrate the instrument and re-used to check the calibration.
- **Secondary Standard.** A solid secondary standard has been purchased from Turner Designs. This standard (which is a dark grey rod) has an indefinite shelf life.

Chemical Reagents

- Acetone, Fisher Optima #A-929
- sodium bicarbonate, certified ACS, Fisher #S-233
- chlorophyll standards, liquid primary, #10-850 purchased from Turner Designs

Have on hand:

- Chlorophyll data sheets,
- Filter remover wire (6" aluminum wire with bent tip)
- Kim-wipe tissues
- Aluminum foil

PREPARATION OF REAGENTS FOR CHLOROPHYLL ANALYSIS

90% ACETONE

EQUIPMENT	STORAGE LOCATION
Acetone (Fisher Acetone Optima #A-929)	Fume Hood rm 019A
1N sodium bicarbonate $NaHCO_3$ (see below)	side lab bench rm 019A
Dropper pipet	Left in small flask next to bottle of $NaHCO_3$
500 ml graduated cylinder labeled "chl only"	fume hood or center lab bench rm 019A
magnetic stirrer	lab bench Rm 019A
1.5" magnetic stir bar	Always left in graduated cylinder
Acetone Repipet labelled "90% acetone"	Fume hood, Rm 019A

To make 500 ml 90% acetone:

- **measure 450 ml acetone into the 500 ml graduated cylinder**
- **add DI water to 500ml mark**
- **add 5 drops 1N sodium bicarbonate ($NaHCO_3$ (1 drop/100 ml)**
- **Stir well with the magnetic stirrer, pour into and store in the Acetone Repipet.**

1N SODIUM BICARBONATE

EQUIPMENT	STORAGE LOCATION
$NaHCO_3$ (Fisher #S-233 Certified ACS)	top shelf, glass chemical cabinet
250 ml beaker	non-acid washed glassware cabinet
Balance weighing to 0.1g	Rm 018
magnetic stirrer and 1" stir bar	Side lab bench, 019A

To make approx. 100 ml 1N sodium bicarbonate:

- **measure 8.4 mg $NaHCO_3$ into beaker,**
- **add D.I. to 100 ml, then stir.**
- **Store in brown glass bottle labeled 1N $NaHCO_3$**

SOP – 4
ESS Laboratory Standard Operating Procedure for Turbidity Analysis

SOP – 5
Field Sampling Standard Operating Procedure
Temperature, specific conductance, dissolved oxygen, salinity

Temperature, specific conductance, dissolved oxygen, salinity - SOP

Equipment- YSI Model 85

Note: Field calibration is not necessary for the aforementioned parameters. However, from time to time it is wise to check the system calibration for conductivity. This should be accomplished in the laboratory by following the protocol provided in the YSI Model 85 manual.

Field Operation

1. Turn the meter on- the instrument will activate all segments of the display for a few seconds, which will be followed by a self-test procedure that will last for several more seconds. During this power on self-test sequence, the instrument's microprocessor is verifying that the instrument is working properly.

2. Select a measurement mode (dissolved oxygen %, dissolved oxygen mg/L, conductivity, specific conductance, or salinity). Temperature is always displayed. Selecting a measurement mode is accomplished by simply pressing and releasing the mode button. If the instrument is reading specific conductance (temperature compensated), the large numbers on the display will be followed by μS or mS. Additionally, the small portion of the display will show the ^{o}C flashing on and off. If the instrument is reading conductivity (NOT temperature compensated), the large numbers on the display will be followed by either a μS or an mS; however, the small portion of the display will show the ^{o}C NOT flashing.

3. Lower electrode to the desired depth (surface, middle, or bottom of the water column). When recording the bottom measurement, be sure to keep the electrode at least 0.5 ft above the bottom. Be sure not to disturb bottom substrates prior to or during measurement.

4. Record measurement

5. Cycle to the next measurement mode and record the next parameter. This step should be continued until measurements for all parameters are recorded.

6. Turn meter off and place electrode into storage chamber.

Note: If sampling sites are relatively close together, it is acceptable to leave the meter on until all measurements are recorded.

APPENDIX E

FIELD EQUIPMENT MANUFACTURER'S OPERATION MANUAL (EXCERPTS)

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insert operations manual