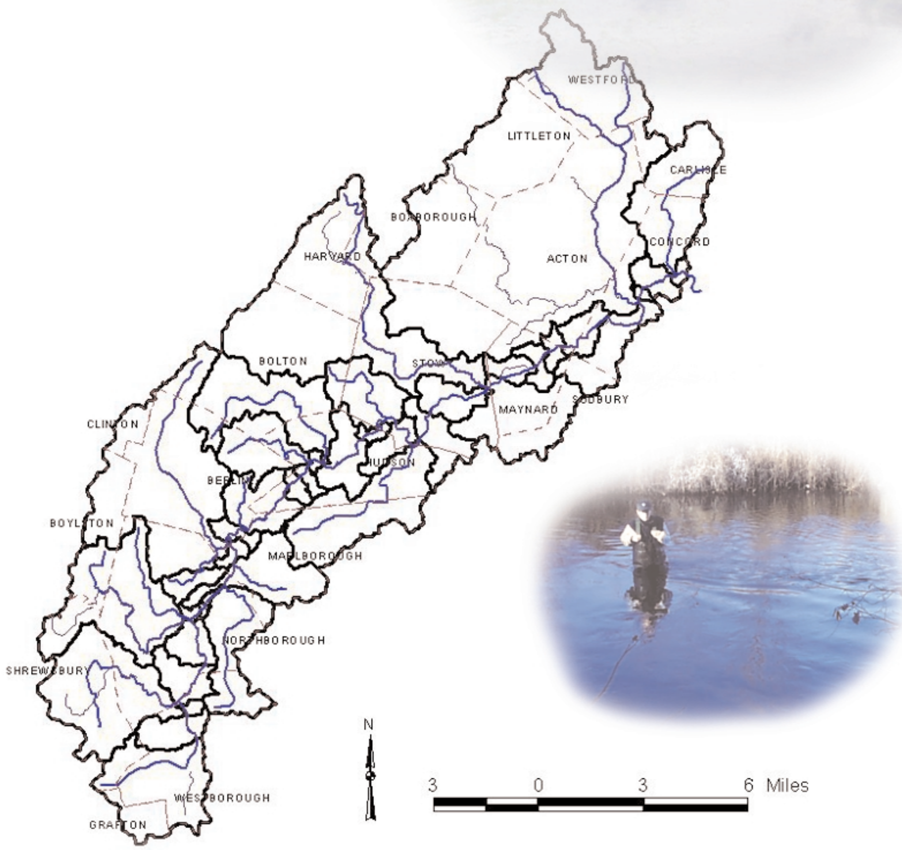
US Army
Corps of Engineers

Quality Assurance Project Plan (QAPP) for SuAsCo Watershed Phased TMDL Study:

Massachusetts
Department of
Environmental
Protection



Assabet River TMDL Assessment Investigation
DEP Project Number 99-09/MWI

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January 18, 2000

(Draft)
QUALITY ASSURANCE PROJECT PLAN
(QAPP)
FOR
SuAsCo Watershed Phased TMDL Study:
Assabet River Tributary and Impoundment Investigation
DEP Project Number 99-09/MWI

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CONTENTS

1.0 PROJECT MANAGEMENT 1

1.1 Project/Task Organization 1

1.2 Problem Definition/Background 3

1.3 Project/Task Description and Schedule 3

1.4 Quality Objectives and Criteria for Measurement Data 13

1.4.1 Quality Objectives 13

1.4.2 Measurement Performance Criteria 13

1.5 Special Training Requirements 15

1.5.1 Training and Certification 15

1.6 Documentation and Records 15

1.6.1 Information Included in the Reporting Packages 15

2.0 MEASUREMENT/DATA ACQUISITION 1

2.1 Sampling Process Design (Experimental Design) 1

2.1.1 Scheduled Project Activities, Including Measurement Activities 1

2.1.2 Rational for the Design 1

2.1.3 Design Assumptions 1

2.1.4 Procedures for Locating and Selecting Environmental Samples 2

2.1.5 Classification of Measurements as Critical or Noncritical 2

2.2 Sampling Methods Requirements 3

2.2.1 Sample Collection, Preparation, Decontamination Procedures 3

2.2.2 Sampling/Measurement System Failure Response and Corrective Action Process 7

2.2.3 Sampling Equipment, Preservation, and Holding Times Requirements 8

2.3 Sample Handling and Custody Requirements 9

2.3.1 Sample Custody Procedure 9

2.4 Analytical Methods Requirements 11

2.4.1 Preparation of the Samples 11

2.4.2 Analytical Methods 13

2.5 Quality Control Requirements 14
2.5.1 QC Procedures 14
2.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements 17
2.6.1 Testing, Inspection, and Maintenance 17
2.7 Instrument Calibration and Frequency 17
2.7.1 Identify the Instrumentation Requiring Calibration 17
2.7.2 Document the Calibration Method that Will Be Used for Each Instrument 18
2.7.3 Document the Calibration Standards 18
2.7.4 Document Calibration Frequency 18
2.8 Data Acquisition Requirements (non-direct measurements) 18
2.8.1 Acquisition of Non-Direct Measurement Data 18
2.8.2 Tracking and Quality Verification of Supplies and Consumables 19
2.9 Data Management 20
2.9.1 Data Recording 20
2.9.2 Data Validation 20
2.9.3 Data Transformation 20
2.9.4 Data Transmittal 20
2.9.5 Data Reduction 20
2.9.6 Data Analysis 22
2.9.7 Data Tracking 22
2.9.8 Data Storage and Retrieval 23

3.0 ASSESSMENT/OVERSIGHT 1
3.1 Assessments and Response Actions 1
3.1.1 Assessment Activities and Project Planning 1
3.1.2 Documentation of Assessments. 1

4.0 DATA VALIDATION AND USABILITY 1
4.1 Data Review, Validation, and Verification Requirements 1
4.1.1 Sampling Design 1
4.1.2 Calibration 1

4.1.3 Data Reduction and Processing 1
4.2 Validation and Verification Methods 1
4.2.1 Describe the Process for Validating and Verifying Data 1

5.0 REFERENCES 1

LIST OF FIGURES **PAGE**

Figure 1-1 Organizational Chart Outlining the Relationship Between the Parties Involved in the Investigation of the Assabet River 2

Figure 1-2 Map 1 in a series of 5 maps illustrating the study area of the Assabet River. 5

Figure 1-3 Map 2 in a series of 5 maps illustrating the study area of the Assabet River. 6

Figure 1-4 Map 3 in a series of 5 maps illustrating the study area of the Assabet River. 7

Figure 1-5 Map 4 in a series of 5 maps illustrating the study area of the Assabet River. 8

Figure 1-6 Map 5 in a series of 5 maps illustrating the study area of the Assabet River. 9

Figure 1-7 Sketch of stormwater sampler to be used for wet-weather sampling. 11

Figure 2-1 Sample chain-of-custody form to be used during the Assabet River water quality investigation. 12

LIST OF TABLES **PAGE**

Table 1-1 Summary of water quality sampling locations for the Assabet River survey. 4

Table 1-2 Measurements to be collected during dry-weather surveys. 10

Table 1-3 Desired precision, accuracy, field blank cleanliness, and MDL for each parameter based on the quality objectives set forth in this QAPP. 14

Table 2-1 Classification of measured water quality parameters as “critical” or “non-critical” 2

Table 2-2 Field analytical equipment and operating ranges. 3

Table 2-3 CMAST Standard Sample Holding Times 5

Table 2-4 CMAST Detection Limits and Accuracy for Laboratory Measurements 6

Table 2-5 CMAST Criteria for Measurement 6

Table 2-6 Summary of analyte, field preservation, and holding time for Assabet River water quality survey for both baseflow and stormflow samples. 8

Table 2-7 Methods of detection for dry and wet-weather surface water analytes. 13

Table 2-8 Monitoring Parameters 15

Table 2-9 Laboratory Analysis[i] 16

Table 2-10 Summary of supplies, inspection requirements, and responsible party 19

Appendices

Appendix I – Quality control plan for Thorstensen Laboratory, Inc.

Appendix II – Standard operating procedures (SOP) for YSI® for water quality meter.

Appendix III – Standard operating procedures (SOP) for flow measurements.

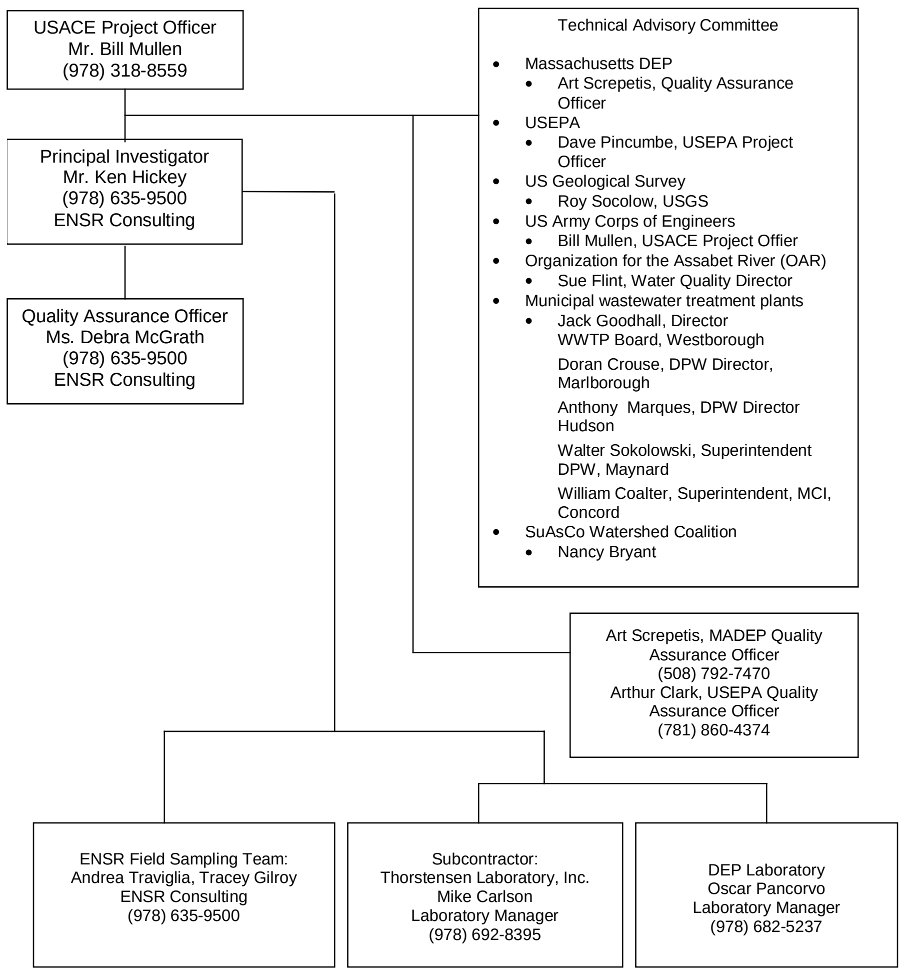
1.0 PROJECT MANAGEMENT

1.1 Project/Task Organization

Funding for this project is managed by the United States Army Corps of Engineers (USACE) New England District. Mr. Bill Mullen is the project coordinator for the USACE and is primarily responsible for working with ENSR to insure that the project scope is met. Mr. Mullen has also had an active role in designing the water quality sampling field efforts and is ENSR's primary contact point at the USACE. Mr. Screpetis of the Massachusetts DEP and Mr. Clark of the USEPA are both involved in the review and approval of the QAPP presented here. Mr. Ken Hickey is ENSR's project manager for this investigation and is responsible for coordinating the specific details of the project and ensuring that the work completed by ENSR meets the scope of the project. Mr. Hickey will be working closely with all interested parties to formulate an effective sampling plan and to solicit feedback regarding sampling efforts. He is also responsible for all budgetary constraints on the project. Ms. Debra McGrath is ENSR's Quality Assurance Officer. Her primary responsibility will be to insure that the data collected throughout this investigation meet the quality objectives set forth in this QAPP.

A group of interested parties designated the Technical Advisory Committee (TAC) has been organized to offer technical guidance throughout the investigation. The TAC includes representatives from the Massachusetts Department of Environmental Protection, the US Environmental Protection Agency, the US Geological Survey, the US Army Corps of Engineers, the Organization for the Assabet River (OAR), municipal wastewater treatment plants, the SuAsCo Watershed Community Council (Water Quality & Water Quantity Task Force), SuAsCo Watershed Coalition, and the SuAsCo Watershed Team. The role of the TAC will be to provide project guidance and review of proposed sampling locations, methodologies, draft and final reports, and to resolve issues that may arise during the course of the project. A team of ENSR scientists will complete sample collection. These individuals will have the responsibility of carrying out the tasks outlined by the USACE, ENSR's project manager, and the TAC. Water samples will be analyzed at a local water quality laboratory located in Westford, Massachusetts and at a DEP laboratory in Lawrence, Massachusetts. Figure 1-1 is an organizational chart outlining the parties involved in this investigation.

Figure 1-1 Organizational Chart Outlining the Relationship Between the Parties Involved in the Investigation of the Assabet River



1.2 Problem Definition/Background

Environmental professionals within the state and federal environmental agencies agree that the Assabet River suffers from eutrophication as a result of excessive nutrient loads to the river. The loading of these nutrients, in particular phosphorus, plays a major role in encouraging the growth of nuisance algae and aquatic plants. The decay of the aquatic algae and vegetation in the Assabet River has been known to cause foul odors and to reduce dissolved oxygen levels in the river. A substantial portion of the nutrients entering the Assabet River are derived from five wastewater treatment plants that discharge effluent at locations along the river. Stormwater runoff and internal recycling from river and impoundment sediments also contribute to the nutrient loading problem. In addition to nutrients, most river flow is comprised of wastewater effluent during low flow periods. At times, the river consists almost entirely of wastewater effluent. Low flow periods tend to occur during the summer and early fall and contribute to the river's eutrophication problem. In addition, dams have altered the natural flow characteristics of the river resulting in nutrient retention in both the water and sediments within the impoundments.

Presently, most sections of the Assabet River are officially categorized as "non-assessed" by MADEP because the agency has not monitored the river's water quality in recent years to determine if it meets applicable Class B water quality standards. Despite the lack of recent published data, MADEP recognizes that the river has a serious eutrophication problem. As a result, the DEP has initiated work to quantify present nutrient loadings and determine the levels of nutrients that the river could receive and still comply with applicable narrative and numeric water quality standards. Specifically, the MADEP is developing a Total Maximum Daily Load (TMDL) allocation for nutrients in the Assabet River. A TMDL allocation analysis results in the establishment of the maximum amount of a pollutant that may be introduced to a waterbody while allowing the waterbody to comply with applicable water quality standards.

1.3 Project/Task Description and Schedule

The non-summertime impoundment and tributary field investigation has been designed to collect sufficient measurements to support evaluation of the extent of nutrient retention within the river system and to quantify non-point source loadings to the river. Field surveys will be conducted to quantify the movement of nutrients through the five largest impoundments in the Assabet River system. Also, nutrient loadings from tributaries will be measured to support assessment of non-point source impacts on water quality in the river system. This investigation will be conducted during wintertime conditions to determine the impact of nutrient loadings through the system during periods of minimal algal growth. In particular, it is important to determine whether or not nutrients are retained in river impoundments during the non-summer months and then geochemically released only to significantly enhance problematic summertime eutrophication in the Assabet River. The data collection portion of the project may be described as the following 5 distinct tasks; 1) dry-weather impoundment/tributary surveys, 2) wet-weather tributary surveys, 3) impoundment sediment nutrient flux survey, 4) impoundment bathymetric and sediment thickness survey and 5) impoundment detention time survey. A description of each specific task is provided below.

1) Dry-weather Combined Impoundment/Tributary Surveys

Surface water quality surveys will be conducted monthly in January, February, and March 2000 for a total of three surveys. The surveys will be performed over a one or two day period and will include measurement of, streamflow, nutrient-related water quality, and in-situ water quality on the river and in selected tributaries. River sampling stations were selected to include locations upstream and downstream of the five major impoundments. The five impoundments under investigation are Powdermill, Ben Smith/Crow Island, Gleasondale, Hudson, and Allen Street Impoundments. These five impoundments were selected primarily because they are the largest impoundments on the Assabet River and are believed to have the most significant potential impact in terms of nutrient cycling throughout the year

Sixteen water-sampling locations, including 10 river locations and 6 tributary locations, have been identified for this investigation and are listed in Table 1-1. River locations were selected based on the proximity to the five impoundments and tributary sample locations have been selected based on the size of contributing watersheds. Figures 1-2 through 1-6 contain maps of sampling locations including river mile and location identification (ID) designations.

Table 1-1 Summary of Water Quality Sampling Locations for the Assabet River Survey

River Mile	River Location
30.7	Maynard Street, Westborough
28.0	School Street, Northborough
25.2	Allen Street, Northborough
19.4	Chapin Road, Hudson
17.9	Route 85, Hudson
15.9	Cox Street, Hudson
8.6	Route 117/62, Maynard
7.7	USGS Gage, Maynard
6.3	Below Powder Mill, Acton
2.6	Route 2, Concord

River Mile	Tributary Location	Area (miles^2)
2.8	Nashoba Brook, Concord	47.6
9.4	Elizabeth Brook, Maynard	20.0
21.2	North Brook, Berlin	18.0
12.3	Fort Meadow Brook, Hudson	13.4
24.5	Cold Harbor Brook, Northborough	11.5
28.7	Hop Brook, Westborough*	9.3
1.3	Spencer Brook, Concord*	7.7
17.3	Mill Brook, Hudson*	6.6
17.5	Hog Brook, Hudson*	6.3
23.1	Stirrup Brook*	4.9
	*Denotes sampled during wet-weather events only.	

Figure 1-2 Map 1 in a Series of 5 Maps Illustrating the Study Area of the Assabet River

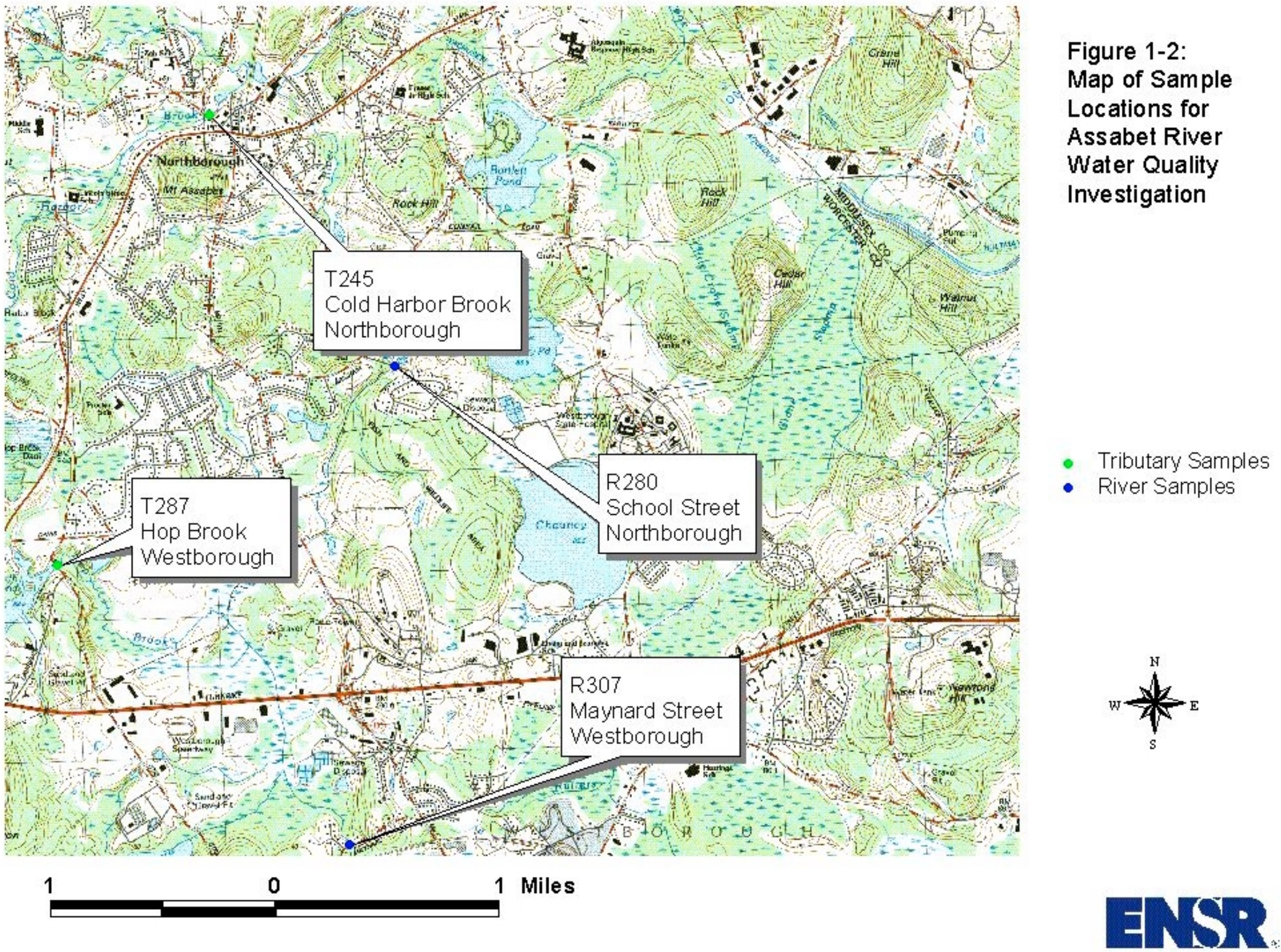


Figure 1-3 Map 2 in a Series of 5 Maps Illustrating the Study Area of the Assabet River

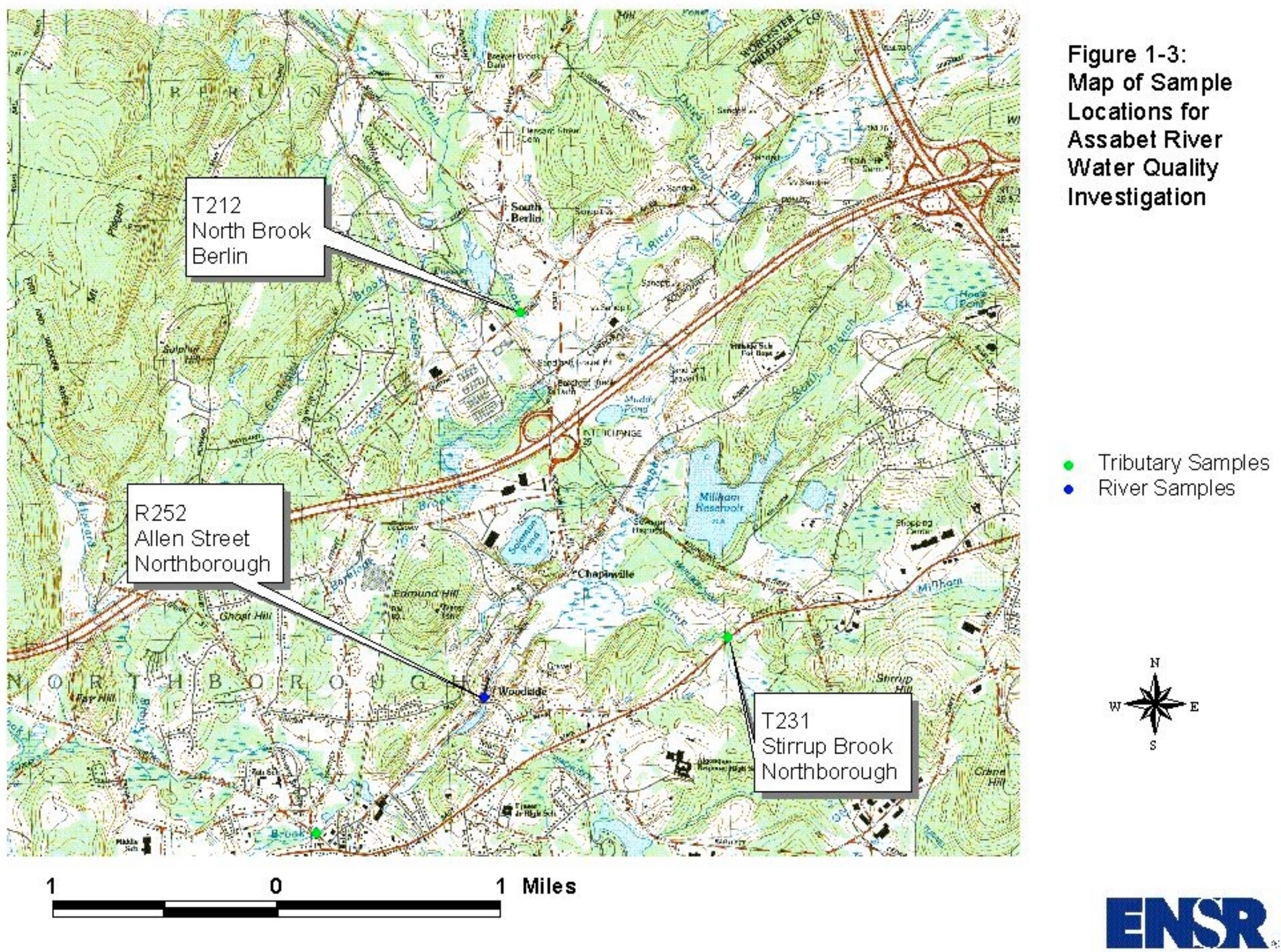


Figure 1-4 Map 3 in a Series of 5 Maps Illustrating the Study Area of the Assabet River

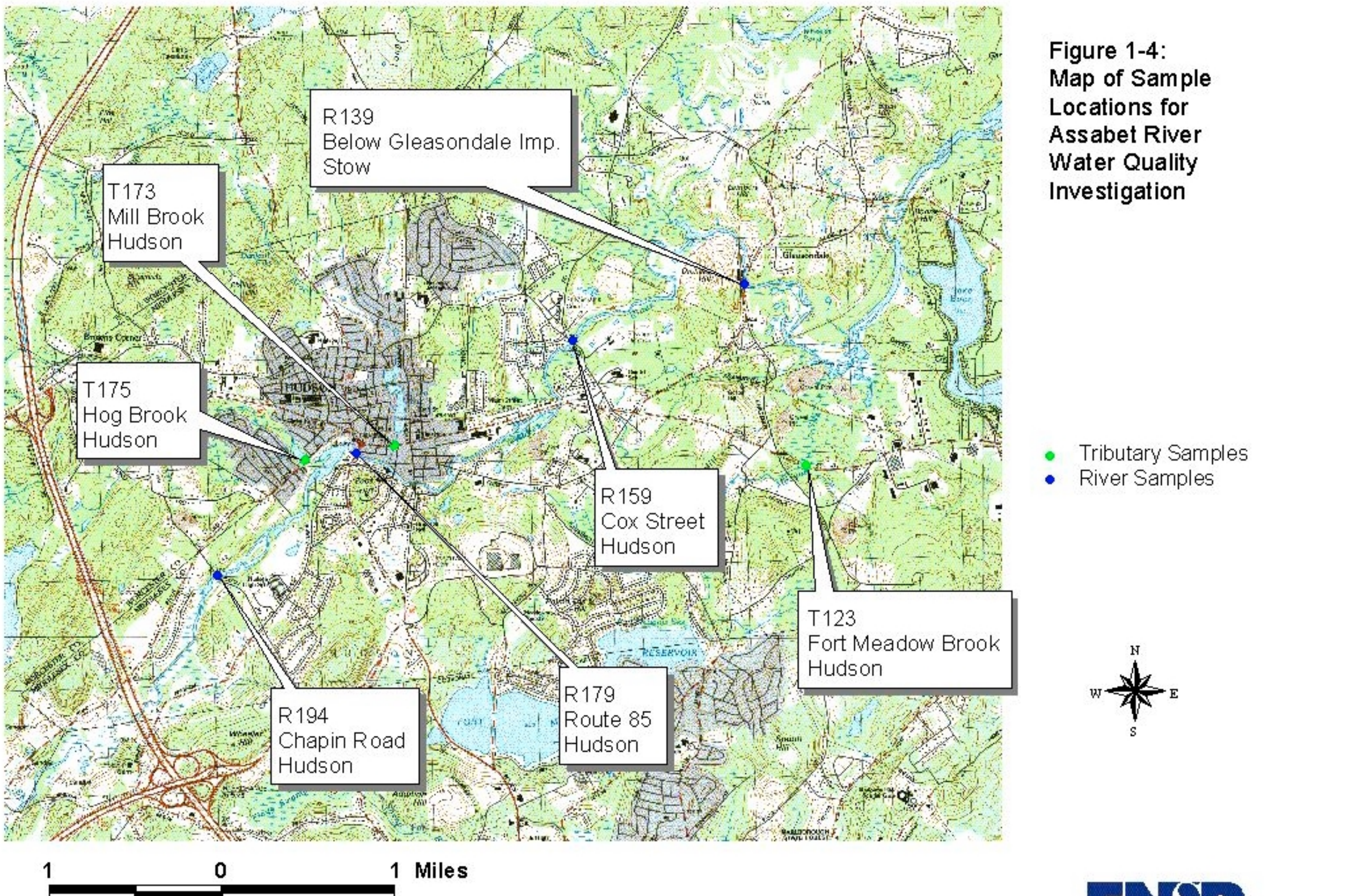


Figure 1-5 Map 4 in a Series of 5 Maps Illustrating the Study Area of the Assabet River

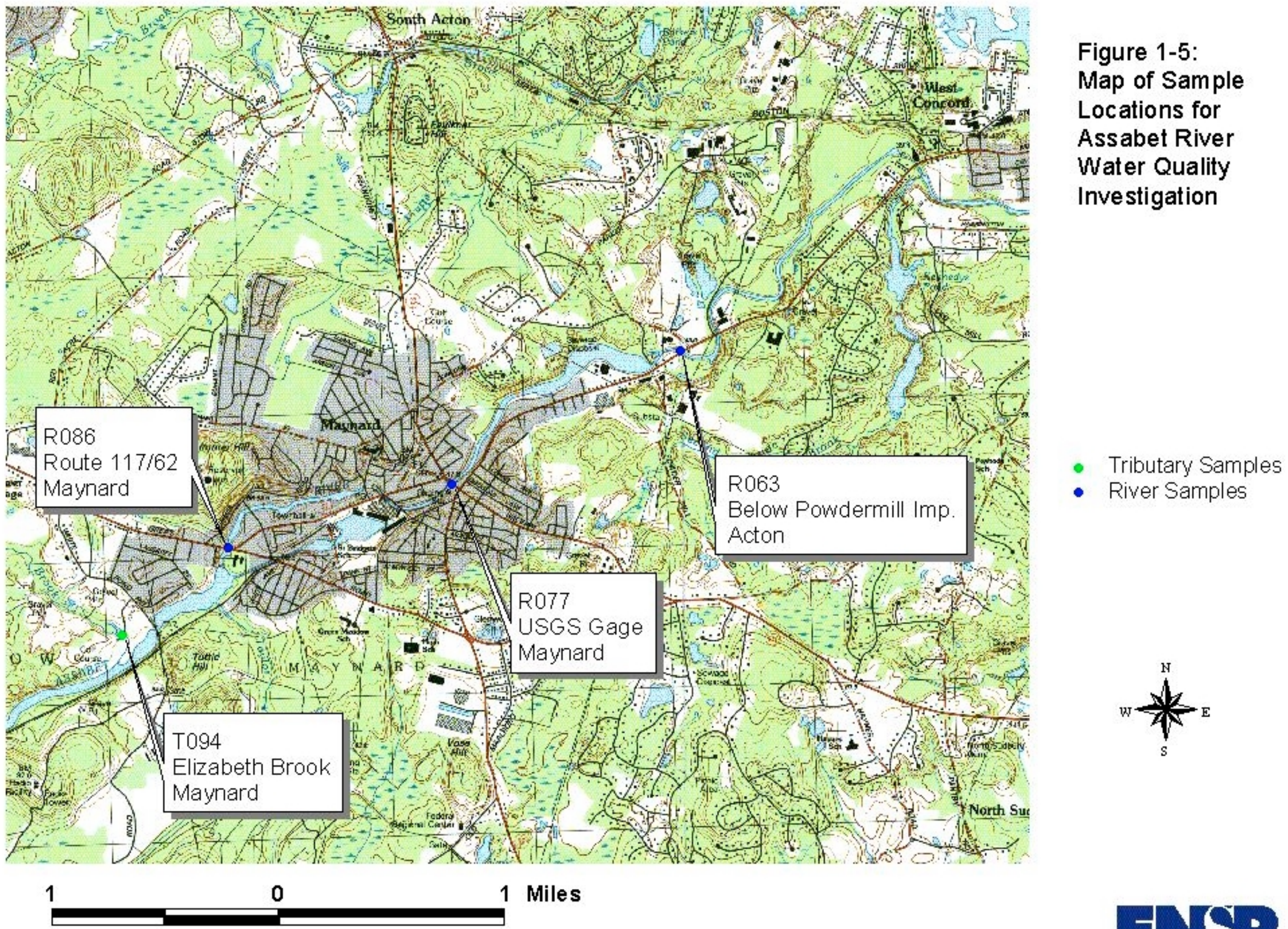
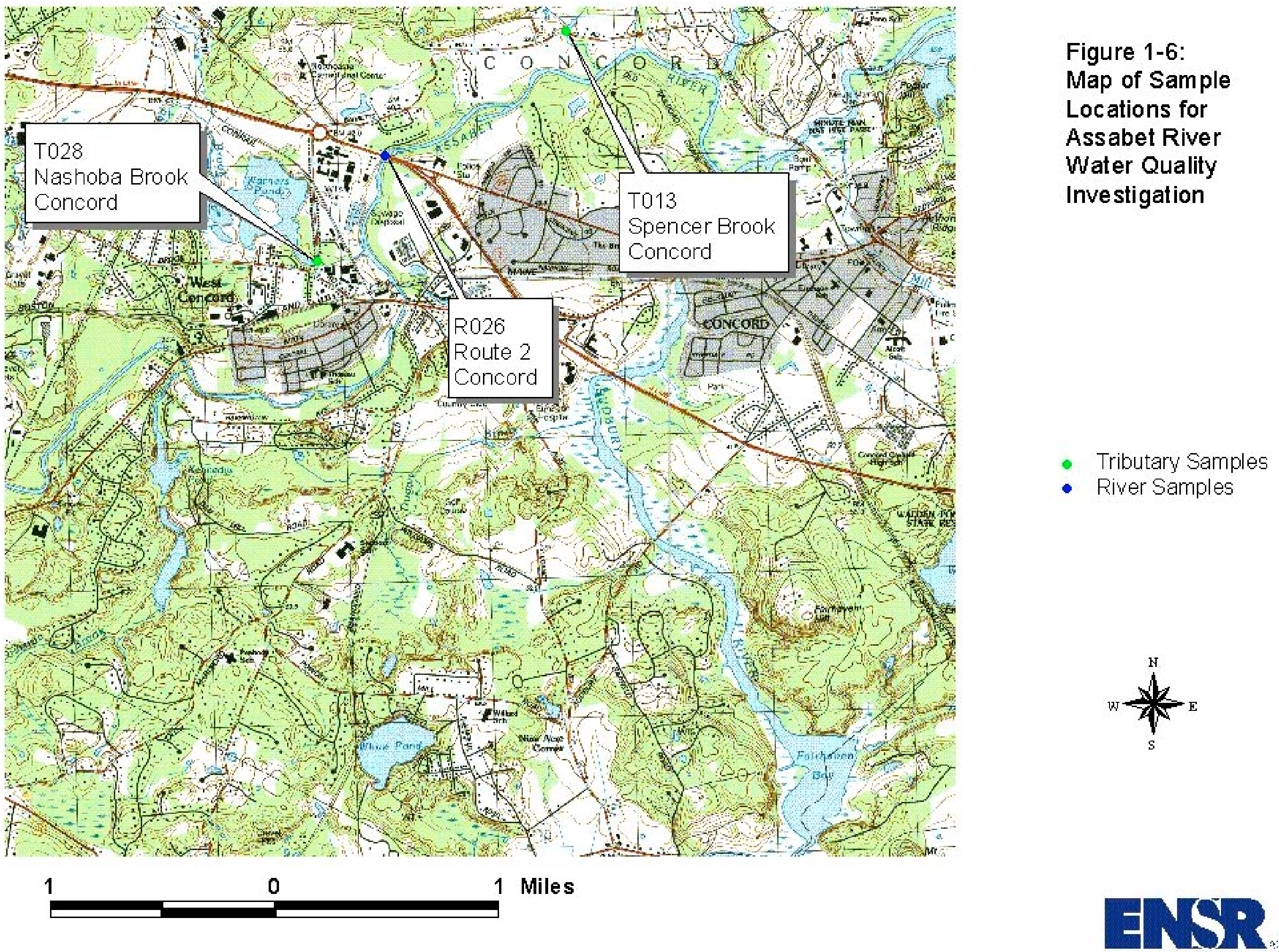


Figure 1-5:
Map of Sample Locations for Assabet River Water Quality Investigation

Figure 1-6 Map 5 in a Series of 5 Maps Illustrating the Study Area of the Assabet River



Water samples will be collected upstream and downstream of each impoundment and in 6 of the 10 listed tributaries, over the course of the dry-weather survey. Sampling will include *in situ* water quality monitoring and grab sample collection for laboratory analysis. *In-situ* water quality measurements will be collected using a portable water quality meter and grab samples will be analyzed for parameters listed in the following Table 1-2.

Table 1-2 Measurements to be Collected During Dry-Weather Surveys

In situ **Measurements**	**Laboratory Measurements**
• Temperature • Conductivity • pH • Dissolved Oxygen • Flow	• Fecal Coliform • BOD-5 • BOD-30 • Nitrate • Ammonia • Total Kjeldahl Nitrogen • Total Phosphorus • Ortho-Phosphorus • Total Suspended Solids • Total Settleable Solids • Particle Size Distribution • (range: 0.50 – 2,000 um)

In addition to making *in situ* measurements and collecting grab samples for laboratory analysis, streamflow will be measured at each sampling location in accordance with USGS protocols as outlined in the document entitled "Measurement and Computation of Streamflow: Volume 1. Measurement of Stage and Discharge" (USGS, 1982). The streamflow measurement protocol includes stringing a tape measure across the stream channel perpendicular to flow and recording width, depth, and water velocities at 20 to 30 locations across the channel for the calculation of flow rate. Velocities will be measured using a mechanical "pygmy" rotating cup current meter (e.g., Price model #6025) and/or an electromagnetic current meter (e.g. Marsh-McBirney Model #2000). Stream flow measurements will then be used to estimate flows and nutrient loadings throughout the river system.

2) Wet-Weather Tributary Surveys

During the period of January through May 2000, three wet-weather sampling surveys will be performed to support assessment of non-point source nutrient loadings associated with precipitation events. Wet-weather samples will be collected during precipitation storm events, defined herein as an accumulation of greater than 0.25" of rain over a 12-hour period.

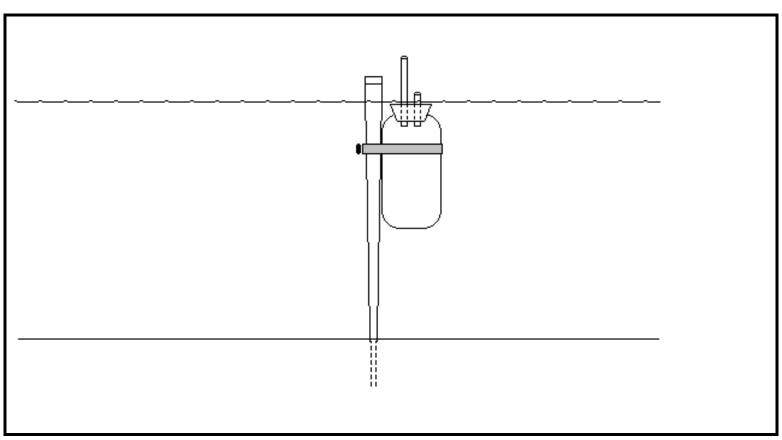
Wet-weather samples will be collected in the 10 largest tributaries to the Assabet River, listed in Table 1-1. Grab samples will be analyzed for the suite of parameters listed in Table 1-2. Wet-weather sampling will be performed using simple automated grab samplers. The automated grab sampler design is shown in Figure 1-7 and consists of a sample bottle equipped with a stopper with two tubes, one shorter (to allow water to enter) and one longer (to allow air to exit). The sample bottle will be attached to a post and placed in the river such that the shorter tube is approximately one inch above the water line (depending on the characteristics of the tributary cross-section). When the water level in the river rises due to storm water runoff, the sample bottle will be filled with water.

Sampling personnel will not be present at the time of automated sample collection. Personnel will visit the sampling location within 20 hours on commencement of the storm event. Upon arrival at the sampling location, sampling personnel will gather the pre-collected grab sample bottle and measure water level and streamflow in the tributary. All analytes (Table 1-2) will be collected using the automated sampler except for fecal coliform bacteria. Fecal coliform samples will not be collected using the automated sampler because of the short holding time (6 to 8 hours) associated with that analyte. Rather, fecal coliform samples will be collected by sampling personnel within 20 hours of the automated sampling event.

Note that streamflow will not be measured concurrently with automated grab sampling. In order to estimate streamflow at the time of automated sample collection, sampling personnel will survey the tributary cross-section and establish a preliminary stage-discharge relationship. Stage-discharge measurements will be recorded and used to estimate streamflow corresponding to the water level at the time of automated sample collection.

As an additional measure of storm water-related flows, the peak water level associated with the storm event will be automatically measured and recorded using a simple technique. To measure peak storm water level, a clear plastic tube will be mounted on a post in the river, such that the water level in the tube is the same as the water level in the river. Cork dust will be placed inside the tube and will float on top of the water. When the water level in the river rises and recedes, cork dust residue will be left on the sides of the plastic tube and will indicate the maximum water level during the runoff event. Sampling personnel will record this level when retrieving storm water samples.

Figure 1-7 Sketch of Stormwater Sampler to be Used for Wet-Weather Sampling



3) Sediment Nutrient Flux Survey

A sediment nutrient flux survey will be performed in the Ben Smith Impoundment. The Coastal Systems Laboratory at the Center for Marine Science and Technology (CMAST) at the University of Massachusetts in New Bedford will perform the sediment nutrient flux survey task. The overall objective of the nutrient flux portion of this study is to quantify the flux of selected nutrients and oxygen between the sediments and their overlying waters in the Ben Smith impoundment. These fluxes can be significant in relation to overall carbon, nutrient, and oxygen dynamics in aquatic systems and the magnitude of flux is influenced by many environmental factors including temperature and the availability of labile organic carbon. In particular, this data will be important to quantify phosphorus retention in the Ben Smith Impoundment including recycling rates and sediment storage capacity. The sediment nutrient flux survey will provide critical information for the determination of phosphorus retention in impoundments in the form of recycling rates and sediment storage capacity.

Nutrient species concentrations will be measured over time and under four scenarios including (1) ambient temperature, (2) moderately increased temperature, (3) summertime temperature, and (4) anoxic conditions. These scenarios will provide valuable measurements of sediment/water column nutrient interactions during both non-summer and summer time conditions, as well as quantifying chemical release of phosphorus from sediments. The sediment flux survey will include measurement of sediment oxygen demand over an extended time period.

4) Impoundment Bathymetry and Sediment Thickness Surveys

A bathymetric and sediment thickness survey will be performed in five impoundments (Powdermill, Ben Smith/Crow Island, Gleasondale, Hudson, and Allen Street). Bathymetry and sediment thickness surveys will support assessment of the impacts of river impoundments on water quality. Bathymetry measurements will support estimation of impoundment volume and average residence time. Sediment thickness measurements will support assessment of sediment impacts on river water quality. Volunteers from the Organization for the Assabet River (OAR), with training and support from ENSR personnel, will perform bathymetry and sediment thickness surveys.

In each impoundment, approximately 120 measurements of water depth and sediment thickness will be made at approximately 12 transects, each containing 10 measurements. Measurements will be made using a graduated pole placed through the water column to determine water depth. The pole will then be forced through the surface sediment to determine soft sediment thickness.

For each impoundment, bathymetry and sediment thickness measurements will be used to estimate impoundment water volume and soft sediment volume. Measurements will also be processed and used to generate maps of bathymetry and sediment thickness in each impoundment.

5) Impoundment Detention Time Survey

A survey will be performed to measure detention time in the Ben Smith impoundment. The survey will include injection of Rhodamine WT dye at the inlet of the Ben Smith Impoundment and continuous-monitoring at the outlet of the impoundment to measure dye concentrations. The dye study will support the assessment of potential water quality impacts associated with river the impoundments. Specifically, the dye study will provide a measurement of residence time of water in the river impoundment. The residence time measurements, along with sediment and water column nutrient measurements, will be used to assess the impact of river impoundments on nutrients and biological activity in the river system.

1.4 Quality Objectives and Criteria for Measurement Data

1.4.1 Quality Objectives

There are three data quality objectives for this investigation. Firstly, to insure that the parameters measured during this investigation will adequately describe nutrient cycling in the system at levels necessary to understand eutrophication processes. Secondly, to insure that sample results are representative of the stream at the time of sampling and that the data produced during this investigation are accurate. Thirdly, to reduce the uncertainty associated with related experimentation that will explain the sediment related nutrient cycling in the system.

1.4.2 Measurement Performance Criteria

The first objective will be met by carefully examining recent data collected on the Assabet River and working closely with the TAC to insure that the stations selected for sampling will provide the information necessary to quantify a nutrient balance in each impoundment. Since relatively low nutrient concentrations can greatly enhance the growth of biomass in aquatic systems, ENSR has required that the water samples be analyzed using a very low detection limit for phosphorus. The second objective will be met by collecting duplicate samples throughout the investigation to insure the quality of the laboratory analysis and to insure the reproducibility of results. The third objective will be met by duplicating the sediment nutrient experimentation to illustrate the variability of results within a benthic system.

Based on the data quality required for this project, and the parameters that will be determined during the field and laboratory analysis, a certain level of precision, accuracy, field blank cleanliness, and maximum detection limits (MDLs) is desired. Table 1-3 lists the parameters to be measured and the desired detection limit for each analyte.

Table 1-3 Desired Precision, Accuracy, Field Blank Cleanliness, and MDL for each Parameter Based on the Quality Objectives Set Forth in this QAPP

Parameter	Field Precision	Lab Precision	Accuracy	Field Blank Cleanliness	MDL
Fecal Coliform	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0 per 100 ml
BOD-5	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	1.0 mg/L
BOD-30	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	1.0 mg/L
Nitrate	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0.01 mg/L
Ammonia	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0.03 mg/L
Total Kjeldahl Nitrogen	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0.05 mg/L
Total Phosphorus	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0.01 mg/L
Ortho-Phosphorus	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0.01 mg/L
Total Suspended Solids	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	1.0 mg/L
Total Settleable Solids	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0.1 ml/L
Particle Size Distribution	< 30% of RPD	< 20% of RPD	75-100% recovery for either blank or matrix spike.	< Detection limit	0.75-2,000 um

1.5 Special Training Requirements

1.5.1 Training and Certification

This investigation includes no non-routine field sampling techniques, field analyses, laboratory analyses, or data validation. Specialized training is therefore not required however; all field personnel are experienced in standard protocols for sampling water, sediment and algae using the equipment identified within this QAPP. Certifications relevant to implementing of this plan are not required.

1.6 Documentation and Records

1.6.1 Information Included in the Reporting Packages

The final evidence file will be the central repository for all documents, which constitute evidence relevant to sampling and analysis activities as described in this QAPP. ENSR is the custodian of the evidence files and maintains the contents of the evidence files for the investigation, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews in a secured, limited access area and under custody of the ENSR Project Manager.

The final evidence files will include at a minimum:

- Field logbooks,
- Field data and data deliverables,
- Photographs, and drawings,
- Sample collection logs,
- Laboratory data deliverables,
- Data validation reports and data assessment reports,
- Progress reports, QA reports, interim project reports, etc.,
- All documentation (forms, airbills, etc.)

2.0 MEASUREMENT/DATA ACQUISITION

2.1 Sampling Process Design (Experimental Design)

2.1.1 Scheduled Project Activities, Including Measurement Activities

This investigation will be performed from January to May 2000. It is anticipated that three dry-weather sampling events will be performed on an approximately monthly basis in January, February, and March. It is also anticipated that three wet-weather surveys will be performed from January through May 2000. The impoundment sediment nutrient flux and detention time surveys will be performed in March 2000. Scheduling of all survey tasks is dependent on weather, streamflow, and ice cover conditions. The impoundment bathymetry and sediment thickness survey is scheduled to be performed during April or May 2000. Flexibility in survey scheduling is required in order to collect measurements under conditions appropriate to support project objectives.

2.1.2 Rational for the Design

The field-sampling program detailed in this QAPP has been designed to quantify nutrient loadings to the Assabet River and to evaluate nutrient cycling in river impoundments. Surveys are scheduled during the wintertime in order to capture nutrient loadings and nutrient movement through the system during periods of reduced biologic activity. One objective of the study is to quantify the accumulation or depletion of nutrients within the impoundments through river and impoundment sampling events. A second objective is to quantify non-point source loadings through tributary sampling events.

The role of river impoundments in retaining and cycling nutrients will be investigated through measurement of nutrient loads into and out of impoundments, measurement of sediment nutrient flux, and measurement of detention time. Sediment nutrient flux measurements will provide an assessment of the role of impoundment sediments as a sink and/or source of available nutrients. Lastly, the volume of water and sediment in each impoundment will be quantified as part of the bathymetric/ sediment thickness task.

The role of non-point sources, in contributing to the overall nutrient load to the Assabet River, will be assessed through measurements of nutrient loadings in 6 tributaries during three dry-weather surveys, and in 10 tributaries during wet-weather conditions. Quantification of non-point source nutrient loadings, coupled with known point source nutrient loadings, will provide sufficient information to support the TMDL assessment objectives.

2.1.3 Design Assumptions

During the collection of dry-weather samples it will be assumed that the system is at or near baseflow conditions. Baseflow conditions will be determined based upon review of the United States Geological Survey (USGS) real-time stream gage at Maynard (gage #01097000) and antecedent rainfall events. Also, during water sampling events it is assumed that, ambient water is laterally and vertically well mixed throughout river cross-sections, and water samples collected are representation of water at that location.

To effectively map the bathymetry and sediment thickness, it is assumed that the impoundments will be mostly full with water during the investigation. Since this type of survey requires the use of a boat, more water in the impoundment will allow for more of the impoundment to be mapped.

2.1.4 Procedures for Locating and Selecting Environmental Samples

All sample locations will be identified on US Geological Survey topographic maps. Field personnel will perform a reconnaissance survey prior to the first sampling event to identify appropriate sampling locations and will carry maps of the study area during all field-sampling operations. During impoundment sampling events, detailed topographic maps of impoundments will be used and locations plotted relative to landmarks (e.g., buildings and bridges). Geographical Positioning Systems (GPS) will not be used during this investigation to locate sample sites.

2.1.5 Classification of Measurements as Critical or Noncritical

Nearly all of the measurements being collected during the dry-weather and wet-weather surveys are considered to be "critical" to the characterization of the system due to the complex interconnection of factors affecting nutrient cycling in aquatic environments. Table 2-1 provides a list of measurements to be collected and identification of critical or non-critical status, and identification of organization responsible for performing the measurement or analysis.

Table 2-1 Classification of Measured Water Quality Parameters as "Critical" or "Non-Critical"

Parameter	Critical/Non-Critical	Measurement made by:
Temperature	Critical	ENSR
Conductivity	Critical	ENSR
pH	Critical	ENSR
Dissolved Oxygen	Critical	ENSR
Flow	Critical	ENSR
Fecal Coliform	Critical	Thorstensen
BOD-5	Critical	Thorstensen
BOD-30	Critical	Thorstensen
Nitrate	Critical	Thorstensen
Ammonia	Critical	Thorstensen
Total Kjeldahl Nitrogen	Critical	Thorstensen
Total Phosphorus	Critical	Thorstensen
Ortho-Phosphorus	Critical	Thorstensen
Total Suspended Solids	Critical	Thorstensen
Total Settleable Solids	Critical	Thorstensen
Particle Size Distribution	Critical	To Be Determined

2.2 Sampling Methods Requirements

2.2.1 Sample Collection, Preparation, Decontamination Procedures

1) Dry-Weather Combined Impoundment/Tributary Surveys

Surface water samples for each suite of analytes will be collected in flowing water. A single pre-cleaned 1-liter plastic container will be filled by first removing the cap, then filling and rinsing the bottle three times prior to filling with sample water. Two 1-liter sample bottles will be filled and sent to Thorstensen Laboratory, Inc in Westford, MA or the DEP Laboratory in Lawrence, MA. Additional 1-liter samples will be collected in cases when duplicated samples are required. Fecal coliform samples will be collected in laboratory sealed 250-ml bottles, in the same fashion as the nutrient samples. Bottles will then be sealed and labeled accordingly.

In situ water quality measurements will be made, immediately following collection of grab water samples, using a YSI® portable water quality instrument. The YSI® meters used during this investigation will be able to measure temperature, conductivity, pH, and dissolved oxygen simultaneously to increase sampling efficiency. The parameters measured, instrumentation, and the associated range of measurement are presented in Table 2-2. The YSI® water quality probe will be placed in an area with water that is flowing and undisturbed to insure that a representative ambient measurement is obtained. Each of the readings will be allowed to become stable before a value is reported in the field notebook.

Table 2-2 Field Analytical Equipment and Operating Ranges

Analyte	Instrumentation	Instrument Operating Range	Matrix
Flow	Mechanical or electro-magnetic current meter	0.05 < V < 3.0 ft/s	Water
Temperature	Water qual. meter (YSI 6920)	-5 to 45 ^oC	Water
Dissolved Oxygen	Water qual. meter (YSI 6920)	0 to 50 mg/L	Water
Conductivity	Water qual. meter (YSI 6920)	0 to 100 ms/cm	Water
pH	Water qual. meter (YSI 6920)	0 to 14 S.U.	Water

Surface water samples will be collected using clean laboratory bottles dedicated to each location. Decontamination of equipment will therefore not be required. Investigation-derived waste (IDW) will not be generated during any part of this investigation.

2) Wet-Weather Tributary Surveys

Wet-weather tributary sample collection will be performed using automated samplers. A minimum of four, 1-liter sample bottles will be placed in the stream prior to the expected storm event, similar to those used during the collection of dry-weather samples with the exception of the modified cap. To insure that sufficient sample volume is collected, at least 1 extra bottle will be placed at each location. Once the sampler bottles are full, any exchange between the sample and the flowing water is unlikely based on the design of the feed tubes into the cap. Immediately after the storm event has occurred the sample bottles will be retrieved and the modified cap will be replaced with a standard cap. In-situ water quality measurements will be collected during sample retrieval activities. Also, fecal coliform samples will be collected during sample retrieval activities following the protocol described under dry-weather surveys above. Samples will be transported by ENSR personnel directly to Thorstensen Laboratory, Inc. in Westford, MA or the DEP Laboratory in Lawrence, MA for analysis.

Surface water samples will be collected using clean laboratory bottles dedicated to each location. Decontamination of equipment will therefore not be required. Investigation-derived waste (IDW) will not be generated during any part of this investigation.

<u>3) Impoundment Sediment Nutrient Flux Survey</u>

Measurements of benthic nutrient flux will be conducted by the measurement of oxygen and nutrient flux across the sediment/water interface in 8 cores (6" diameter) collected from the Ben Smith impoundment. Cores will be diver collected and will be maintained at *in situ* temperatures in a boat until return to the shore laboratory. Incubations will be performed at a "field" laboratory very near the impoundment to prevent disturbance to the cores in transit. All of the sediment incubations will be incubated immediately upon return to the remote field laboratory. CMAST has the equipment required for this purpose and has routinely conducted these incubations in a variety of field sites (including a remote interior site in Antarctica). The potential for disturbance to the sediment matrix of the cores due to transport over land (even a short distance) requires this procedure because it is nearly impossible to prevent vibrational mixing of the surfical sediment matrix during long distance transport over land. The problem with benthic flux measurements is that both disturbed and undisturbed cores yield linear rates, the only difference being that highly disturbed cores sometimes show less inter-core variance. Baffles and appropriate anti-mixing procedures will be used during the transport of the cores. While a significant degree of effort is generally spent in achieving highly accurate chemical assays (accuracy to 1%) to determine flux rates, handling of the sediment cores themselves (the source of the fluxes) is generally not well controlled and yet can create several fold errors in rates. In fact, CMAST's long experience in these measurements, in a variety of coastal sediment systems, indicates that core handling is the single major source of error in benthic oxygen and nutrient flux measures.

Analyses will be performed for most parameters by the Coastal Systems Laboratory at the Center for Marine Science and Technology (CMAST) at the University of Massachusetts in New Bedford, MA. The laboratory follows strictly follows Standard Operating Procedures (SOPs) as described in more detail below.

The methods to be employed in this effort are the standard methods of research level environmental laboratories. The CMAST Coastal Systems Laboratory focuses on analysis of nutrients (and other biogeochemical parameters) in ecosystems and natural waters (freshwater, estuarine and marine). The CMAST Lab has provided analytical support (and filed detailed QAPPs) for work with the

Buzzards Bay Project's Buzzards Bay Monitoring Program (since 1992), the MWRA HOM Program (1995-1998, including lab intercalibrations), USGS's Namskaket Marsh Project (included laboratory intercalibration with the USGS Central Lab), National Science Foundation and NOAA funded research programs, and many monitoring and research programs involving ecosystem functioning and assessment. The methods used by the laboratory have been through many EPA and other agency reviews as part of QAPP procedures over the past almost 2 decades (3 years at CMAST, 15 years Woods Hole Oceanographic Institution). Dr. Brian Howes, the manager of the Coastal Systems Program at CMAST has more than 25 years experience in biogeochemical sampling of natural waters. He has served as the QA Officer on numerous research programs both within the U.S. and internationally. The laboratory has produced the nutrient analysis for more than 100 publications and technical reports, several on analytical techniques, methods and sampling approaches.

The CMAST laboratory will use accepted approaches for the present effort. Samples will be logged-in upon delivery to the CMAST Coastal Systems Laboratory based upon field logs and Chain of Custody forms prior to signature by the authorized laboratory staff member. Staff will be on-call 24 hours when the field team is sampling, both to assist in any sample handling issues which might arise and to allow drop-offs and assay within the proscribed holding times. During log-in, sample integrity and clarity of label are checked and any unusual sample characteristics (identified by visual inspection or information from sample courier) noted on the COC and in the appropriate laboratory notebook. All frozen and/or archived samples are stored in a locked freezer (-20^{o}C) accessible only to authorized laboratory personnel. The laboratory analysts are responsible for the samples from arrival to analysis and data entry.

Assays will be within the recommended holding times specified in Table 2-3. All chemical assays for dissolved constituents are filtered upon collection. Initial sample processing is generally undertaken immediately upon receipt by the laboratory. Analytical detection limits, accuracy and precision for laboratory analyses are listed in Table 2-4.

Table 2-3 CMAST Standard Sample Holding Times

Assay	Project Team Holding Time (*)	Laboratory
Nitrate +Nitrite	48 hrs	CMAST
Dissolved Ammonia (NH_3 + NH_4^+)	12-24 hrs	CMAST
Total Dissolved Nitrogen	12-24 hrs	CMAST
Ortho-Phosphate	12-24 hrs	CMAST
Total Phosphorus	24 hrs	CMAST
(*) Samples will be kept between 0 and 4 degrees C during storage in the field.		

Table 2-4 CMAST Detection Limits and Accuracy for Laboratory Measurements

Variable (Lab)	Matrix	Units	Lower Detection Limits	Accuracy and Precision* (Better Than)
Nitrate +Nitrite	water	mg/l	0.001	5%
Dissolved Ammonia	water	mg/l	0.001	5%
Total Diss. Nitrogen	water	mg/l	0.003	5%
Ortho-Phosphate	water	mg/l	0.003	5%
Total Phosphorus	water	mg/l	0.006	5%
Oxygen Uptake	water	mg/l	NA	5%
*Accuracy based on results of laboratory control standards and spiked samples; however, no spikes are available for POC/PON analysis; precision based on relative %difference of duplicate samples.				

Table 2-5 CMAST Criteria for Measurement

Parameter Comments	Lab	Precision/Detection Accuracy	Desired Limit	Laboratory Parameters
Nitrate + nitrite	CMAST	<5%	0.001	variable field levels
Dissolved ammonia	CMAST	<5%	0.001	variable field levels
Total dissolved nitrogen	CMAST	<5%	0.003	variable field levels
Ortho-Phosphate	CMAST	<5%	0.003	variable field levels
Total phosphorus	CMAST	<5%	0.006	variable field levels
Oxygen	CMAST	<5%	NA	variable field levels

4) Impoundment Bathymetry and Sediment Thickness Survey

Bathymetry and sediment thicknesses will be measured using a pole and/or secchi disk to detect the sediment/water interface and the soft sediment/hard sediment interface. The bathymetry/sediment thickness survey will be a boat-based survey and measurements will be made along transects. There will not be any analyses conducted as part of the bathymetry and sediment thickness survey and therefore no samples or associated holding times a required.

Bathymetry and sediment thickness surveys will be performed in 5 river impoundments. In each impoundment, measurements will be collected along at least 12 transects, each containing 10 measurements. At each sampling location, depth to bottom and thickness of soft sediment will be recorded. These measurements will be used to generate a map of bathymetry and of sediment thickness for each of the five river impoundments.

The river impoundments are long and narrow in shape. When traveling by boat, the shoreline is always nearby and affords numerous landmarks as reference locations. Thus, locations of measurements will be identified using landmarks and recorded on topographic maps. A Geographic Positioning System will not be used for the survey.

In each of five impoundments, water depth and thickness of soft sediments will be measured by probing with a graduated rod. The following method will be employed:

- Depth from water surface to sediment surface will be recorded; an attachment may be placed on the bottom of the rod if the sediment is too loose to allow easy detection of the sediment-water interface.

- Depth from water surface to first refusal (rock, tight sand, gravel or clay) will be measured with the same graduated rod.

- Soft sediment depth (sediment-water interface to first refusal) will be calculated as the difference between the two measurements described above.

Decontamination of equipment will not be required and investigation-derived waste (IDW) will not be generated during any part of this investigation.

5) Impoundment Detention Time Survey

A fluorescent dye will be introduced to the Assabet River upstream of the Bed Smith Impoundment at a concentration capable of being recorded by the *in situ* Turner® fluorometer located at the outlet of the impoundment. This experiment will be conducted during a time period when no precipitation is anticipated for at least 5 days to minimize the possibility of storm water flow effecting the travel time and dispersion estimate. The recording fluorometer will be set up prior to the injection of dye and recordings will be made at a predetermined interval approximately once every 10 minutes during the next several days or until the fluorescence level is reduced to background levels.

The concentration of the dye will be continuously monitored at the downstream end of the impoundment using a recording Turner Model 110 fluorometer and a graphic representation of the dye concentration leaving the impoundment can be determined. The dye study will be conducted prior to a forecasted period of zero precipitation and will continue until measured dye concentrations reach background levels. Detention time information together with water column nutrient loading measurements and sediment nutrient flux measurements will provide a strong evaluation of nutrient mass balance in the impoundments.

2.2.2 Sampling/Measurement System Failure Response and Corrective Action Process

Corrective action in the field may be needed when the sample network is changed (i.e., more/less samples, sampling locations other than those specified in the QAPP, etc.), or when sampling procedures and/or field analytical procedures require modification, etc. due to unexpected conditions. In general, the field team may identify the need for corrective action. The field staff in consultation with the ENSR Project Coordinator will recommend a corrective action. The ENSR Project Manager will approve the corrective measure, which will be implemented by the field team. It will be the responsibility of the ENSR Project Manager to insure the corrective action has been implemented.

Corrective actions will be implemented and documented in the field record book. No staff member will initiate corrective action without prior communication of findings through the proper channels.

Corrective action in the laboratory may occur prior to, during, and after initial analyses. A number of conditions such as broken sample containers, multiple phases, low/high pH readings, and potentially high concentration samples may be identified during sample log-in or just prior to analysis. Following consultation with laboratory analysts and Section Supervisors, it may be necessary for the Laboratory QA/QC Officer to approve the implementation of corrective action.

The bench chemist will identify the need for corrective action. The Section Supervisor, in consultation with the staff, will approve the required corrective action to be implemented by the laboratory staff. The Laboratory QA/QC Officer will insure implementation and documentation of the corrective action.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action files, and the narrative data report sent from the laboratory to the ENSR Project Coordinator. If the corrective action does not rectify the situation, the laboratory will contact the ENSR Project Coordinator.

2.2.3 Sampling Equipment, Preservation, and Holding Times Requirements

Samples collected for laboratory analyses will be stored on ice in coolers and holding times will be met to insure the accuracy of the results (Table 2-6). Because of the 6-hour holding time of the fecal coliform samples these samples will be collected over a relatively short period of time. A courier will meet the field team at a predetermined location and will transport all sample bottles to Thorstensen Laboratory, Inc. in Westford, MA or the DEP Laboratory in Lawrence, MA in a timely fashion in order to meet the holding times of all analytes.

Table 2-6 Summary of Analyte, Field Preservation, and Holding Time for Assabet River Water Quality Survey for both Baseflow and Stormflow Samples

Parameter	Method of Preservation	Holding Time
Fecal Coliform	Stored on ice at 4^oC	6 hours
BOD-5	Stored on ice at 4^oC	24 hours
BOD-30	Stored on ice at 4^oC	24 hours
Nitrate	Stored on ice at 4^oC	24 hours
Ammonia	Stored on ice at 4^oC	24 hours
Total Kjeldahl Nitrogen	Stored on ice at 4^oC	24 hours
Total Phosphorus	Stored on ice at 4^oC	24 hours
Ortho-Phosphorus	Stored on ice at 4^oC	24 hours
Total Suspended Solids	Stored on ice at 4^oC	7days
Total Settleable Solids	Stored on ice at 4^oC	48 hours
Particle Size Distribution	None	Indefinite

2.3 Sample Handling and Custody Requirements

2.3.1 Sample Custody Procedure

Field logbooks will provide the means of recording the data collecting activities performed during the investigation. As such, entries will be described in as much detail as possible so that persons going to the site could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in the project files when not in use. The project-specific document number will identify each logbook.

The title page of each logbook will contain the following:

- Person to whom the logbook is assigned,
- The logbook number,
- Project name and number,
- Project start date, and
- End date.

Entries into the logbook will contain myriad information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be entered. The names of visitors to the site, field sampling or investigation team personnel, and the purpose of their visit, will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. Weather permitting, all entries will be made in ink, signed, and dated and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark, which is signed and dated by the sampler. Whenever a sample is collected, or a measurement is made, a detailed description of the sampling location will be recorded. The number of photographs taken of the sampling location, if any, will be noted.

The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume, and number of containers. Sample identification numbers will be assigned prior to sample collection according to the following sample identification scheme.

Sample ID Code Format:

A1xyzzzaabb

Where:

- "A1" denotes "Assabet River Survey #1" and will be the same for all samples.
- "x" denotes sampling round and will be a "1" or "2" (there will be two sampling rounds)
- "y" denotes type of sampling location and will be R, T, or M for river, tributary, or impoundment.
- "zzz" denotes river mile (e.g. 28.3) and will vary by station
- "aa" denotes type of analysis and will be "NS" for nutrient suite, "FC" for fecal coliform
- "bb" denotes type of sample and will be "SA" for sample, "BL" for blank, and "DU" for duplicate.

Sample labels will include the name of the investigation, the date and time of collection, the sample unique ID, the name and river mile location of sample collection, the round of sample collection, and the type of analysis required. An example label is given below.

ENSR/Assabet River July 1999 WQ Survey
Date: Time:
A11M11OCHDU
Crow Island Imp SW 11.0
Round 1 chlorophyll

All of the sample label information excepting the date and time of sample collection will be filled on the self-adhesive label prior to the collection of the sample.

The sample packaging and shipment procedures summarized below will insure that the samples will arrive at the laboratory with the chain-of-custody intact.

- The field sampler is personally responsible for the care and custody of the samples until they are transferred or dispatched properly. Field procedures have been designed such that as few people as possible will handle the samples.
- All bottles will be identified by the use of sample labels with sample numbers, sampling locations, date/time of collection, and type of analysis. Sample labels will be completed for each sample using ink.
- A properly completed chain-of-custody form will accompany samples. The sample numbers will be listed on the chain-of-custody form (Figure 2-1). When transferring the possession of

samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents the transfer of custody of water samples from the sampler the laboratory for analysis.

- Water samples will be properly packaged on ice at 4°C for shipment and dispatched to the appropriate laboratory for analysis within the prescribed holding times for the analytes. Since the analytic lab in near the study area, sample bottles will be dropped off by ENSR personnel with the signed custody record.

Information regarding the sample ID number, the date and time of sample collection, the method of preservation and filtration (if any) and other relevant information will be recorded on a chain-of-custody form. This form will be filled out by each of the water quality sampling teams after collection and prior to the transport of the samples to Thorstensen Laboratory, Inc. in Westford. Upon arrival of the samples at the laboratory the chain-of-custody will be used to insure that each of the samples is accounted for by going through each sample with the technician at hand. An example of the chain-of-custody form follows. Once the laboratory has accounted for all of the intended samples for delivery the receiving party and the ENSR courier delivering the samples will sign the chain-of-custody.

2.4 Analytical Methods Requirements

2.4.1 Preparation of the Samples

1-2) Water Quality Samples Collected During Dry-Weather and Wet-Weather Surveys

During the collection of water samples for the dry-weather and wet-weather sampling events, duplicate samples will be collected on regular intervals to determine the comparability between samples collected at the same time. Duplicate samples will be collected at a rate of 5-10% of the total number of samples collected.

Duplicate samples will be collected using the exact sample protocols as for collecting water quality samples. Duplicate samples will be collected at the same time as water quality samples and by the same individual(s). These samples will be immediately stored on ice in the same cooler used for holding the water quality samples for a given site and transported to the laboratory at the same time.

Field blanks collected as part of this investigation will be used to determine the quality of field measurements. Differences between the duplicates of less than 20% will be considered to be reasonable when at concentrations in excess of 0.050 mg/L. However, at lower concentrations a greater percent difference between the duplicates could be considered acceptable because of the reporting increment used. For example, the difference in phosphorus concentration between duplicates of 0.020 and 0.030 mg/l (0.010 mg/l, the smallest possible increment) yields a 40% difference. As a consequence, small absolute differences between duplicates can yield higher percent differences. Sample results not in conformance with the acceptable QC criteria will be rejected and excluded from the final analysis of project results.

Figure 2-1 Sample Chain-of-Custody Form to be Used During the Assabet River Water Quality Investigation

ENSR		CHAIN OF CUSTODY RECORD	
Assabet River Water Quality Investigation		Event ID:	
Chief Scientist:		Field Logbook No:	
Signature:		Chain of Custody Tape No:	
Send Results To	ENSR 35 Nagog Park Acton, MA 01720	Analytical Laboratory (Destination)	
Relinquished by: (print name) Signature	Date: Time:	Received by: (print name) Signature	Date: Time:
Relinquished by: (print name) Signature	Date: Time:	Received by: (print name) Signature	Date: Time:
Relinquished by: (print name) Signature	Date: Time:	Received by: (print name) Signature	Date: Time:

#	Cooler	Bottle No.	Date	Time	Analysis	Media	Preserv.	Contain.	Filtered?

3) Impoundment Sediment Nutrient Flux Survey Samples

Preparation of samples collected during the Sediment Nutrient Flux Survey is described in Section 2.4.2 below.

4) Impoundment Bathymetric and Sediment Thickness Measurements

To insure that water depth and sediment thickness is accurately measured measurements from two transects will be duplicated by a second individual during the survey through two complete transects. It is expected that transect measurements will be easily reproduced and that the only differences will arise from measuring depth and thickness in slightly different locations in the impoundment.

2.4.2 Analytical Methods

1-2) Water Quality Samples Collected During Dry-Weather and Wet-Weather Surveys

Both the dry-weather and wet-weather samples will be analyzed at Thorstensen Laboratory, Inc. or the DEP laboratory using the methods listed in Table 2-7.

Table 2-7 Methods of Detection for Dry and Wet-Weather Surface Water Analytes

Parameter	Method of Detection	Detection Limit	Laboratory For Analysis
Fecal Coliform	SM9222D	0 per 100 ml	Thorstensen
BOD_5	EPA 405.1	1.0 mg/L	Thorstensen
BOD_{30}	EPA 405.1	1.0 mg/L	Thorstensen
Nitrate	EPA 300.0	0.01 mg/L	Thorstensen
Ammonia	EPA 350.3	0.03 mg/L	Thorstensen
Total Kjeldahl Nitrogen	EPA 351.3	0.05 mg/L	Thorstensen
Total Phosphorus	EPA 365.2	0.01 mg/L	Thorstensen
Ortho-Phosphorus	EPA 365.2	0.01 mg/L	Thorstensen
Total Suspended Solids	WPA 160.2	1.0 mg/L	Thorstensen
Total Settleable Solids	EPA 160.5	0.1 ml/L	Thorstensen
Particle Size Distribution	ASTM	0.75-2,000 um	Thorstensen

3) Impoundment Sediment Nutrient Flux Survey

Upon arrival at the field laboratory flux cores are sealed from the atmosphere with machined core tops fitted with magnetic stirrers that gently mix the overlying water without disturbing the sediment surface. Oxygen will be determined using an Orbisphere meter and electrode (the probe fitted through an opening in the core top) calibrated at 100% and 50% of atmospheric equilibration at the temperature and salinity of the headspace water of the cores. The headspace of the cores from each of the seven stations will be replaced with 0.22 micron filtered water (collected from each core site). Subsamples of the filtered water will be incubated to control for oxygen and nutrient changes in the headspace not associated with sediment flux. The incubation will continue until a significant flux is detected or to 48 hours. The headspace will be set so as to maximize the signal and minimize the incubation time (ideally 18 hours).

At least four to five time-points (plus time zero) will be conducted per core incubation. Dissolved oxygen will not be allowed to decline to less than 50 percent of air equilibration. Since oxygen disappearance rates may exceed those of other solutes, we will continue the incubations after completion of the oxygen uptake assay, aerating the headspace until the solute flux assays are completed. At each time-point, headspace water will be removed through a port in the gas tight headspace with equal replacement with the setup water; samples are immediately filtered (Millipore 0.22 micron in-line filtration) into acid leached 60cc polyethylene bottles upon removal. The CMAST system allows water removal without even brief pressure changes to the headspace (negative pressures can increase fluxes in some incubation systems). All fluxes will be adjusted for water removals and measured activities within the headspace water.

Ammonium, nitrate + nitrite and ortho-phosphate will be analyzed for each of the time point sample volumes. Total dissolved nitrogen and total phosphorus will be analyzed at time zero and time final samples. Accumulations in the headspaces will be used to calculate flux rates. The time-course measures will be used to ensure calculations from linear increases. Samples for ammonia, nitrate/nitrite, and phosphate will be analyzed against reference standards having nutrient concentrations bracketing those of the samples. Standards will be analyzed daily, and checked for linearity (r^2 >0.99) and acceptability of blanks. All standards and blanks are run in duplicate. The dissolved oxygen meter will be calibrated against air-saturated water and the calibration will be checked prior to each oxygen measurement. Deviations from 100% saturation will be noted and appropriate corrections will be applied to the data following the manufacturer's manual.

This process will be repeated under four scenarios including (1) ambient temperature, (2) moderately increased temperature, (3) summertime temperature, and (4) anoxic conditions. These scenarios will provide valuable measurements of sediment/water column nutrient interactions during both non-summer and summer time conditions, as well as quantifying chemical release of phosphorus from sediments. The sediment flux survey will include measurement of sediment oxygen demand over an extended time period.

2.5 Quality Control Requirements

2.5.1 QC Procedures

1-2) Water Quality Samples Collected During Dry-Weather and Wet-Weather Surveys

For all parameters analyzed in the field, field duplicates will be collected at a frequency of 5 to 10% or once per field team per field sampling event, whichever is more frequent. Furthermore, the station at which field duplicates are collected and/or analyzed will vary with each event. Field duplicates will be collected at the aforementioned frequency for both *in situ* measurements and for water samples to be forwarded to Thorstensen Laboratory, Inc. for analysis. Laboratory duplicates will be measured at a frequency of 5 to 10% or once per analytical batch, whichever is more frequent; spiked samples will be measured for all nutrient parameters and BOD at a frequency of 5 to 10% or once per analytical batch, whichever is more frequent.

Outlier data points will be considered on an individual basis and may be disregarded depending on both upstream and downstream data measurements and on concentrations measured at different times.

Both Thorstensen Laboratory, Inc. and the EPA laboratory routinely conduct an in-house quality control plan whereby laboratory duplicates, spiked samples, and laboratory blanks are analyzed. This data may be obtained from either laboratory and reviewed to insure acceptable ranges are maintained.

3) Impoundment Sediment Nutrient Flux Survey

Monitoring parameters, sample volumes, containers, sample processing and storage for this project are listed in Table 2-8. Analytical methods and associated references are listed in Table 2-9. Complete standard curves are generated for each analytical run. If more than a 10-fold range of concentrations is encountered in the samples, then both a high and low standard curves is created. In all cases, the standards are prepared new each day and are chosen to give at least 5 points over the sample concentration range. Standards well above the sample range are not used. Nitrate+Nitrite (run in duplicate) by autoanalysis has additional standards run before and after every five (5) samples. Failure of these additional standards (run as samples) to agree within 10% of their known value halts the assay line for complete recalibration and the re-running of the last sample set.

Table 2-8 Monitoring Parameters

Parameter	Volume	Container (*)	Processing & Storage
Nitrate + Nitrite	60 ml	polyethylene (HCl leached)	0.45 um membrane field filtration stored on ice (dark)
Dissolved ammonium ($NH_3 + NH_4^+$)	60 ml	polyethylene (HCl leached)	0.45 um membrane field filtration stored on ice (dark)
Total Dissolved Nitrogen	60 ml	polyethylene (HCl leached)	0.45 um membrane field filtration stored on ice (dark)
Ortho-Phosphate	60 ml	polyethylene (HCl leached)	0.45 um membrane field filtration stored on ice (dark)
Total Phosphorus	1000 ml	polyethylene (HCl leached)	stored on ice (dark)
Oxygen Uptake	NA	core	NA
(*) The acid used for acid-washed bottles consists of 10% hydrochloric acid.			

Table 2-9 Laboratory Analysis[i]

Parameter	Matrix	Units	Method	Reference
Nitrate + Nitrite	water	ug/L	Autoanalyzer	a
Dissolved Ammonium (NH_3 + NH_4^+)	water	ug/L	Indophenol	b
Total Dissolved Nitrogen	water	ug/L	Persulfate Digest	c
Ortho-Phosphate	water	ug/L	Molybdenum Blue	e
Total Phosphorus	water	ug/L	Persulfate Digest Molybdenum Blue	f
Oxygen uptake	sediment	$mg/m^2/h$	time-course O_2 uptake	g
Nutrient flux	sediment	$mg/m^2/h$	time-course [conc.]	h

a Lachat Autoanalysis procedures based upon the following techniques

- Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Ass. U.K. 47:23-31.
- Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in sea water. J. Mar. Res. 11: 87-96.

b Scheiner, D. 1976. Determination of ammonia and Kjeldahl nitrogen by indophenol method. Water Resources 10: 31-36.

c D'Elia, C.F., P.A. Stuedler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22: 760-764.

d Murphy, J. and J. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27: 31-36.

e Persulfate Digestion Method for Total Phosphorus; Standard Methods 4500-P B.5 (18th ed.)

f Total Suspended Solids dried at 103-105^oC, Standard Methods 2540 D (18th ed.)

g Jorgensen, B. 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnol. Oceanogr. 22:814-832.; Albro, C., J. Kelley, J. Hennessy, P. Doering, J. Turner. 1993. Combined Work/Quality Assurance Project Plan (CW/QAPP) for Baseline Water Quality Monitoring: 1993-1994. MWRA, Boston MA.

h Klump, J. & C. Martens. 1983. Benthic nitrogen regeneration In: Nitrogen in the Marine Environment, (Carpenter & Capone, eds.). Academic Press.

i The techniques used by the CMAST laboratory are methods generally used by state-of-the-art research laboratories. All of the methods and QA/QC are routinely performed by the CMAST laboratory have been accepted by EPA, USGS, MCZM, DEP, NSF and NOAA as part of previous studies conducted by the CMAST lab under their review.

For Nitrate+Nitrite, dissolved ammonium, total dissolved nitrogen, ortho-phosphate, and total phosphorus, non-automated assays are all run in duplicate (at a frequency of at least 10% of the samples) with a <5% tolerance between duplicates required for acceptance. After completion of analyses, remaining sample is frozen, for possible reanalysis if required.

Reagent blanks and standards are prepared and analyzed with each new batch of reagent. These blanks are compared to previous data on blanks to evaluate the potential of contamination and the standard curve compared to previous records. If this initial blank and standard curve is deemed satisfactory, samples are then analyzed. Calibration blanks are prepared and analyzed simultaneously with the creation of each standard curve that is created for each sample series. Nutrient samples are analyzed against reference standards having nutrient concentrations bracketing those of the samples. Standards are analyzed daily, and checked for linearity (r^2>0.98) and acceptability of blanks.

2.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

2.6.1 Testing, Inspection, and Maintenance

1-2) Water Quality Samples Collected During Dry-Weather and Wet-Weather Surveys

The YSI® water quality meters used during this investigation will be visually inspected prior to use and tested and testing in the form of comparing to standard solutions of pH and conductivity.

The current meter will be inspected prior to use and tested by conducting a "free spin" test to insure that the rotating current meter cups are free of obstruction and have freedom of movement during operation.

Stormflow samplers will be inspected prior to placement for clogged tubes and other obstructions that would cause the bottles to not fill during a rise in stage.

3) Impoundment Sediment Nutrient Flux Survey

Analytical equipment (Bausch and Lomb, Genesis Spectrophotometers, Lachat Autoanalyzer, conductivity meters, etc.) will be calibrated through the processing of standards in the normal analytical procedure. Meters and electrodes will be multi-point calibrated. Laboratory analytical balances are under annual manufacturer service and calibration. CMAST also maintains and routinely uses certified calibration weights and thermometers. The freezer has a chart record of temperature and a temperature alarm to ensure the maintenance of frozen samples below -20ºC.

4) Impoundment Detention Time Survey

The fluorometer used during the dye study investigation will be inspected and tested according to the manufacturer instructions. The EPA will provide the fluorometer.

2.7 Instrument Calibration and Frequency

2.7.1 Identify the Instrumentation Requiring Calibration

Each survey day, water quality meters will be pre-calibrated prior to the commencement of field activities and post-calibrated following the completion of field activities in accordance with manufacturer's instructions.

2.7.2 Document the Calibration Method that Will Be Used for Each Instrument

The YSI® water quality meter used in this investigation will be calibrated for dissolved oxygen, pH, and conductivity. Dissolved oxygen will be calibrated to air saturation. This method allows the meter to measure the dissolved oxygen concentration in moist air at a given temperature and barometric pressure. After the meter makes a stable reading the instrument is calibrated by forcing it to consider that the reading under those conditions is at 100% saturation. The water in the Assabet River system is known from previous measurements to be slightly alkaline. For this reason, the water quality will only be calibrated to pH 4 and pH 10 solutions. If, however, pH readings at or below pH 7 are encountered the meter will be immediately calibrated to pH 4 and measurements will continue. The pH is calibrated at pH 7 and pH 10 (and potentially pH 4) by inserting the pH probe in the appropriate solutions and once a stable reading has been made, forcing the meter to report the pH of the standard solution. The conductivity is calibrated in the same manner. Water temperature will be measured immediately prior to beginning each field collection and compared with the temperature reported by the YSI® meter. Any deviation between the two measurements will be recorded in the field notebook.

The fluorometer to be used during this investigation will be provided by the MADEP and calibration will be done according to the manufacturer instructions.

2.7.3 Document the Calibration Standards

All standard solutions used during the calibration process for the water quality instrumentation will be unused, within any expiration data, will be purchased from a reputable manufacturer, and will be specifically designed for the instrument(s) being calibrated.

2.7.4 Document Calibration Frequency

All instruments will be calibrated twice per sampling day. Once prior to the collection of water quality data at the beginning of the day and once at the end of the day to verify that the instrument has remained calibrated throughout the day and that the instrument has not drifted from the original calibration. The following limits are proposed as a verification of drift as 5-10% (depending on the parameter) of the range of values expected to be measured; pH $\pm$ 0.20 S.U., conductivity, $\pm$ 50 uS/cm, temperature $\pm$ 1^{o}C, and dissolved oxygen, $\pm$ 1.0 mg/L. All pre- and post-calibration procedures will always be recorded in the field notebook.

2.8 Data Acquisition Requirements (non-direct measurements)

2.8.1 Acquisition of Non-Direct Measurement Data

Accuracy of laboratory analysis will be assessed for compliance with the criteria established in Section 3 of the QAPP using the analytical results of method blanks, MS/MSD samples, and LCSs. The percent recovery (%R) for MS/MSD samples will be determined according to the following equation:

$$\%R = \frac{(Amount\ in\ Spiked\ Sample - Amount\ in\ Sample)}{Known\ Amount\ Added} x100$$

%R for LCSs will be determined according to the following equation:

$$\%R = \frac{Experimental\ Concentration}{Known\ Amount\ Added} x100$$

The relative percent difference (RPD) between the matrix spike and matrix spike duplicate, or sample and sample duplicate in the case of metals, and field duplicate pair is calculated to compare to the criteria in Section 3 of this QAPP. The RPD will be calculated according to the following formula.

$$RPD = \frac{(Amount\ in\ Sample\,1 - Amount\ in\ Sample\ 2)}{0.5\,(Amount\ in\ Sample\,1 + Amount\ in\ Sample\ 2)} x100$$

Completeness is the ratio of the number of valid sample results to the total number of samples analyzed with a specific matrix and/or analysis. Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$Completeness = \frac{(number\ of\ valid\ measurements)}{(number\ of\ measurements\ planned)} x100$$

2.8.2 Tracking and Quality Verification of Supplies and Consumables

For this project, critical supplies will be tracked through ENSR's system in the following manner outlined in Table 2-10.

Table 2-10 Summary of Supplies, Inspection Requirements, and Responsible Party

Critical Supplies and Consumables	Inspection Requirements and Acceptance Criteria	Responsible Personnel
Sample bottles	Visually inspected upon receipt for cracks, breakage, cleanliness	Field team
Chemicals and reagents	Visually inspected for proper labeling, expiration dates, appropriate grade	Field team
Water quality monitor/ current meter	Functional checks to insure proper calibration and operating capacity	Field team
Sampling equipment	Visually inspected for obvious defects, damage, and contamination	Field team

Supplies and consumables not meeting acceptance criteria will initiate the appropriate corrective action, e.g., replacement, return to vendor.

2.9 Data Management

2.9.1 Data Recording

Data that is transposed from field notebooks to an electronic database, and from laboratory reports to an electronic database, will be checked 100% after transcription.

2.9.2 Data Validation

Detail the process of data validation to insure that the system performs the intended function consistently, reliable, and accurately in generating the data.

2.9.3 Data Transformation

It is expected that data transformations made during this investigation will be relatively simplistic and all calculations made during data transformation will be checked 100% prior to dissemination of the transformed information.

2.9.4 Data Transmittal

During the transfer of data from one place (field notebook or data report) to another (electronic data spreadsheet) the data will be copied and checked by one individual and then checked 100% by a second individual to insure accuracy.

2.9.5 Data Reduction

Raw data from field measurements will be recorded directly in field notebooks or on sample logs. If errors are made, results will be legibly crossed out, initialed and dated by the person recording the data, and corrected in a space adjacent to the original (erroneous) entry. Logbooks will be periodically reviewed by the ENSR Project Coordinator to insure that records are complete, accurate, and legible.

Reduction of current meter and water quality monitoring data will be made by entering all field-collected data in an Excel® computer spreadsheet. The use of a spreadsheet is desired to facilitate east access and graphic representation of the information.

Laboratory data reduction procedures will be performed according to the following protocol. All information related to analysis will be documented in controlled laboratory logbooks, instrument printouts, or other approved forms. All entries that are not generated by an automated data system will be made neatly and legibly in waterproof ink. Information will not be erased or obliterated. Corrections will be made by drawing a single line through the error and entering the correct information adjacent to the cross out. All changes will be initialed, dated, and, if appropriate, accompanied by a brief explanation. Unused pages or portions of pages will be crossed out to prevent future data entry. Analytical laboratory records will be reviewed by the Section Supervisors on a regular basis and by the Laboratory QA/QC Officer periodically, to verify adherence to documentation requirements.

Prior to being released as final, laboratory data will proceed through a tiered review process. Each analyst will be responsible for reviewing the analytical and QC data that he/she has generated. As part of this review, the analyst will verify that:

- The appropriate methodology was used,
- Instrumentation was functioning properly,
- QC analyses were performed at the proper frequency and the analyses met the acceptance criteria,
- Samples were analyzed within holding times,
- All analytes were quantitated within the calibration range,
- Matrix interference problems were confirmed,
- Method-specific analytical requirements were met (e.g., correlation coefficients), and
- Calculations, dilution factors, and detection limits were verified.

Prior to releasing the final data, the Section Supervisor will review the data to:

- Verify the appropriate methodology was used,
- Verify QC analyses were performed at the proper frequency and the analyses met the acceptance criteria,
- Verify samples were analyzed within holding times,
- Verify data in logbooks and instrument printouts were correctly entered into LIMS,
- Review and document problems encountered during the analysis, and
- Prepare case narratives.

The final data report will be reviewed and approved by the Laboratory QA/QC Officer, Laboratory Project Manager, or Laboratory Manager prior to its release. This review will verify that the report format and content meet client specifications, that the data were reported correctly, and that analytical or QA problems were addressed, documented in the file, and, if appropriate, described in the case narrative.

Data Reduction in Support of the Sediment Nutrient Flux Survey

Raw data is maintained in duplicate notebooks. Data reduction involves the process of converting raw numbers into data that have direct chemical meaning or can be compared statistically. Calculation to concentration is done in an adjacent column for easy comparison. The calculation is based upon the regression equation calculated from the chemical standards. The results will be reported in terms of concentration, as means and standard errors. All data are subject to 100% check at all stages by everyone. All data reported are reviewed to check for errors in transcription, calculation, or computer input. If data points are judged to be aberrant, the reserved sample will be reanalyzed. Data are also reviewed for adherence to analytical protocols and to pre-established criteria (e.g., holding times, surrogate recoveries, initial and continuing calibration, matrix spikes, laboratory duplicates, blank contamination). Students t-test for paired samples, analysis of variance, are used for interpretation. Data is transcribed only for the statistical analysis and each point is checked for accuracy. Sample logs associated with field and laboratory custody and tracking are maintained in the project files.

Laboratory data will be reviewed relative to reagent and calibration blanks and standard curves. Performance and evaluation standard data for nutrients will also be available from the CMAST Coastal Systems Laboratory. Results will be checked against the expectations of precision and accuracy as detailed in the analytical sections. Data entry will be independently compared to the raw data sheets by a second analyst. Randomly selected samples will be recalculated from the raw data to final form in these checks. Samples which do not meet the validation (either recalculation or based on performance criteria) will require a re-check of all data from that sampling event.

All data developed for this project must be demonstrated to be comparable to similar data generated by other laboratories or by other studies at the same or similar sites. This is to be accomplished by the employment of sampling methods and analyses that have been previously approved by EPA and other regulatory agencies. The methodologies employed by the CMAST laboratory have been used in a wide variety of systems and are identical or comparable to those used by previous researchers at comparable sites.

Representativeness of laboratory procedures will be insured by proper handling, storage and analysis of samples so that the material analyzed reflects the material collected as accurately as possible.

2.9.6 Data Analysis

The data generated during this investigation will be used to calculate nutrient budgets for the six impoundments during the sampling periods. Concentrations and flows will be used to calculate loading to and from the systems and calculations will be made to determine the flux of nutrient to or from the sediment. Much of this evaluation will be focused on determining if the nutrient budget indicates how much, if any, phosphorus is stored in the impoundments during periods of relatively low biologic activity.

2.9.7 Data Tracking

Data will be recorded in the field notebooks and upon return completion of the associated date collection information will be transposed to an electronic spreadsheet format. Copies of field data will be made and stored in project file on a daily basis. Laboratory data will also be transposed to an electronic spreadsheet format upon receipt.

2.9.8 Data Storage and Retrieval

Data will be maintained in electronic format using Microsoft Excel® for data analyses and presentation purposes. Backup copies of all data files will be made intermittently throughout the project and upon completion of the project a CD containing all of the electronic data will be burned with copies available for distribution.

3.0 ASSESSMENT/OVERSIGHT

3.1 Assessments and Response Actions

3.1.1 Assessment Activities and Project Planning

3.1.1.1 Assessment of the Subsidiary Organizations

The laboratory as part of their QA Program will conduct laboratory performance and system audits. System audits will be done on an annual basis, at a minimum and will include an examination of laboratory documentation on sample receiving, sample log-in, sample storage, chain-of-custody procedures, sample preparation and analysis, instrument operating records, etc.

3.1.1.2 Assessment of Project Activities

Field audits will include examination of field sampling records, field screening results, field instrument operating records, sample collection, handling, and packaging in compliance with the established procedures, maintenance of QA procedures, chain-of-custody, etc. Follow-up audits will be conducted to correct deficiencies, and to verify that QA procedures are maintained throughout the investigation. The audits will involve review of field measurement records, instrumentation calibration records, and sample documentation. This will occur once during the investigation.

3.1.2 Documentation of Assessments.

3.1.2.1 Reporting and Resolution of Issues

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out-of-limit QC performance that can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation, and data assessment. All corrective action proposed and implemented should be documented in the QA sections of project deliverables. Corrective action should only be implemented after approval by the ENSR Project Manager, or his designee. If immediate corrective action is required, approvals secured by telephone from the ENSR Project Manager should be documented in an additional memorandum.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem is responsible for notifying the ENSR Project Manager.

Any nonconformance with the established QC procedures in the QAPP will be identified and corrected in accordance with the QAPP. The ENSR Project Manager, or his designee, will issue a nonconformance report for each nonconformance condition.

4.0 DATA VALIDATION AND USABILITY

4.1 Data Review, Validation, and Verification Requirements

4.1.1 Sampling Design

Sample collection plans will be developed and used during the sample collection periods. These plans will include a detailed map of the sample locations, and the types of samples to be collected. The project manager will develop the sample collection plan and brief the sample collection team on the objectives of the sampling.

4.1.2 Calibration

Suspect calibration information will be highlighted in the field data notebook upon discovery of the information. Data collected during the period of suspect information will be footnoted as being questionable.

4.1.3 Data Reduction and Processing

Once these goals and objectives are evaluated and chosen, analytical data quality will be assessed to determine if the objectives have been met. In addition, the data will be reviewed by ENSR's Quality Assurance Officer for indications of interference to results caused by sample matrices, cross contamination during sampling, cross contamination in the laboratory, and sample preservation and storage anomalies (e.g., sample holding time or analytical instrument problems).

4.2 Validation and Verification Methods

4.2.1 Describe the Process for Validating and Verifying Data

The procedures used to evaluate field data will include checking procedures utilized in the field, ensuring that field measurement equipment was properly calibrated, checking for transcription errors, and comparing the data to historic data or verifying its "reasonableness". Evaluation of the field data will be the responsibility of the Project Coordinator or his designee (a qualified individual who is not a part of the field team).

An independent assessment of the data will be performed by ENSR. The overall completeness of the data package will be evaluated. Completeness checks will be administered on all data to determine whether deliverables specified in the QAPP are present. At a minimum, deliverables will include sample chain-of-custody forms, analytical results, and QC summaries. The reviewer will determine whether all required items are present and request copies of missing deliverables. In addition, holding times and the results of all blanks, MS/MSDs, LCSs, and duplicate analyses will be reviewed/ evaluated.

The need for corrective action may be identified during either data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory. These actions are dependent upon the ability to mobilize the field team and whether the data to be collected is necessary to meet the required QA objectives (e.g., the holding time for samples is not exceeded, etc.). If the ENSR data assessor identifies a corrective action situation, it is the ENSR Project Manager who will be responsible for approving the implementation of corrective action, including resampling, during data assessment. The ENSR Project Coordinator will document all corrective actions of this type.

5.0 REFERENCES

USGS, 1982. Measurement and Computation of Streamflow: Volume 1. Measurement of Stage and Discharge. Geological Survey Water Supply Paper 2175.

QUALITY ASSURANCE PROJECT PLAN

For

SuAsCo Watershed Phased TMDL: Assabet River Part One

(Revision 1)

September 1999

Prepared by:
ENSR CORPORATION

Prepared for:
United States Army Corps of Engineers

ENSR Project Manager	Date
ENSR Project Quality Assurance Officer	Date
US Army Corps of Engineers Protection Project Officer	Date

Appendix I

Quality Control Plan for Thorstensen Laboratory, Inc.

Appendix II

Standard Operating Procedures for YSI® Water Quality Meter

FIELD EQUIPMENT OPERATION AND MAINTENANCE PROCEDURES –

YSI 6920 MULTI-PARAMETER WATER QUALITY MONITOR

SOP DESCRIPTION

This Standard Operating Procedure (SOP) describes the procedure that will be followed by field staff for measuring water column characteristics using a YSI-6920.

The Model 6920 system is a multi-parameter, water quality measurement and data collection system designed for use in research, assessment and regulatory compliance applications. The unit features field replaceable sensors, an on-board data logging system and internal power supply, self-cleaning turbidity probe and a stirring-independent dissolved oxygen sensor. The YSI 6920 configured for ENSR is equipped with sensors for the measurement of dissolved oxygen (DO), conductivity, specific conductance, salinity, total dissolved solids, resistivity, temperature, pH, ORP, turbidity and depth. The fast sensor response makes the unit ideal for profiling and monitoring water conditions in industrial and wastewater effluents, lakes, rivers, wetlands, estuaries, coastal waters and monitoring wells. Data can be viewed in real-time using a YSI 610-DM hand-held data logger.

EQUIPMENT - PRINCIPLES OF OPERATION

Specific Conductivity

Conductivity is the ability of a material to conduct electrical current. The principle by which conductivity is measured is to immerse two plates in a sample solution, apply a voltage potential (E) across the plates and measure the resultant current (I). Conductivity (G) is then determined from the voltage and current values according to Ohms Law G = I (amps) /E volts). The 6920 utilizes a cell with four pure nickel electrodes for the measurement of solution conductance. The four-electrode cell uses a reference voltage to compensate for any polarization or fouling of the electrode plates. The reference voltage ensues that the measurements indicate actual conductivity independent of electrode condition, resulting in higher accuracy. Since cell geometry affects conductivity values, standardized measurements are expressed in specific conductivity units (μS/cm) to compensate for variations in electrode dimensions. Specific conductivity (C) is then obtained from the product of measured conductivity (G) and the electrode cell constant (L/A), where L is the length of the column of liquid between the electrodes and A is the area of the electrodes. The cell constant for the 6920 is approximately 5.0/cm; this value is automatically confirmed with each deployment of the system when the calibration procedure is followed.

Conductivity is also highly dependent on temperature and the nature of the ionic species present in solution. The 6920 uses the temperature and raw conductivity values (G) associated with each determination to generate a specific conductance value (C) compensated to 25^{o} C.

pH

The pH of a solution measures the degree of acidity or alkalinity relative to the ionization of water. Pure water dissociates to yield 10^{-7} M of $[H^+]$ and $[OH^-]$ at 25°C; thus the pH of water is 7, the point of neutrality by the following relationship $pH_{water} = -\log [H^+]$. pH values less than 7.0 are classified as acidic while a value greater than 7.0 is tend to be more alkaline. The 6920 employs a field replaceable pH electrode for the determination of hydrogen ion concentrations. The probe is a combination electrode consisting of a proton selective glass reservoir filled with a buffer at approximately pH 7.0 and a Ag/AgCl reference electrode that utilizes gelled electrolyte. A silver wire coated with AgCl is immersed in the buffer reservoir. Protons (H^+ ions) on both sides of the glass (media and buffer reservoir) selectively interact with the glass, setting up a potential gradient across the glass membrane. Since the hydrogen ion concentration in the internal buffer solution is invariant, this potential difference, determined relative to the Ag/AgCl reference electrode, is proportional to the pH of the media.

Dissolved Oxygen

To measure dissolved oxygen (DO), a thin Teflon membrane is placed over a thin layer of electrolyte and three metal electrodes, a thin linear gold cathode placed between two silver rectangles which serve as the anode and reference electrode. The sensor is continuously polarized at a voltage sufficiently negative to cause oxygen to diffuse through the membrane at a rate proportional to its partial pressure – the greater the oxygen partial pressure, the more oxygen diffuses through the membrane. This diffusion process results in oxygen being reduced to a hydroxide ion at the cathode and silver metal to be oxidized to silver chloride at the anode. The current associated with this process is proportional to the oxygen present in the solution outside the membrane. To minimize the depletion of oxygen in the medium by this electrochemical process and the resultant decrease in the apparent oxygen concentration that would be recorded, the 6920 employs a Rapid Pulse oxygen system which allows for reliable measurements in minimal flow conditions.

Turbidity

Turbidity is the measurement of the content of suspended solids (cloudiness) in water and is typically determined by shining a light beam into the sample solution and then measuring the light that is scattered off of the particles and directed back to the detector. The light source is a light emitting diode (LED) which produces radiation in the near infrared region of the spectrum and the detector is a highly sensitive photodiode. The turbidity probe on the 6920 conforms to recommendations of the International Standards Organization (ISO); the light source emits a wavelength between 830 and 890 nm and the angle between the emitted and detected radiation is 90 degrees in accordance with ISO-7027. The turbidity probe is also equipped with a mechanical wiper to periodically clean the sensor.

Temperature

Temperature is measured by a thermistor of sintered metallic oxide that changes predictably in resistance with variations in temperature. The algorithm for conversion of resistance to temperature is incorporated into the unit's internal software, providing accurate measurements of temperature automatically in either degree Fahrenheit, Celsius or Kelvin.

Equipment – Calibration

The YSI 6920 shall be calibrated in accordance with the manufacturer's instruction manual prior to field use. The required calibration procedures are summarized below.

SAFETY NOTE: Reagents used to calibrate and check this instrument may be hazardous to your health. Some calibration standards solutions require special handling. Review pertinent health and safety information attached.

REQUIRED APPARATUS

- Calibration standards
    - pH 7.0 standard buffer solution
    - pH 4.0 or pH 10.0 standard buffer solution (depending on field conditions expected)
    - 0.0 NTU Turbidity Standard (deionized or distilled water)
    - 100 NTU Turbidity Standard
    - Conductivity standard appropriate for field conditions expected
- YSI 6920 Transport Cup
- 600 ml glass beaker
- YSI 6920 Probe Guard
- Kim-wipes and Paper Towels
- YSI 6920 DO Calibration Kit (electrolyte solution and Teflon membranes)
- Ring stand and clamps suitable for holding YSI 6920 unit during calibration
- Barometer

GENERAL NOTES:

- Insure that all sensors are immersed in the standard solutions during calibration procedures. Used recommended volumes when performing calibrations The recommended volume for use with the 6920 Transport Cup is 300 ml with turbidity probe installed and 350 ml without turbidity probe installed. The fluid level measured from the top lip of the cup is 2.50” and 1.75” respectively.

- During many calibrations the readings acquired by other sensors (e.g. temperature probe) are factored into calibration algorithms.

- Rinse the sonde between calibration solutions using clean ambient temperature water. For maximum accuracy, follow up by pre-rinsing the sonde with a small amount of the calibration solution required next.

- Have clean adsorbent paper towels to dry the sonde between rinses and calibration solutions. It is important to remove as much residual liquid as possible from the sonde after each rinse. Drying the sonde in this way reduces carry-over contamination of calibrator solutions and increases the accuracy of the calibration.

After powering up the YSI6920, the Main Menu will be displayed. To access the calibration menu select option “2-Calibrate” from the Main Menu, the unit will display all the installed sensors which necessitate a pre-calibration prior to deployment and data acquisition i.e., conductivity, dissolved oxygen, pressure, pH and turbidity. The calibration procedure for each of the sensors is explained individually as follows:

Calibration of Conductivity Sensor

Select the conductivity sensor off the Calibrate Menu to access the conductivity calibration procedure, then select SpCond to access the specific conductance calibration procedure. Enter the calibration value of the standard you are using (mS/cm at 25 ^{o}C) and press ENTER. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

Observe the readings under SpCond, when no significant change occurs in the display for approximately 30 seconds, press ENTER. The screen will indicate that the calibration has been performed successfully and will prompt you to press ENTER again to return to the Calibrate Menu.

Rinse the sonde unit in clean tap water and thoroughly dry.

Calibration of the Dissolved Oxygen (DO) sensor

Place approximately 1/8” (3 mm) of water into the YSI transport cup and engage 1 or 2 threads on the sonde unit. Make certain that the DO and temperature probes are not immersed in the water. Do not tighten, a loose connection which allows the transport cup to freely vent to the atmosphere is required to properly complete this calibration step. Wait approximately 10 minutes for the air in the calibration cup to become water saturated and for the temperatures of the thermistor and the oxygen probe to equilibrate.

Select 2-Dissolved Oxy from the Calibrate Menu, then select 1-DO% to access the DO% calibration procedure. Enter the current local barometric pressure in mm Hg (inches Hg x 25.4 = mm Hg). Do not use barometer readings obtained from meteorological reports, these are corrected to sea level will produce an inaccurate calibration.

A countdown timer will be displayed on the lower left of the screen that allows for the proper warm up time for the DO sensor. After the warm up time is complete, the readings just before and just after calibration are displayed. A message that indicates to press ENTER to continue will appear. Pressing ENTER will return the display to the DO calibration. When the DO% values are reach a stabilized value, pressing ENTER will accept the calibration. Immediately proceed with depth sensor calibration

NOTE: Calibration of the DO sensor following the DO% procedure will simultaneously achieve calibration in the DO mg/L mode and vice versa.

Calibration of Depth Sensor

Following the DO calibration, with the sonde still in the water saturated environment of the transport cup, select 3-Pressure-Abs from the Calibrate Menu to access the depth calibration procedure. Input 0.00 or some known sensor offset in feet. NOTE: With the standard sensor guard attached to the sonde, the depth sensor is approximately 0.50 feet above the bottom of the probe compartment). Press ENTER and monitor the stabilization of the depth readings with time. When no significant change occurs for approximately 30 seconds, press ENTER to confirm the calibration. This action will zero the sensor with regard to current barometric pressure. Then press ENTER to return to the Calibrate Menu.

Calibration of pH Probe (2-Point Calibration)

Place the appropriate volume of pH 7.0 standard buffer solution into a pre-rinsed transport cup and allow 1 minute for temperature equilibration before proceeding. From the Calibrate Menu select 4-ISE1 pH to access the pH calibration procedure and select 2-2-point. Press ENTER and input the value of the buffer (7.0) at the prompt. Press ENTER and the current values received from the sensors will be displayed. When the unit has stabilized and there are no significant changes for approximately 30 seconds, press ENTER to accept this calibration step.

Press ENTER to continue with the second point in the calibration procedure. Rinse the sonde in water and dry the sonde before proceeding. Select either a pH 4.0 of pH 10.0 standard buffer solution to encapsulate the range of pH values expected in the field. Place the appropriate volume of the second standard buffer solution into pre-rinsed transport cup. Press ENTER and input the value of the second buffer at the prompt. Following the same procedure as above, Press ENTER and the current values received from the sensors will be displayed. When the unit has stabilized and there are no significant changes for approximately 30 seconds, press ENTER to accept and complete this calibration step.

Thoroughly rinse the sonde and the calibration container in water and dry.

Calibration of the Turbidity Probe

Select 8- Turbidity from the Calibrate Menu and then select 2-2-point.

NOTE: One standard must be 0.0 NTU, and this standard must be calibrated first.

Place 250 ml of 0.0 NTU standard (clear deionized or distilled water) into the clear calibration cup or a 600 ml glass beaker. With the probe guard installed, immerse the sonde in the water. Input the value 0.00 NTU at the prompt and press ENTER, real-time sensor values will then be displayed. Activate the wiper 1 or 2 times by pressing the 3-Clean Optics key as shown on the display to remove any trapped bubbles. After stabilization is complete, press ENTER to confirm the first calibration, press ENTER to continue.

After drying the sonde carefully, place the unit in 250 ml of the second turbidity standard (100 NTU is suggested). Input the correct turbidity value in NTU, press ENTER, real-time sensor values will again be displayed. Activate the wiper 1 or 2 times by pressing the 3-Clean Optics key as shown on the display to remove any trapped bubbles. After stabilization is complete, press ENTER to confirm the turbidity calibration procedure.

Thoroughly rinse and dry the sonde and calibration cups.

Equipment - Data Collection

The YSI 6920 unit is capable of collecting data in two distinct modes; discrete sampling or unattended sampling. Each mode allows the operator to save data electronically to file. The complete details of each mode are specified in the manufacturer's user manual and are defined as follows:

- <u>Discrete Sampling</u> – employed in short term, spot sampling applications when the user is present on site and the unit is attached to a 610-DM data logger or laptop PC.

- <u>Unattended Sampling</u> – used in long term deployments of the battery powered sonde when user is not present on site. The sonde is configured to automatically log data to instrument memory after long sampling intervals (15 to 30 minutes) for extended periods of time, upwards of 30 to 40 days depending on sampling frequency and suite of active sensors.

The mode of data collection for this monitoring effort will be discrete sampling at each station at three depths, surface (YSI submerged to the lifting bail), mid-depth and bottom (YSI depth at 3 feet off bottom). Prior to the start of the survey the discrete sampling location (comprised of station location and YSI depth) can be entered into a pre-established site list on the 610-DM data logger. Once on station the appropriate file can be opened off the site list allowing the operator to capture sensor data from the YSI unit and store the information electronically. A supplemental written log of the data is recommended as a back up.

The site list can be generated by the following procedure:

- Turn on the 610-DM by pressing the POWER key, the Main menu will be displayed. If the sonde unit is already connected the display will automatically default to the Run menu, simply hit ESC to return to Main menu.
- Use the ↓ key to scroll to the System Setup menu, press ENTER.
- Scroll to Setup Site List, press ENTER.
- The 610 will now prompt for a file name (8 characters maximum), enter title, press ENTER.
- Scroll to Site Item, enter descriptors for each sampling site (10 characters maximum)
- Once complete, ESC to verify the Site List, edits can be made to the site list by selecting the item you wish to change, then Move, Insert, Revise or Delete accordingly.

The following procedure will permit the operator to "Add" data that is collected by the sonde unit and subsequently displayed on the 610-DM. The procedure assumes that the 610-DM is properly attached to the YSI-6920 sonde unit and that the 610-DM is in the Run Mode displaying data.

- Press "A" to add a data point to a file (the 610-DM will offer the filename of the last file that was added to.
    - To Add to this file, press ENTER
    - To Add to a new file, type that files name and press ENTER.
    - To Add to a file whose filename is on the Site List, press ↓ or ↑ to select the desired filename then press ENTER. The data point is immediately appended to the data file.
    - Continue until all sites have been visited.

<u>NOTE</u>*: *Do not collect data until the sensor display has stabilized, particularly the parameters of DO and pH. Allow the DO sensor to warm up from 40 to 180 seconds after being immersed on station, depending on the water temperature.

QA/QC

- The YSI-6920 must be calibrated on a daily basis in accordance with the manufacturers instruction manual prior to use.

Operating Guidelines (Sensors)

- DO Probe - Keep the DO probe moist when not in use, either by immersing in water or by placing damp sponge in the transport cup. For long term storage, remove the probe from the sonde and store it in water with the Teflon membrane and electrolyte in place. The Teflon membrane and the KCL reagent should be changed prior to the first deployment of the sonde on any particular survey and at least once every 30 days during a sampling study. In addition, the membrane should be changed if bubbles are visible under the membrane; if significant deposits of dried electrolyte are visible on the membrane or the O-ring; or if the probe shows unstable readings.

- Conductivity Cell – The openings that allow fluid access to the conductivity electrodes must cleaned regularly with mild detergent and a small brush provided in the 6570 Maintenance Kit.

- Depth Sensor – The depth sensor is exposed to the water column via a small through-hole in the side of the sonde. The port should be cleaned on a regular basis to ensure the opening is unobstructed. A syringe is supplied in the maintenance kit to aid in cleaning the pressure port.

- Turbidity Probe – Inspect the optical surface of the probe after each deployment and clean if necessary by gently wiping the probe face with moist lens cleaning paper. Replace the wiper regularly, especially if poor water quality conditions are encountered. DO NOT rotate the wiper by hand – Damage to the internal operating mechanisms will result.

- pH Probe – Be sure to remove deposits or contaminants from the glass probe using clean water clean water and a soft clean cloth or lens cleaning paper –" Use caution". Remove any material that may be fouling the circular reference electrode junction of the sensor.

Operating Guidelines (General)

- Attach the field cable to the sonde and hand tighten – DO NOT use tools!

- Be sure to attach the strain relief connector to the sonde bail prior to deployment.

- DO NOT deploy the sonde without installing the probe guard.

- Lower the sonde through the water column slowly and avoid impacting the sonde on the bottom.

- Make sure all port plugs are installed in all port connections where probes are not installed, it is extremely important to keep these electrical connections dry.

Procedures for Special Conditions

The following procedures address special conditions.

- If the sonde unit becomes fouled with oily materials or sediments, gently remove these coatings using clean Kimwipes followed by a distilled-water rinse. Properly dispose of the Kimwipes along with used safety gloves.

Contamination Avoidance

- If it is anticipated that field conditions will expose the YSI-6920 sonde to hazardous materials, rinse the unit thoroughly with clean water between stations. Special precautions exposure i.e., Latex gloves, Tyvek sleeves, rubber boots, should be exercised by personnel operating the YSI in order to adequately protect from hazardous material exposure.

Health and Safety

- A approved site specific Health and Safety Plan will be developed, incorporating guidelines for employee safety consistent with OSHA and other applicable and appropriate standards and requirements, prior to implementation of the field effort.

- All ENSR field personnel will be outfitted in the appropriate protective clothing and safety equipment required by the H&S Plan during field efforts, including steel-toed boots, safety glasses, chemical resistant gloves and an approved USCG work vest for all work performed afloat or near the waters edge.

Sensor Specifications

Depth
Sensor Type: Stainless Steel Strain Gauge
Range: 0 to 200 feet (61 meters)
Accuracy: +/- 0.4 feet (0.12 meters)
Resolution: 0.001 feet (0.001 meters)

Temperature
Sensor Type: Thermistor
Range: -5 to 45 ^oC
Accuracy+/- 0.15 ^oC
Resolution: 0.01 ^oC

Dissolved Oxygen, % Saturation
Sensor Type: Rapid Pulse – Clark Type, polargraphic
Range: 0 to 500% air saturation
Accuracy: 0 to 200% air saturation, +/- 2% air saturation
200 to 500% air saturation, +/- 6% air saturation
Resolution: 0.1% air saturation

Dissolved Oxygen, mg/L (Calculated from % air saturation, temperature and salinity)
Sensor Type: Rapid Pulse – Clark Type, polargraphic
Range: 0 to 50 mg/L
Accuracy: 0 to 20 mg/L, +/- 0.2 mg/L
20 to 50 mg/L, +/- 0.6 mg/L
Resolution: 0.001 mg/L

Conductivity
Sensor Type: 4-electrode cell with autoranging
Range: 0 to 100 mS/cm
Accuracy: +/- 0.5% of reading + 0.001 mS/cm
Resolution: 0.001 mS/cm to 0.1 mS/cm (range dependent)

Salinity
Sensor Type: Calculated from Conductivity and Temperature
Range: 0 to 70 ppt
Accuracy: +/- 1.0% of reading or 0.1 ppt, whichever is greater
Resolution: 0.01 ppt

pH
Sensor Type: Glass Combination Electrode
Range: 0 to 14 standard units
Accuracy: +/- 0.2 standard units
Resolution: 0.01 standard units

Turbidity
Sensor Type: Optical, 90o scatter, mechanically cleaned
Range: 0 to 1000 NTU
Accuracy: +/- 5% of reading or 2 NTU (whichever is greater)
Resolution: 0.1 NTU

Appendix III

Standard Operating Procedures for Streamflow Measurements

Procedure for Measuring Average Stream Velocity and Discharge Using a Current Meter
(Summarized from USGS, 1982)

1. Select a cross-section from a straight, uniform reach with parallel streamlines and a relatively uniform bottom. The depth of the section and the velocity of flow that can be measured are limited by the dimensions of the current meter used. The pygmy current meter can measure velocities in water that is approximately 2 inches deep or greater and at velocities of 0.05 feet per second or more. If possible, the section should be free of large eddies with upstream circulation near the banks, slack water, or excessive turbulence caused by upstream bends, radical changes in cross-section shape, and irregular obstructions such as boulders, trees, vegetation, and other debris in the vicinity.
2. Select a time period for measurement when the flow is not expected to change. If the flow changes rapidly during the flow measurement the reading will have to be abandoned. The determination of flow variability during a measurement will be made by noting the before and after water levels.
3. String a tape measure across the stream channel perpendicular to flow. This will allow for a record of the transverse location of the current meter during a measurement. Visually divide up the flow through the cross-section into at least 20 compartments (depending on the width of the channel) such that each compartment has roughly the same amount of flow passing.
4. According the channel cross-section diagram illustrated in Figure 1, measure the distances (b) and depths (d) for each average velocity measurement. The mean velocity is measured at a point six-tenths of the depth from the stream surface at each location (b). The partial area flows are calculated by multiplying the width of the individual areas by the corresponding depths in those areas. This calculation is made according to the following equation with locations of the variables defined in Figure 1 of this appendix.

$$q_x = v_x\left[\frac{b_x - b_{(x-1)}}{2} + \frac{b_{(x+1)} - b_x}{2}\right]d_x$$

5. Compute the total flow as the sum of the partial flows using the equation:

$$Q = \Sigma q_x$$

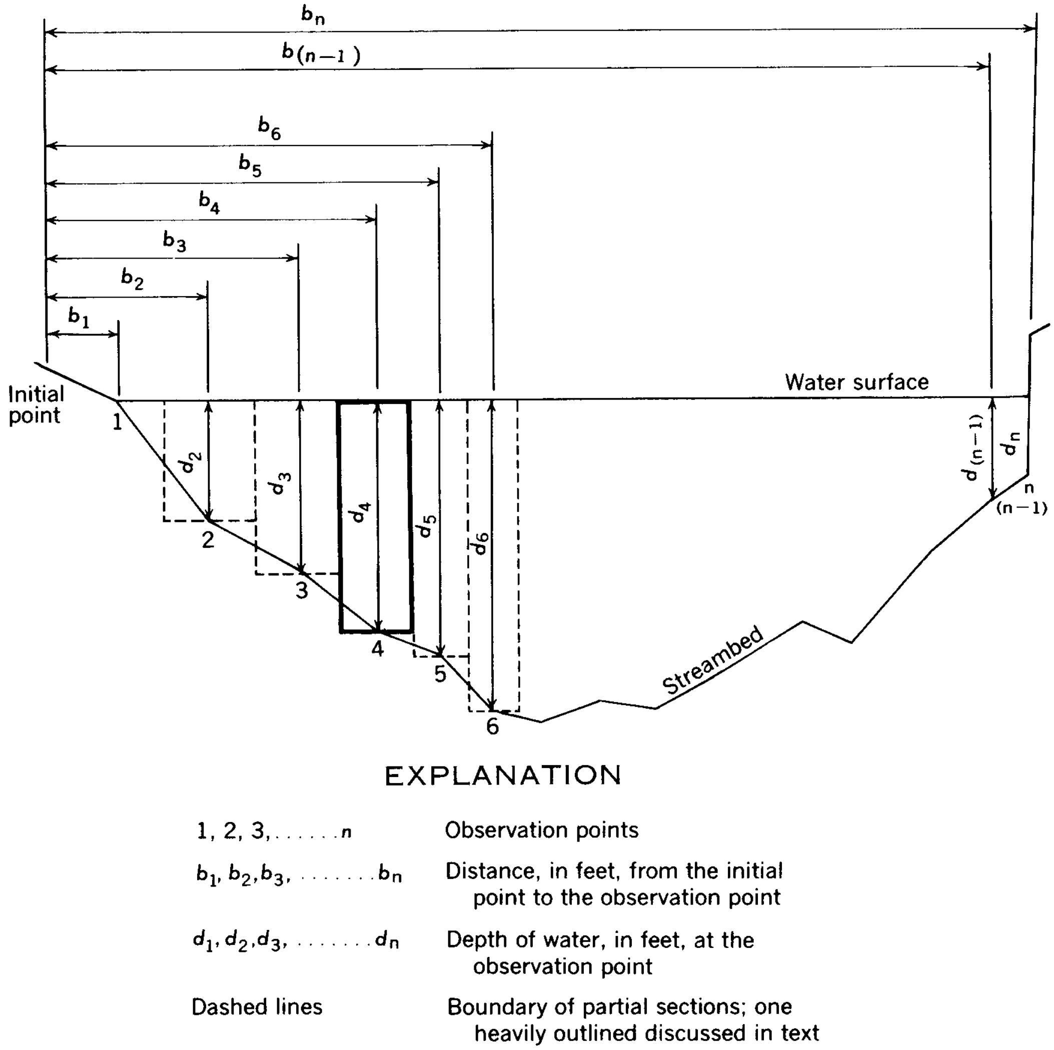


Figure 1 – Illustration of channel cross-section showing the distances of the measured velocities from the shore and the depths of the partial area cross-sections (USGS, 1982).

USGS. 1969. Discharge Measurements at Gaging Stations. Techniques of Water-Resources Investigations of the United States Geological Survey. Book 3, Chapter A8.