QUALITY ASSURANCE PROJECT PLAN

Narragansett Bay
Fixed-Site Monitoring Network (NBFSMN)
Seasonal Monitoring

Rhode Island Department of Environmental Management

June 1, 2020

Project Manager

Sue Kiernan

7/31/20
Date

Sue Kiernan
RIDEM, Office of Water Resources
235 Promenade Street
Providence, RI 02908
Tel: 401.222.4700 ext. 7613
sue.kiernan@dem.ri.gov

Quality Assurance Officer

H Stoffel

7/31/20
Date

Heather E. Stoffel
University of Rhode Island's Graduate School of Oceanography (URI/GSO)
South Ferry Road
Narragansett, RI 02882
Tel: 401.874.6860
stoffel@uri.edu

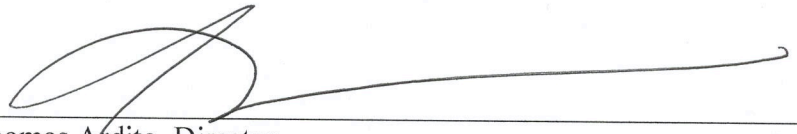
EPA QA Manager

NORA CONLON Digitally signed by NORA CONLON
Date: 2020.08.04 12:37:47 -04'00'

Nora Conlon, Quality Assurance
EPA New England Regional Laboratory
11 Technology Drive North Chelmsford, ME 01863
617.918.8335 conlon.nora@epa.gov

Date

Restore America's Estuaries/ Southeast New England Watershed Grants Program



3 AUG 20

Thomas Ardito, Director
PO Box 476
Saunderstown, RI 02874
(401) 575-6109
tardito@estuaries.org

Date

SNEP Oversight Officers

Margherita Pryor

4/5/2020

Margherita Pryor, Project Officer
5 Post Office Square, Suite 100
Boston, MA
617.918.1597
Pryor.Margherita@epa.gov

Date

Network Officers

URI/GSO Site Officers

H Stoffel 7/31/20

Heather E. Stoffel
University of Rhode Island's Graduate School of Oceanography (URI/GSO)
South Ferry Road Narragansett, RI 02882
Tel: 401.874-6860 stoffel@uri.edu

Date

Candace Oviatt 8-3-20

Dr. Candace Oviatt
URI/GSO Marine Ecosystems Laboratory (MERL)
South Ferry Road Narragansett, RI 02882
Tel: 401.874-6661 oviatt@uri.edu

Date

NBNERR Site Officer

August 10, 2020
Date

Dr. Daisy Durant
Narragansett Bay National Estuarine Research Reserve (NBNERR)
Prudence Island Prudence Island, RI
Tel: 401.683.7368 daisy.durant@dem.ri.gov

NBC Site Officers

Molly Welsh
Narragansett Bay Commission (NBC)
2 Ernest Street Providence, RI 02905
Tel: 401.461.8848 ext. 389 mwelsh@narrabay.com

10/1/2020
Date

Karen Cortes
Narragansett Bay Commission (NBC)
2 Ernest Street Providence, RI 02905
Tel: 401.461.8848 ext. 274 kcortes@narrabay.com

09/24/2020
Date

MassDEP Site Officer

8/14/20

Richard Chase
Massachusetts Department of Environmental Protection
8 New Bond Street Worcester, MA 01606
Tel: 508.767.2859 richard.f.chase@mass.gov

Date

8/19/20

Dr. Richard Carey
Massachusetts Department of Environmental Protection
8 New Bond Street Worcester, MA 01606
Tel: 508.767.2894 richard.carey@mass.gov

Date

Table of Contents

List of Tables

List of Figures

Acronyms and Agency Abbreviations

ABBREVIATION	FULL NAME
NBC	Narraganset Bay Commission
NBNERR	Narragansett Bay National Estuarine Research Reserve
RIDEM-OWR	Rhode Island Department of Environmental Management's Office of Water Resources
RIDEM-F&W	Rhode Island Department of Environmental Management's Office of Fish & Wildlife
MASSDEP	Massachusetts Department of Environmental Protection
EPA	United States Environmental Protection Agency
URI/GSO	University of Rhode Island's Graduate School of Oceanography
MERL	Marine Ecosystems Research Laboratory
SNEP	Southern New England Estuary Program
NBFSMN	Narragansett Bay Fixed Site Monitoring Network
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
QC	Quality Control
QAPP	Quality Assurance Project Plan
NBEP	Narragansett Bay Estuary Program
NERACOOS	Northeast Regional Association of Coastal Ocean Observing Systems
CHLA	Chlorophyll *a*
BGA	Blue Green Algae

Distribution List

Table 3.1 Distribution List.

QAPP Recipient	Organization	Telephone Number	Address
Sue Kiernan	RIDEM-OWR	401.222.4700 ext. 7600	235 Promenade Street Providence, RI 02908 sue.kiernan@dem.ri.gov
Dr. Kenny Raposa	NBNERR	T 401.683.7849 F 401.683.7366	55 South Reserve Dr. Prudence Island, RI 02874 kenneth.raposa@dem.ri.gov
Dr. Daisy Durant	NBNERR	401.683.7368	55 South Reserve Dr. Prudence Island, RI 02874 daisy.durant@dem.ri.gov
Molly Welsh	NBC	401.461.8848 ext. 389	2 Ernest Street Providence, RI 02905 mwelsh@narrabay.com
Tom Uva	NBC	401.461.8848 ext. 470	2 Ernest Street Providence, RI 02905 tuva@narrabay.com
John Motta	NBC	401.461.8848 ext. 471	2 Ernest Street Providence, RI 02905 jmotta@narrabay.com
Karen Cortes	NBC	401.461.8848 ext. 274	2 Ernest Street Providence, RI 02905 kcortes@narrabay.com
Walter Palm	NBC	401.461.8848 ext. 437	2 Ernest Street Providence, RI 02905 wpalm@narrabay.com
Heather Stoffel	RIDEM/ URI/GSO	401.874.6860	215 South Ferry Road Narragansett, RI 02882 stoffel@uri.edu
Dr. Candace Oviatt	URI/GSO	401.874.6661	215 South Ferry Road Narragansett, RI 02882 oviatt@uri.edu
Edwin Requintina	URI/GSO	401.874.6652	215 South Ferry Road Narragansett, RI 02882 erequintina@uri.edu
Laura Reed	URI/GSO	401.874.6651	215 South Ferry Road Narragansett, RI 02882 lweber@uri.edu
Richard Chase	MassDEP	508.767.2859	8 New Bond Street Worcester, MA 01606 richard.f.chase@mass.gov
Dr. Richard Carey	MassDEP	508.767.2894	8 New Bond Street Worcester, MA 01606 richard.carey@mass.gov
Kalman Bugica	MassDEP	508.767.2867	8 New Bond Street Worcester, MA 01606 kalman.bugica@mass.gov
Thomas Ardito	SNEP	401.575.6109	PO Box 476 Saunderstown, RI 02874 tardito@estuaries.org
Margherita Pryor	EPA, SNEP	617.918.1597	5 Post Office Square, Suite 100 Boston, MA Pryor.Margherita@epa.gov
Nora Conlon	EPA, SNEP	617.918.8335	11 Technology Drive North Chelmsford, ME 01863 colon.nora@epa.gov

4.0 Project Organization

4.1 Project Organizational Chart

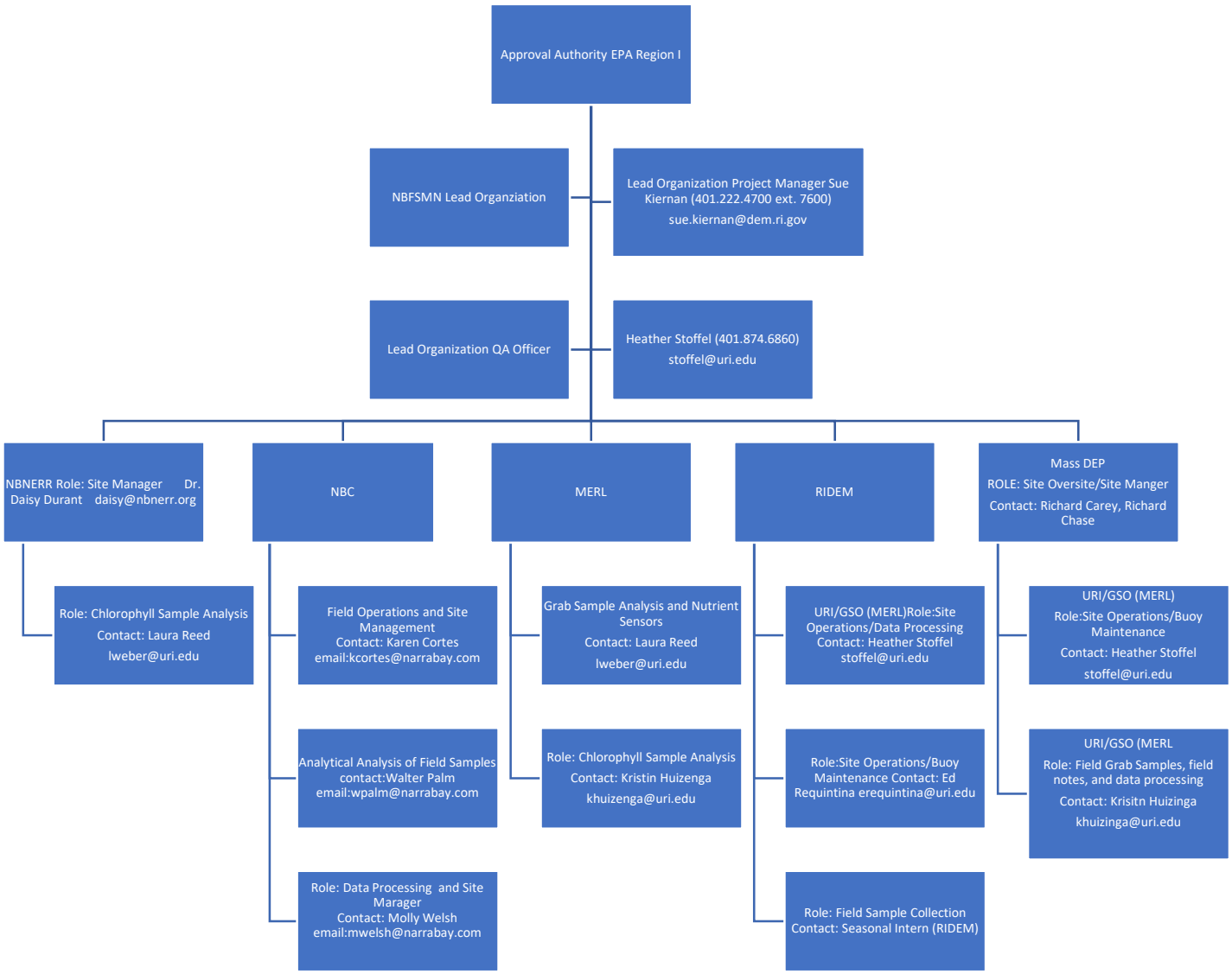


Figure 4.1 Project Organizational Chart.

4.2 Communication Pathways

The monitoring efforts of the Narragansett Bay Fixed-Site Water Quality Monitoring Network (NBFSMN) occur at a minimum during summer season, generally from May through October. Some monitoring efforts are conducted year-round when applicable (land-based stations where it does not freeze over). The teams will be comprised of RIDEM employees, URI/GSO- MERL lab, NBNERR, MassDEP, NBC staff, interns, and volunteers. NBFSMN will collaboratively determine sampling needs and identify the critical stations each year prior to the sampling season.

The QA officer and project manager will contact all potential monitoring agencies prior to the monitoring season for a collaborative meeting/discussion. The premise is to identify monitoring locations, outline each agency's responsibilities during the monitoring season (e.g. site management, funding, and data management), and resolve any issues before the monitoring season is to begin. The QA officer will keep track and archive all the monitoring station's data and metadata on an annual basis.

It is probable that changes to the sampling plan will occur during the monitoring season. Some stations may be inaccessible during certain weather conditions. All changes made in the field by the field samplers will be documented in the field notes. The QA and site operations officers will try to discuss these changes with the field sampler within one week after the problem or changes have occurred. It may become necessary to add and drop stations prior or during the monitoring season. The QA officer, project manager, and the site operations officer will make this decision jointly. The site operator will report all changes to the QA Plan in the site's metadata document.

The NBFSMN will convene for formal or informal meeting/discussions as needed. The purpose of these discussions is to communicate monitoring issues and the future of the program. Each station operator is responsible for generating formatted data and the accompanied metadata. The QA officer will combine all the stations' reports to produce a final report that will be reviewed by and distributed to the members of the NBFSMN. The finalized data sets (raw, edited, and corrected for each station) and accompanied metadata document will be made available for public use after each agency's internal review processes are complete through the RIDEM-OWR website (http://www.dem.ri.gov/programs/emergencyresponse/bart/netdata.php).

The network historical data can be found at the RIDEM website (see above) for annual downloads and through searchable databases to improve public access to data and provide a more user-friendly platform to examine the data generated by the NBFSMN. Since many of the NBFSMN stations have real-time capabilities, stations will report in real-time to the site manager's base station computer. Once data are received, they will be made available for public access at the site manager's discretion. Several stations have real-time data links available to meet the associated agency's protocols.

Real-time data links are below:

NBC reports real-time data: http://snapshot.narrabay.com/app
NBNERR real-time: http://cdmo.baruch.sc.edu/get/realTime.cfm?stationCode=NARTBWQ
RIDEM-OWR stations real-time: http://www.neracoos.org
RIDEM-OWR is also working with Rhode Island Consortium for Coastal Ecology Assessment, Innovation & Modeling (RI C-AIM) to develop a searchable data portal to the NBFSMN historical data. http://ridatadiscoverycenter.org/
MassDEP-data available upon request through MassDEP site manager contact. Data from the two sites collected using MassDEP-owned equipment will only be distributed through the NBFSMN website after the initial URI/GSO review process and the final MassDEP review and validation process are completed.

4.3 Site Manager Duties

Every station operator will inform the QA Officer and NBFSMN with their monitoring plans. Each operator will outline the station locations and sampling protocol before sampling begins. The locations of each sampling station will be designated by name and GPS coordinates.

All agencies' site managers oversee all aspects of their designated sampling stations. Site managers are responsible for reporting data and metadata to the QA officer on a yearly/seasonal basis, unless otherwise agreed upon by site manager and project manager. In addition, site managers of the critical stations (Bullock's Reach, Greenwich Bay, Conimicut Point, and North Prudence; http://www.dem.ri.gov/programs/emergencyresponse/bart/latest.php) will report data and comments to the QA officer twice a month from Memorial Day through Columbus Day. Alternately, if data are publicly available for download on an external site, data will be downloaded directly by the QA officer regularly and will be provided to the QA officer by the site manager upon request. The URI/GSO MERL Laboratory and NBC laboratory will analyze the field chlorophyll samples throughout the sampling season and report results to each site manager annually.

Other data products may consist of public outreach documents, website updates, and further data analysis reports. These reports will be generated at the NBFSMN discretion. All the data reports will be archived by the lead agency, RIDEM-OWR. In addition, a weekly blog will be written for the RIDEM website regarding the water quality of the Bay.

4.4 Training

Training is required for new staff or individuals who feel uncomfortable with the equipment or procedures and when new equipment becomes available. For those unfamiliar with the equipment being used, training will include an introduction to all possible monitoring equipment. Training is provided or arranged through each station operator and webinars from the equipment manufacturer. The training can involve extensive one-on-one training, group training meetings, and/or webinars. When possible, technicians should periodically be trained from the equipment manufacturers, such as YSI.

The QA officer will provide procedure training such as deployment, retrieval, and site setup options when requested by site managers. Each operator will be given an overview on station deployment and retrieval and urged to use a vessel familiar with buoy station deployments. If help is needed for station deployment, the QA and site officers will provide it. This is on a need basis since every deployment is different.

The QA and operations officers will keep a list of all individuals trained. This list will include the names of the individuals trained, how long they have worked with the equipment, and if they have received manufacturer training.

Here are some training videos for site managers to use:

EXO training- EXO-University.com
Buoy Platform setups-https://video.ysi.com/ysi-webinar-set-up-floating-platforms-for-lake
Seabird SUNA V2-https://www.youtube.com/watch?v=UO4Ea_Z2QI4

5.0 Problem Definition/Background

5.1 Problem Definition/Background of Program

Narragansett Bay experiences intermittent low oxygen events in over 32% of the bay throughout the summer period (May-October). Low dissolved oxygen or hypoxia is a complex issue (NBEP, 2013). Low oxygen can be linked to nutrient over-enrichment, particularly nitrogen, which contributes to over-production of phytoplankton (algae). In turn, the excess algae die, sink to the bottom, and decompose, a process that consumes oxygen. Oxygen levels can also be impacted by whether or not the water is stratified (when there are distinct layers of water identified by their different densities). Stratification is amplified by the input of fresher, lighter water which floats on top of saltier, heavier water. Fresh water flowing into the Bay can form a layer that sits on top of the water column like a cap, preventing oxygen in the air from reaching saltier bottom water. During times with stratification, bottom waters are not readily re-oxygenated, leading to oxygen depleted bottom waters, as observed in Narragansett Bay (Codiga et al., 2009). Many factors affect nutrient loadings, and ultimately dissolved oxygen concentrations, throughout the bay:

- Weather (rainfall, temperature, wind)
- Circulation patterns (tides, flushing rates, and currents)
- River flows into the bay from the watershed
- Discharges, both point and non-point, that result in nutrient over-enrichment
    - Point discharges include wastewater treatment facilities
    - Non-point discharges include stormwater runoff from developed and agricultural lands.

Ultimately, excess nutrients and its effects can hinder the natural ecosystem's ability to maintain aquatic life and support designated uses, such as fisheries. DEM F&W work show quahogs, in the Providence River, exhibit low meat to shell weight ratio (RIDEM et al., 2000). One of the causes of low ratios is low oxygen stress.

Excess nutrients are one likely cause of lack of re-growth of critical habitat like eelgrass beds in the upper half of the Bay. In addition, fish kills, and other evidence of low-oxygen conditions extend beyond the tidal river section of the estuary.

Shifts in physical and/or chemical properties of the water column cause hydrographic changes in estuarine waters. These shifts affect the water's ability to sustain life. To address the negative impacts on aquatic life, estuarine managers must first have knowledge of how the ecosystem responds to nutrient loading and what natural processes control the magnitude of the impacts, in particular low dissolved oxygen levels (hypoxia). Temperature, salinity, pH, DO, chlorophyll, and turbidity are among the most important parameters needed to assess the hypoxia issue.

To understand these shifts throughout Narragansett Bay, a small group of researchers were established in 1999 to monitor physical water quality parameters on a continuous basis. Over the next few years other agencies expanded this type of research approach. This collaborative officially became the NBFSMN in 2004. In 2005, RIDEM, NBNERR, NBC, and URI GSO were the original members of NBFSMN. Rhode Island Department of Environmental Management's Office of Water (RIDEM-OWR) is the lead agency for the NBFSMN. Then in 2008, the Sally Rock Buoy was added to increase spatial awareness of water quality in Greenwich Bay. Most recently (2016-2017), two new buoys were added in Mount Hope Bay at Taunton River and Cole River as MassDEP joined the water monitoring efforts. RIDEM-OWR is working with its partners to continue a comprehensive and coordinated monitoring program to analyze the spatial and temporal distribution of low oxygen in Narragansett Bay during the summer. RIDEM-OWR will also use the information generated by the network to assess the bay's water quality conditions using the state's established water quality

criteria for dissolved oxygen for estuarine waters. MassDEP will use the data collected from their buoys to assess water quality in Mount Hope Bay.

RIDEM-OWR and MassDEP have an ongoing responsibility to assess state waters for exceedances of criteria related to low oxygen. State criteria are used to identify impaired waterbodies with the goal of removing the bay and its tidal rivers from the list of impaired waters. RIDEM's oxygen criteria are based upon duration and intensity exposure rates adapted from the EPA's guidance document of 2000 (USEPA, 2000). Rhode Island's state criteria can be found at http://www.dem.ri.gov/pubs/regs/regs/water/h2oq10.pdf. MassDEP's dissolved oxygen criteria specify protective concentration thresholds and can be found at https://www.mass.gov/regulations/314-CMR-4-the-massachusetts-surface-water-quality-standards. The network provides continuous data on a 15min time scale to document intermittent hypoxia that occurs in the bay. This information can be used by the states as a tool to help assess their waters. The network data provides a more thorough account compared to spot checks or grab samples. Ultimately, the water quality monitoring information from the NBFSMN provides the continuous information necessary to assess oxygen levels based on the criteria's exposure rates that provide protection to living resources (water quality to support crabs, oysters, and fish) and vital habitats (water quality to support submerged aquatic vegetation - SAV). Water quality information also supports refinement, calibration and validation of the water quality models throughout the bay.

The data from the network will also be used to assess trends over time, identify impaired waters, and assess effectiveness of management decisions (e.g. wastewater treatment facilities (WWTF) upgrades, TMDL efforts, and stormwater treatment). This is a long-term monitoring strategy to aid in gathering baseline information, provide support for other programs, and evaluate management decisions.

The network will achieve the goal by documenting the bay's summer season water quality conditions to determine the extent of damaging effects of eutrophication in Narragansett Bay. Continuous long-term monitoring provides information needed to define the temporal variability of water quality. This level of observation will capture events that occur on short time scales (hours to days) or during times when it is impractical to deploy field crews. Continuous monitoring captures the daily variability in water quality to provide scientists with the information necessary to fully assess criteria attainment throughout the bay. Continuous monitoring provides early warning of potential harmful algae blooms and low- dissolved oxygen related fish kills, allowing managers to coordinate appropriate supplemental sampling (e.g., plankton sampling). Having these stations operational for the long term allows for all parameters to be examined for trends. In addition, inter-annual variability can be described, evaluation can be conducted of implemented management initiatives, and potential effects of climate change can be examined.

5.2 Narragansett Bay Watershed

Narragansett Bay covers approximately 147 square miles with an undulating shoreline that creates a string of sheltered coves where water circulation may be restricted. These characteristics, and other factors such as the location of urban areas within its watershed, make it difficult to characterize the water quality of all the small coves and harbors. In general, there is a clear north to south gradient of pollution in the main channels of the Bay. The highest pollutant levels have been documented in the urbanized Providence / Seekonk tidal rivers and the Fall River /Taunton River area, and slightly lower levels in the urbanizing areas such as Greenwich Bay and the upper Bay (between Conimicut Point and Prudence Island). Levels of pollutants in the open bay channels continue to decrease south towards the mouth of the Bay, with lowest levels at the openings to Block Island Sound. Small harbors and coves, such as Wickford Harbor and Newport Harbor can experience significant pollutant impacts due to poor flushing, which exacerbates the level and impact of local pollutant sources (Oviatt, 2008).

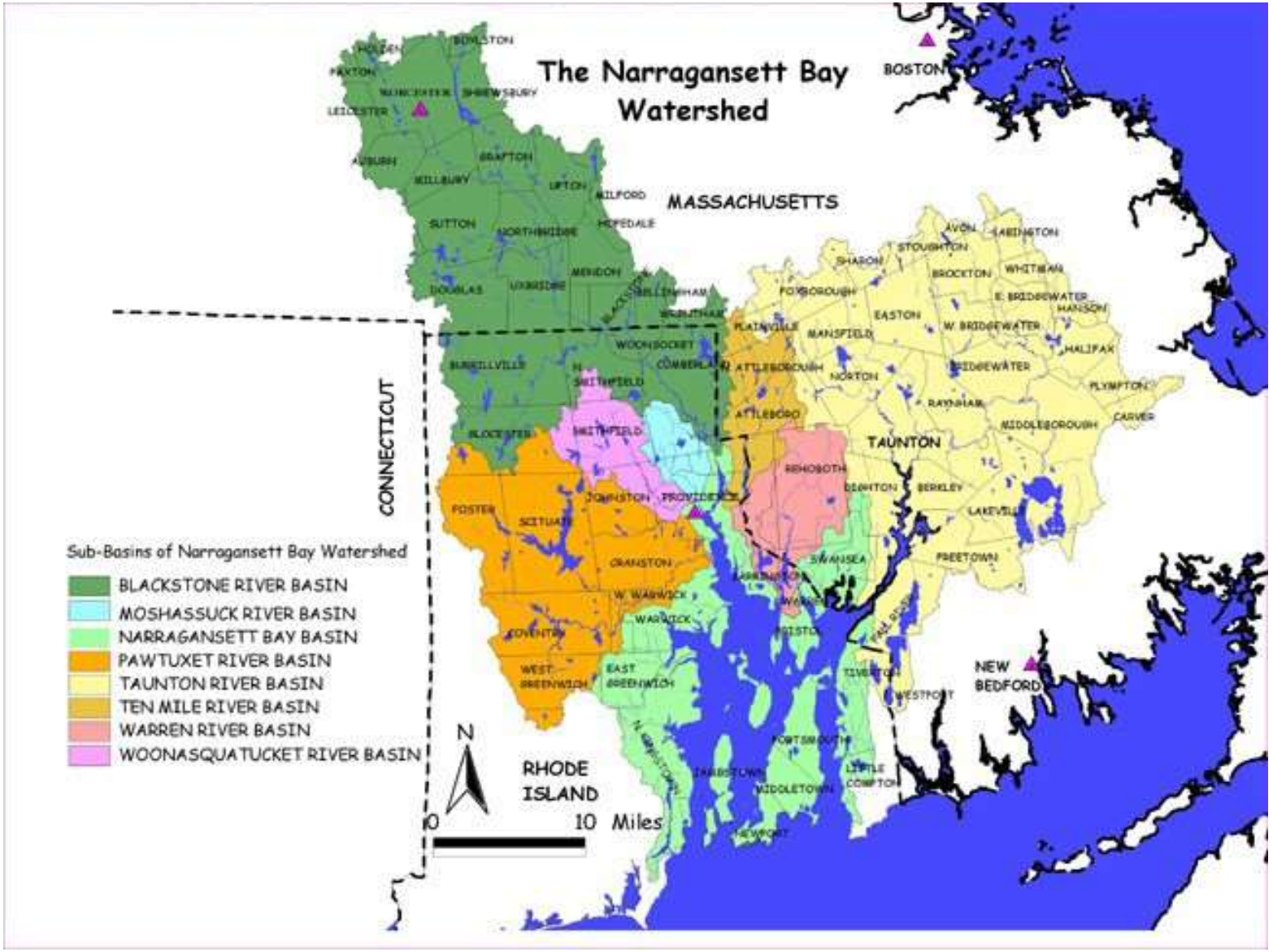


Figure 5.1 Narragansett Bay Watershed. The Narragansett Bay watershed covers a land area of 1,657 square miles. Forty percent of the Bay's watershed is in Rhode Island; the remaining 60% is in Massachusetts (Figure 5.1).

5.3 Water Quality History

Poor water quality conditions have been known to exist in the Greenwich Bay, Seekonk, and Providence Rivers prior to 1999 (Deacutis, 1999; Doering, et.al., 1990). From 2001-2013, several studies observed lower than expected oxygen concentrations (< 2 mg/L) in the Upper Bay region (Bergondo., et. al, 2005; Deacutis, et. al., 2003; Deacutis, et. al., 2006; Saarman, et.al., 2008; NBEP, 2017). The data revealed that hypoxic events extend into the Upper Bay, the upper East Passage, and parts of the upper West Passage during summer, at times crossing more than a third of the Bay. Presently, over 32% of Narragansett Bay is impaired for dissolved oxygen based on data analysis from the NBFSMN (NBEP, 2013).

The states of Rhode Island and Massachusetts have dissolved oxygen criteria for Narragansett Bay to protect marine life (RIDEM, 2010; MassDEP, 2013). These standards are used to assess each state's waterbodies using the data generated from the NBFSMN. These assessments have revealed the upper 2/3rds of Narragansett Bay is impaired for dissolved oxygen (NBEP, 2013). These areas include the Seekonk and Providence Rivers, which are located in the major urban center of Rhode Island, to the Mt View area in the West Passage and the Poppasquash Point area in the East Passage. The impaired waters of Narragansett Bay also include two embayments, Greenwich Bay and Mt. Hope Bay. To address the concerns in these areas, starting in 2004, work began on TMDLs to improve water quality with respect to eutrophication through nutrient (nitrogen) reductions from the watershed's WWTFs, primarily focusing on the effluent that empties into the Providence River.

The Bay experiences seasonal intermittent hypoxic events with the potential to threaten ecological health seasonally (May-October). Low oxygen or hypoxic events can have adverse effects on aquatic life. The persistent lack of oxygen in the bottom waters is one of the leading causes of aquatic life die-off. One low oxygen event can severely negatively impact all stages of marine life (e.g. growth rate reductions and fish kills). These negative effects on finfish and shellfish populations have implications for commercial fisheries (Codiga, et.al., 2009).

These stresses on marine life became even more apparent during the summer of 2003. In August 2003, data confirmed that dissolved oxygen levels had declined causing a hypoxic event the bottom waters throughout the Upper Bay. In the western section of Upper Narragansett Bay, known as Greenwich Bay, bottom conditions became anoxic. This resulted in the largest fish kill recorded by officials. Large events causing fish kills, like in 2003, are sporadic. Small fish kills in Narragansett Bay, including its coves, occurred occasionally, such as in 2001, 2006, 2008, and 2018. Although fish kills do not occur every year, low oxygen events occur each year in impaired areas causing adverse effects on the marine ecosystem (RIDEM-OWR, 2003).

RIDEM fish kill and 303b reports target low dissolved oxygen and nutrient enrichment (eutrophication) among the major causes for impairments and stressors on marine life in the estuary.

Unlike the other parts of the Narragansett Bay, Mount Hope Bay lies within the dominion of both Massachusetts and Rhode Island. Although two thirds of the bay fall within Rhode Island, a calculated 90% of the bay's drainage comes from Massachusetts. In the past, the bay has been susceptible to pollution from sewage and industry which flushed heavy metals and waste out of the cities into nearby rivers such as the Taunton and Cole River, which then flowed into Mount Hope Bay (RIDEM-OWR, 2010). While the bay has recently become cleaner due to the enforcement of stricter regulations, improvement of infrastructure, and monitoring, it continues to have various hypoxic events and faces trouble arising from pollution and eutrophication. Power plants have also contributed to the anthropogenic impacts on Mount Hope Bay as they released heated water, notably Brayton Point

Power Station. Due to the recent closure of Brayton Point, there may be a shift in temperature and mixing dynamics of Mount Hope Bay which may or may not impact the observed oxygen levels.

Management and monitoring strategies have now been adopted and implemented to address eutrophication issues throughout Narragansett Bay (RIDEM-OWR, 2005, Colt, A., 2008). The major management strategies are to evaluate facility upgrades for urban waste entering the system from point sources. Recent history shows over 50% of the nutrient loadings entering the bay throughout the watershed come from urban sewage (Vadeboncoeur, A., et.al, 2010). Other strategies include monitoring physical conditions to better understand the spatial extent of hypoxia conditions throughout the bay. Along with monitoring conditions, the data generated by NBFSMN will be used to evaluate management plans for nutrient reductions. NBFSMN has also been highlighted as one of the key monitoring programs for sentinel monitoring for climate change (NERACOOS, 2016).

The NBFSMN is in place to document the management initiatives. Many of the WWTFs in the Narragansett Bay watershed have completed most upgrades to work towards meeting the mandated 50% reduction in nitrogen loading. A few WWTFs are still working to complete upgrades to their facilities throughout the Narragansett Bay watershed to further reduce the amount of nutrient loading to the bay. These efforts are designed to minimize the adverse effects of a eutrophic system. Monitoring the changes that occur in the Bay is imperative to assess the management initiatives as the WWTFs and others work to meet requirements for nutrient loadings to the bay throughout the watershed.

A list of some applicable studies appears in Table 5.1. More details about each study can be found in the Preliminary Data Report.

5.4 NBFSMN History and Funding Sources

The Narragansett Bay Fixed Site Monitoring Network (NBFSMN) was officially established in 2005. The network of agencies agreed to conduct and report monitoring in Narragansett Bay using the same QAPP approved protocols to provide the best comparability between datasets. All agencies use YSI products to monitor physical water quality parameters at near surface and near bottom locations where possible. The buoy stations were agreed to be operational seasonally, and land-based stations are operational year-round where icing is not an issue. The agencies involved in this effort have changed slightly over the years. Presently, as of 2017, Rhode Island Department of Environmental Management's Office of Water Resources (RIDEM-OWR), University of Rhode Island's Graduate School of Oceanography Marine Ecosystems Research Laboratory (MERL), Narragansett Bay Commission (NBC), Narragansett Bay National Estuarine Research Reserve (NBNERR), and Massachusetts's Department of Environmental Protections (MassDEP) have active stations within the network. RIDEM-OWR serves as the lead agency for this project and act as the data clearing house for all network data. URI/GSO MERL maintains all 8 of RIDEM-OWR's stations (B3, B2, F5, B14, B6, B7, B13, B12), 2 of URI/GSO stations (B3W, F7) and 2 of MassDEP's stations (B10, B11) (Figure A1). NBC maintains 2 stations that report to the network (F4, B4) and NBNERR maintains one station that reports to the network (F3). This is a total of 15 stations, as of 2017, throughout the bay with a concentration in the upper bay where low oxygen is to be a known issue. MERL processes chlorophyll and nutrient grab samples for all RIDEM-OWR's stations, NBNERR's T Wharf station (network station), and MassDEP's stations. NBC processes its own samples for chlorophyll and nutrients.

Each agency funds and oversees the maintenance of their stations. Present funding sources include: RIDEM-OWR, NERACOOS, NBC, NBNERR, and MassDEP. RIDEM-OWR also received partial funding in 2019 through a Southeast New England Watershed Grants Program (SNEP) RFA19091 for three buoys at Conimicut Point, North Prudence and Poppasquash Point (figure A1).

Table 5.1 Dissolved Oxygen Studies Conducted in the Narragansett Bay Watershed.

Primary Organization	Title	Date of Report	Approximate Date of Study
URI/GSO	Characterizing Late Summer Water Quality in the Seekonk River, Providence River, and Upper Narragansett Bay, Final Report	1990	1989
Rhode Island Sea Grant (RI Sea Grant)	Historical Trends in Water Quality and Fisheries Resources, Narragansett Bay, Rhode Island	1991	1990
URI/GSO	The Basic Hydrography and Mass Transport of Dissolved Oxygen in Providence and Seekonk Estuaries	1994	1990-1993
URI/GSO	Chemical Variability in Coastal and Mixed Layer Waters	1997	1995-1996
RI Sea Grant, NBEP	Nutrients and Narragansett Bay: Proceedings of a Workshop on Nutrient Removal from Wastewater Treatment Facilities	1999	1999
RIDEM Narragansett Bay Estuary Program & Narragansett Bay	Narragansett Bay Water Quality: Status and Trends 2000 A Summary of Water Quality	2000	1998-1999
Narragansett Bay EPA Laboratory	Determination of Lethal Dissolved Oxygen Levels for Selected Marine and Estuarine Fishes, Crustaceans, and a Bivalve	2002	2000-2001
URI/GSO	Time-Series Observations During the Low Sub-Surface Oxygen Events in Narragansett Bay During Summer 2001	2004	2001-2002
BROWN, NBEP	Nighttime Surveys of Dissolved Oxygen in Upper Narragansett Bay (1999-2003)	2004	1999-2003
RIDEM-OWR	State of Rhode Island and Providence Plantations Water Monitoring Strategy 2005-2010	2005	2005-2010
BROWN, NBEP	Hypoxia in the Upper Half of Narragansett Bay, RI, During August 2001 and 2002	2006	2001-2002
URI/GSO	Time-Series Observations During the Low Sub-Surface Oxygen Events in Narragansett Bay During Summer	2008	2001-2006
URI/GSO, RIDEM-OWR	Narragansett Bay hypoxic Event Characteristics Based on Fixed-site Monitoring Network Time Series: intermittency, geographic distribution, spatial synchronicity, and inter-annual variability	2009	2001-2006
RIDEM-OWR	State of Rhode Island and Providence Plantations Water Monitoring Strategy 2010-2015	2012	2010-2015
NBEP, RIDEM-OWR	Narragansett Bay Watershed Counts 2013 Report	2013	2001-2013
BROWN	Summer-Season survey of dissolved oxygen in upper Narragansett Bay beginning in 2005.	2014	2001-2013
NOAA CHRP Narragansett Bay	Modeling efforts for Hypoxia in Narragansett Bay	2016	2005-2015
NBEP	Status and Trends for Narragansett Bay	2017	2015-2017

6.0 Project Description and Schedule

6.1 Tasks

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

Task 1 NBFSMN: QAPP Preparation/Revision (with approval every five years and annual addendums as necessary)

Table 5.1 includes various studies that have been completed in the Narragansett Bay watershed over the over recent years, highlighting studies that have focused on dissolved oxygen issues. Monitoring efforts have been consolidated to be more effective and efficient in acquiring and distributing data.

During a review of the existing data, the network decided that monitoring efforts are to be collected using similar methodology. As part of the QAPP development/revision, the NBFSMN will review sampling methods and develop or revise standard operating procedures for this program.

The QAPP will be used to guide monitoring efforts and outline the chain of command.

Task 1A NBFSMN: Site Review (yearly)

The monitoring sites and station locations are determined prior to each sampling season. Each agency will designate station locations based on their own research needs and other factors. Other factors that influence the selection of sample sites include accessibility to the site, tidal influences at the site, and receiving water classification. Annually, a review of the sampling stations will take place to identify any data gaps and incorporate the gaps into monitoring strategies. If a change or addition needs to be made, a decision will be determined by consensus and the approval of the project manager as to which station data collected throughout the year will be included in the NBFSMN. Representative station selection will consider factors, such as, data quality, budgeting to run the station, and relevancy to Narragansett Bay. Station selection is also will be determined by the consensus and the approved by the project manager.

Task 2 Site Preparation (yearly)

Prior to the sampling season (buoy deployment or station installation), all site equipment will be prepared for deployment. Since each site uses different equipment, preparation protocols are at the site manager's discretion.

Each site will be responsible for the following preparation activities:

- Replacing old/damaged equipment or ordering new site setups
- Program equipment to meet monitoring SOP (e.g. standard time, 15-min. sampling intervals)
- Setup mooring systems
- Equipment preparations (calibrations, painting, cleaning, etc.)
- Function tests prior to deployment
- Buoy deployment and/or station installation (this can be coordinated through QA Officer)

The QA officer and SOPs provide guidance for site preparation. Equipment needs should be completed at the end of the previous sampling season. Any concerns or suggestions for improvement should be discussed with the QA officers and the project manager.

Task 3 Monitoring (season & year-round)
All stations, with a depth greater than 3 meters, will at a minimum monitor surface and bottom conditions of physical water quality parameters (temperature, salinity, dissolved oxygen, pH, depth, and surface chlorophyll). There are differences between stations on additional parameters due to cost and instrument capabilities. For example, stations equipped with EXOs have the ability to also monitor for chlorophyll at depth if cost effective for the individual agency. Turbidity, although an important parameter, is only collected at the NBC and NBNERR stations because of expense of the sensor.

The sampling period may vary from seasonal to year-round depending upon station location and the site operator's discretion. Routine maintenance will be conducted at each site by lab/field technicians.

Sonde maintenance (including instrument calibrations and field maintenance) will be conducted twice a month for a minimum sampling period of June to October. A longer deployment period may be used when applicable (e.g. winter months when fouling is minimal). Calibration procedures are conducted using the same protocols based on the YSI manual (see appendix B). These procedures were agreed upon by the NBFSMN.

During the sonde swap or field maintenance, all components should be checked and confirmed to be operational. In addition, the tube and sonde supports should be cleaned to remove biofouling. Debris should be cleared from the inside and outside of the tube as well as from any telemetry cables or the floating mechanism (if applicable). Once everything has been cleaned, the new sonde is deployed (Appendix B).

In the field, during the sonde swap process, a three-way *in-situ* match-up is conducted. The new (freshly calibrated) sonde reading will be checked against the old (retrieved) sonde reading and a third reading using a profiler sonde at the same depth. The last reading of the retrieved sonde is compared to the profile results and the first reading of the newly deployed sonde. This three-way comparison assures that the new and old sondes are both reading each parameter within a 90-95% confidence level or within one standard deviation tolerance based on parameters at each station. This triple sonde check also allows for notation on whether the parameters are normal, fluctuating, or stable. All QC data will be documented and provided to the QA officer annually.

For more information and guidance with monitoring, see appendix B and C.

Task 3A Laboratory Analysis (yearly)
Chlorophyll and nutrient samples will be collected whenever possible throughout the field season. Field samples are taken at a minimum during the sonde swaps. If samples are not taken, it should be noted in the field notes. The filtered chlorophyll field samples can be frozen and processed during the year. The designated labs are to report the results to the respective site managers before or during the year-end review period.

Task 4-Year End Review (yearly)
At the end of each field season, the data gathered are processed using QA/QC guidance adapted from the NERRS CDMO manual. Each site is responsible for quality controlling its own data unless otherwise arranged with the project manager. Any problems or concerns about the data processing will be discussed with the QA officer. All data from all stations are gathered by the QA officer for review on an annual basis.

The goal is to have the QA/QC of the data completed during the winter of the following year the data were collected. The data will be available for distribution the following year from when the data were collected. Three forms of the data will be made available (raw data, edited data, and corrected data) and accompanied by a metadata document (document explaining the dataset and changes that have occurred between the three formats). All agencies conduct internal reviews of annual datasets as part of the QA/QC process. MassDEP will conduct an internal review after the NBFSMN QA/QC process is complete for all MassDEP owned sites' datasets and metadata before it is considered finalized. The final validated datasets and metadata from MassDEP owned stations will be published by MassDEP following the end of each deployment season. The final validated datasets and metadata, as published by MassDEP, will additionally be distributed to the public via the NBFSMN website hosted by RIDEM (http://www.dem.ri.gov/programs/emergencyresponse/bart/stations.php).
For more information and guidance with QA/QC procedures see Appendix C.

Task 4A Equipment Assessment (yearly)
Water quality stations are to be assessed on a minimum of a seasonal basis. Buoy stations require replacement of some mooring equipment (such as shackles and line) yearly. Other equipment repairs and replacements are to be conducted during the year-end review. All equipment must be purchased before or during the site preparation task.

Station upgrades, replacements, and repairs are to be discussed with the project manager during the year-end review. The quality assurance officers will provide guidance on equipment assessments.

Task 4b Final Report (yearly)
Each year the site managers will provide the project manager with an annual report of the stations. This report will consist of the formatted raw data, metadata, and edited data (when applicable). The quality assurance officer and the project manager will produce a collective annual report. The collective report will consist of a program metadata file, all forms of the data (raw, edited, & corrected) from all sites, QC data, and each site's metadata document. In addition, the data will be made available for distribution through RIDEM, MASSDEP, NBC, and NBNERR. Each agency will release data to the public at the agency's discretion. RIDEM-OWR will serve as the official NBFSMN data distribution website. The NBFSMN finalized data for a given year will be published publicly through http://www.dem.ri.gov/programs/emergencyresponse/bart/netdata.php

6.2 Project Schedule

Table 6.1 Project Schedule.

Task	Deliverable	Annual Monitoring											
		J	F	M	A	M	J	J	A	S	O	N	D
QAPP Preparation	QAPP Document	■	■	■									
Site Review	Monitoring Plan	■	■	■									
Site Preparation	NA			■	■	■	■						
Monitoring*	NA					■	■	■	■	■	■		
Laboratory Analysis	Laboratory Report										■	■	■
Year End Review	Final Data Report	■	■	■	■	■							

The shaded areas refer to the months these tasks will take place

*Monitoring is minimally collected from May-October, but not limited to this time period. Some stations collected data year-round when weather permissible.

7.0 Project Quality Objectives and Measurement Performance Criteria

Collecting high quality data is one of the most important goals of the network. Specific data quality objectives include precision, accuracy, representation, comparability, and completeness. All the data quality objectives will be met if all the data are collected and managed in a similar fashion.

7.1 Measurement Performance Criteria

Precision

With minor exception (nitrate sensors, every hour), data are collected every 15 minutes using compatible equipment on a bi-monthly servicing schedule, with exceptions based on seasonal biofouling. For the year round stations, from November-April, sampling schedules are monthly since the biofouling is decreased. NBNERR also follows a 3-week deployment schedule from May through October. The stations further up bay experience more biofouling, so a 2-week schedule is needed from May-October. All agencies follow the same procedures for lab calibrations, field sampling, and post deployment checks to ensure precise methodology. This gives the network confidence in the data collected.

Accuracy

The QA/QC methods check the accuracy of the data collected. Field samples are taken with independent instruments to provide quality assurance of the data. This is done through grab samples and a three-point field check of all sensors ensures the accuracy of the data for each deployment.

Representativeness

The selected stations and sampling frequency were chosen for their depiction of conditions in the Narragansett Bay watershed during the summer season. The sampling targets the summer because this is the highest potential for water quality standard violations with respect to dissolved oxygen. The continuous monitoring will measure environmental conditions throughout the season. In addition, real-time connections to the data will be used to minimize the risk of erroneous data caused by instrumentation failures.

Comparability

To maximize the quality of the data collected, and to collect data that are comparable with other studies, accepted sampling procedures will be used during this study. All samples collected will be sent to laboratories that use Standard Methods. Other environmental data (e.g., flow rates, rainfall, weather conditions) will be gathered to support assessments of the water quality monitoring data.

The Project Manager and the QA Officer will study the results of these analyses. If discrepancies exist between the samples, the data will be used with qualifications and discussed in the final report.

Sensitivity

The sensors used are selected to be sensitive enough to measure the expected low-level measurements in Narragansett Bay. The normal ranges for Narragansett Bay are expressed in table 7.1. If sensors do not pass calibration, they are to be troubleshooted and re-calibrated. If they still do not calibrate based on criteria in table 7.1 then the sensors are to be replaced if possible. A sensor not meeting acceptable criteria is not to be deployed. Documentation of all sensor calibrations are to be maintained and archived by the site operator/manager.

Completeness

The monitoring strategy for this program is to have continuous data throughout the most critical times

to assess the hypoxia issue. Measurement performance criteria help determine the completeness of a data set.

Table 7.1 and 7.2 documents the measurement performance criteria for this project. Table 7.1 is based on the YSI sensor calibration criteria. The calibration software (Ecowatch and KOR) are used to calibrate the 6-series and EXO sonde sensors respectively. If a sensor does not pass calibration criteria set by the software, it is not to be deployed. Any changes to a sonde (such as; QA scores or sensor changes) should be documented on the calibration sheets and included in the metadata for the affected site. All sensors that require trouble shooting should also be documented on steps taken in accordance to the respective YSI manual on troubleshooting for sensors and/or sondes.

As for field grab samples, field notes are to be included in metadata documentation and any irregularities noted during the analysis process in the comments section of the data file, so the user is aware of any potential issues with the data analysis. If a sample does not meet performance criteria, it will not be included in the final dataset. All data analysis for CHL will be included in the annual downloadable file. Since there is a lag in the nutrient analysis, this data is available upon request through Laura Reed (MERL nutrient analyst).

Table 7.1 Measurement Performance Criteria for Automated Sensors During Calibration.

Sampling SOP	S-1				**Check/ Calibration Criteria**
Medium/Matrix	Sensor performance				
Parameter	**SOP Reference**	**Sensor Accuracy**	**Reported Resolution**	**Range**	
Temperature (º C)	YSI 6-Series Manual EXO 2-Series Manual	6-Series: +/- 0.15 °C EXO: +/-0.01 °C for-5-35 °C +/-0.05 °C for 35-50°C	6-Series: 0.01 °C EXO: 0.001 °C	-5 to 45 °C EXO -5 to 50 °C Normal Range in Narragansett Bay: -5-30 °C	outside of factory specified limits Function check within 0.5°C of lab NIST thermometer
Specific Conductivity (mS/cm); Salinity (ppt)	YSI 6-Series Manual EXO 2-Series Manual	6-Series: +/- 0.5% of reading + 0.001 mS/cm or +/- 0-1.0% of reading EXO: 0-100mS/cm: +/-0.5% of reading or +/- 0.001 mS/cm, whichever is > 100-200 mS/cm +/- 1% of the reading 0.1 ppt	6-Series: +/- 0.001 mS/cm to 0.1 mS/cm EXO: 0.0001 to 0.01 mS/cm range-dependent 6-Series: 0.01ppt EXO: 0.01 ppt	0-100 mS/cm or 0-70 ppt EXO 0 to 200 mS/cm Normal Range in Narragansett Bay: 0-52 mS/cm 0-70 ppt Normal range in Narragansett Bay 0-34 ppt	Cond constant: An ideal cell constant for the wiped conductivity sensor is 0.47 ± 0.1 6-series: 5.1±0.2 (sensor is calibrated using SpC standard)
Depth (Pressure)(m)	YSI 6-Series Manual EXO 2-Series Manual	6-Series: +/- 0.06 ft (0.018 m) EXO: +/-0.013ft (0.004m) for 0-33ft +/-0.13ft (0.04m) for 0-328ft	0.001 ft (0.001 m)	0-100 ft (0-38.5m) EXO 0-328ft (0-100m) (Max depth at stations 14m)	Non vented outside of factory specified limits (+/- 0.1m at zero air calibration)
Dissolved Oxygen (%, mg/L)	YSI 6-Series Manual EXO 2-Series Manual	6-Series: 0-200% +/- 2% of reading or air saturation EXO: 0-200% +/- 1% of reading or air saturation	0.1% air saturation	A0-500% Normal Range in Narragansett Bay 0-300%	DO gain range: based on a gain factor, relates to the magnitude of coefficient change (0.87-1.25)
Total Chlorophyll (BGA-PE) (µg/L)	YSI 6-Series Manual/ MERL CHL analysis / NBC CHL analysis	6600: +/- 4 ug/L EXO: +/- 4 ug/L	0.1 µg/L; 0.1% FS	S/A0-400 µg/L; 0-100% FS	Full scale: 0-500 ug/L +/- 4 µg/L of cal solution (di water=0)
Turbidity EXO – FSU	EXO 2-Series Manual	EXO: +/-2% of reading or 0.3NTU	EXO: 0.01 FNU	EXO 0-4000 FNU 0-200 normal range	Full scale: 0-1000 µg/L +/-4 NTU (6-series)
pH	YSI 6-Series Manual EXO 2-Series Manual	+/- 0.2 units	0.01 units	0 to 14 units 6-9.5 normal range	pH mvolt range: pH 7-10: 180 mV +/- 40mV
Nitrate-Nitrogen (mg/L)	SUNA Manual SUNA V2	10mm pathlength: +/- 2µm (0.028mgN/L)	2.4µM (0.034 mgN/L)	2-3000 µM Normal Range in Narragansett Bay: 0-40 µM	10mm pathlength: +/- 2µm

Table 7.2 Measurement Performance Criteria for Grab Samples.

Sampling SOP	S-2 and S-8	
Medium/Matrix	Sensor	

Parameter	**SOP Reference**	**Precision**	**MDL/IDL**	**Sample Accuracy**	**Ranges**	**Instrument Accuracy**
Chlorophyll *a* MERL	SOP 2	Value reported must be +/– 10% of Certificate of Analysis values	Instrument Detection Limit (IDL) 0.02µg/L	Duplicate samples ≤15% RPD	The RPD for phaeophytin a might typically range from 10% to 50%. Normal Range for CHL*a* in Narragansett Bay: 0-500 µg/L	If the SRM value is greater than 5% different from nominal, then the instrument must be recalibrated as described in Section 3.1.
Chlorophyll *a* (NBC)	SOP 2-B	Value reported must be +/– 10% of Certificate of Analysis values.	Instrument Detection Limit (IDL) 0.02µg/L	Duplicate samples within +/–10%.	Over range results If the RFU units for the pre-acidification >167000, the sample is higher than that of the highest cal standard. (100µg/L)	Low concentration and high concentration second source standards to be run after calibration and annually. % RPD must be +/–10% of true value.
Total Nitrogen	SOP 8	± 0.1 µM at 10 µM level ± 0.3 µM at 60 µM level	MDL: 0.45 µM	Duplicate samples ≤15% RPD	Normal Range in Narragansett Bay 0-80 µM	R^2 within +/- 10%
Total Phosphate	SOP 8	± 0.04 µM at 1 µM level	MDL: 0.06 µM	Duplicate samples ≤15% RPD	Normal range in Narragansett Bay 0-12 µM	R^2 within +/- 10%
Dissolved Inorganic Nutrients (µMol)	SOP 8	NO3+NO2 = ±0.10 PO4 = ± 0.3 SiO2=± 0.1 NH3= ± 0.1 NO2 = ± 0.1	NO3+NO2 = 0.10 PO4 = 0.05 SiO2 = 0.07 NH3= 0.05 NO2 = 0.02	Duplicate samples ≤15% RPD	Normal Range NB: NO3+NO2 = 0-40 µM PO4 = 0-8 µM SiO2 = 0-100 µM	R^2 within +/- 10%

8.0 Sampling Process Design

8.1 Sampling Design Rationale

Task 1A Real Time Continuous Monitoring

Task 1 outlined in Section 6.2 describes the process for deciding sampling stations. Stations were chosen based on existing information and the need for real-time data by managers and users throughout the monitoring season. To aid in choosing stations, sources were ranked based on monitoring importance to the watershed. Detailed information for each location is found in Table A.2 in Appendix
A. Tables A.2 and A.3 in Appendix A describe the exact location and monitoring protocol for each station. In general, continuous monitoring will occur during the summer months.

Task 1B Chlorophyll Monitoring: Measuring Total Chlorophyll

Table A.3 documents the monitoring protocol for sampling. At all locations, chlorophyll readings will be taken on a continuous basis using the YSI 6-Series and EXO sondes measuring total chlorophyll (YSI, 2011 and YSI, 2019). Total chlorophyll is in various forms and is bound within living cells of photosynthetic organisms, such as phytoplankton and cyanobacteria (blue-green algae). The amount of chlorophyll found in a water sample is used as a measure of the concentration of phytoplankton. These measurements contribute to the understanding of the general biological "health" of the system, such as its trophic status or primary production. Chlorophyll measurements can also identify algal bloom events and their effects on water quality, as well as anticipate toxic algal blooms (YSI, 2011).

Chlorophyll fluoresces when irradiated with light of a particular wavelength (435-470 nm). For field measurements, *in-situ* fluorometers induce chlorophyll to fluoresce by shining a beam of light of the proper wavelength into the water and then measuring the higher wavelength light which is emitted. These real-time chlorophyll measurements complement extractive lab analysis (YSI, 2011).

Field grab samples are collected at each station and are analyzed using the agency's CHL*a* extraction method. These methods can be found in SOP 2 and SOP 2B. Ideally, the water samples will be taken on the same interval as the sonde swaps for quality assurance purposes (generally, twice a month during May-October). Based on the MERL procedure for example, the field technician will collect water in a 125ml sample bottle (1000ml, NBC method) and filter each 10ml sample within a 4-hour holding time limit in accordance to standard operation procedures (S-2). Three 10 ml (60-100ml, NBC method) replicates (2 replicates, NBC method) will be completed for each site. If samples cannot be filtered in the lab within 4 hours, the samples will be filtered and preserved in the field using a 10-ml syringe. Each filter will be stored individually in a labelled foil packet on ice until it can be frozen at the lab for later analysis. The field notes will include documentation for each sample, including the depth and time at which the sample was taken and filtered. The chlorophyll analysis information will be documented and provided with the annual dataset. MERL Laboratory will use the referenced method to analyze all chlorophyll samples (S-2). Table 8.1 contains information about sampling and analysis methods. Since total chlorophyll can be higher than the extracted CHL*a* samples, regressions can be performed to assess relationship between the sonde data and analyzed samples at the data user's discretion. NBFSMN does not provide this information in the public accessible dataset. The NBFSMN will, however, provide the total chlorophyll data from the sondes and the field grab samples of CHL*a* and distribute this information in the annual dataset report through the NBFSMN website (http://www.dem.ri.gov/programs/emergencyresponse/bart/stations.php).

Table 8.1 Sampling and Analysis Method/SOP Requirements for water samples.

Lab	Med./ Matrix	Depth	Analytic	SOP		Container			Container		Holding
			Paramete	Sampling	Analytical	No.	Size	Type	Requirements	Temperature	Time
MERL NBC	Surface Water	1m or Sonde depth	CHL *a*	S-2	S-2	3	10-125 ml	Brown Bottle or Field Filtration	Ice	4°C	4 Hours

Task 1C Nitrate Monitoring: Measuring Nitrate-Nitrogen

Table A.2 documents the monitoring protocol for sampling. At 4 locations (2 land-based stations (GD, GB) and 2 buoy locations (CR, TR) (MassDEP buoys), nitrate readings will be taken on a continuous hourly basis using SUNA V2 Nitrate Sensor. The sensor will be tested monthly using a clean DI water sample. The instrument will be reference checked according to SOP S-8. If the sensor does not meet the acceptance criteria (+/- 2 µmol in DI water), a reference update will be conducted according to the SUNA manual.

Water samples will also be collected for nutrients (dissolved inorganic nutrients (NO3+NO2, PO4, NH3, SiO2, NO2), total nitrogen, total phosphate) analysis every two weeks during the field season at NBFSMN locations equipped with SUNA sensors (GSO, GD, CR, and TR). Ideally, the water samples will be taken on the same interval as the sonde swaps for quality assurance purposes. The field technician will collect water for total nitrogen, total phosphorus, and dissolved inorganic nutrient samples. Dissolved inorganic nutrient samples are filtered within a holding time limit in accordance to standard operation procedures (S- 8). Documentation of the sample collection information is to be included in the field notes. The nutrient analysis information will be documented in the metadata. MERL Laboratory will use a standardized method to analyze all nutrient samples. Table 8.1B contains information about sampling and analysis methods.

Table 8.1B Sampling and Analysis Method/SOP Requirements for Nutrient Samples

Lab	Med./ Matrix	Depth	Analytic	SOP		Container			Container		Holding
			Parameter	Sampl	Analytical	No.	Size	Type	Requirements	Temperature	Time
MERL NBC	Surface Water	1 meter	nutrients	S-8	S-8	1	10-125 ml	Brown Bottle	Ice	4°C	6 Hours

Task 2 Narragansett Bay Fixed-Station Water Quality Monitoring Sites

Table 8.2 Buoy Station Selection

Station	Year data Added to Network	Justification for Adding Station	Ownership
Phillipsdale (PD)	2004	Representative of Seekonk River	NBC
Bullock's Reach (BR)	2001	Representative of Providence River (PVD)	NBC
Conimicut Point (CP)	2003	Representative of Upper Bay and mouth of PVD River	RIDEM
Upper Bay (UB)	2008	Winter representation Upper Bay	RIDEM
North Prudence (NP)	2001	Representative of Upper Bay	RIDEM
Mount View (MV)	2004	Representative of upper West Passage	RIDEM
Quonset Point (QP)	2005	Representative of mid-West Passage	RIDEM
GSO Dock (GD)	2005	Representative of lower West Passage	URI/GSO
Poppasquash Point (PP)	2005	Representative of upper East Passage	RIDEM
Mount Hope Bay (MH)	2005	Representative of Mt Hope Bay proper	RIDEM
Taunton River (TR)	2017	Representative of Upper Mt Hope Bay at mouth of Taunton river (near power plant)	MASSDEP
Cole River (CR)	2017	Representative of Upper Mt Hope Bay	MASSDEP
T Wharf (TW)	2005	Representative of Mid-East Passage	NBNERR
Greenwich Bay (GB)	2003	Representative of western Greenwich Bay	RIDEM
Sally Rock (SR)	2008	Representative of mid Greenwich Bay	RIDEM

9.0 Sampling Procedures and Requirements

9.1 Sampling Procedures

Standard operating procedures (SOP) for field sampling are in Attachment A of this report.

Table 9.1 Project Sampling SOP Reference Table.

Reference Number /Title	Originating Organization	Equipment Identification	Modified for Work	Comments
Field Sampling SOP 1 (S-1) Calibration Procedures	RIDEM-OWR	YSI 6-Series Sondes and EXO	No	
Field Sampling SOP 2 (S-2) CHL Sampling Procedures	URI/GSO-MERL	Non-applicable	No	
Field Sampling SOP 2 (S-2b) CHL Sampling Procedures	NBC	Non-applicable	No	
Field Sampling SOP 3 (S-3) Sonde Swap Protocols	RIDEM-OWR	YSI 6-Series Sondes	Yes	Modified from CDMO manual
Field Sampling SOP 4 (S-4) QA/QC Procedures	RIDEM-OWR	Non-applicable	Yes	Modified from CDMO manual
DCP communications and programming Guidance SOP-5 (S-	YSI/other	Manuals: YSI 6200/Campbell Scientific/Loggernet/Nexsen	No	Custom to each site
Station Preparation Guide SOP-6 (S-6)	URI/GSO	Buoy Manuals	No	Custom to each site
SUNA Preparation Guide SOP-7 (S-7)	URI/GSO MassDEP	SUNA V2 (SUNA manual)	No	
Field Sampling SOP 2 (S-8) Nutrients Sampling Procedures	URI/GSO-MERL	Non-applicable	No	

9.2 Equipment Cleaning

All, seasonally deployed, station equipment will be cleaned and tested for functionality prior to deployment. Equipment can be prepped with anti-fouling agents to reduce damage during deployment.

Equipment, maintained throughout the season, is to be cleaned after post-calibration checks. During each sonde swap, field technicians are to inspect all station equipment. Field technicians are responsible for keeping the critical components clean and operational throughout the sampling season.

9.3 Field Equipment Calibration and Maintenance

The site operator will ensure that all field equipment is operating properly. Table 9.3 provides details to which calibration procedures are followed in the manufacture's manual.

Table 9.2 Field Sampling Equipment Calibration Table.

Equipment	Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	SOP Reference
YSI 6-Series Sondes*	Calibration	Bi-Monthly to Monthly	In accordance to the YSI Manual for each Parameter	Send to Factory	S-1
YSI DCP and communications electronics	Program	Before Sampling Season	Functionality, 15 min sampling rate	Send to Factory	S-5
YSI EXO-Sondes*	Calibration	Bi-Monthly to Monthly	In accordance to the YSI Manual for each Parameter	Send to Factory	S-1B

Table 9.3 YSI and SUNA Equipment Calibration Table.

Parameter	YSI Instrument Type/Sensor	Calibration Procedure	CalibrationSolutions	Frequency	SOP
DO	EXO Optical DO 6 series optical	ODO % Sat	Bubbling tap water at air saturation	Every 2 weeks	S-1 6-series manual 5-10 EXO manual 4.12
Salinity	EXO Wiped C/T 6-series optical	SpC	50,000 µS/cm	Every 2 weeks	S-1 6-series manual 5-2 EXO manual 4.6
pH	EXO Wiped pH 6 series pH (flat glass and guarded)	2 point	7 and 10 pH units	Every 2 weeks	S-1 6-series manual 5-4 EXO manual 4.19
Total CHL	EXO TAL-PE	1 point 2 point*	DI water 0.625 mg/L Rhodamine*	Every 2 weeks	S-1 EXO manual 4.22
BGA (phycoerythrin)	EXO TAL-PE	1 point	DI water	Every 2 weeks	S-1 EXO manual 4.22
Turbidity	EXO Optical turbidity	2 point	DI water and 126 NTU (124 FNU) solution	Every 2 weeks	S-1 EXO manual 4.24
SUNA V2	SUNA V2 nitrate sensor	1 point	DI water	monthly	S-2

*Is preferred option if cost effective and individual agency can dispose of hazardous waste. Metadata will specify method used. Two-point calibration method with rhodamine is in testing phase as of 2020.

Each lab (MERL, NBC, and NBNERR) calibrates it instrumentation based on YSI procedures since a mix of YSI instrumentation is used, references for the SOPs can be found in designated manufacture manuals. These procedures in the manuals are followed for calibration procedures based on instrumentation and sensors used. Calibrations are conducted a day or two prior to deployment. If a sensor does not pass calibration, it is not to be deployed. All calibration notes are included in the metadata for each site annually.

The SUNA V2 sensors are checked in the field with DI water on a monthly basis, since swapping intruments in not available. Therefore, seasonally, the SUNA V2 sensors are checked pre and post season using 0, 15, and 30 umol solutions for a reference check. These sensors are manufacture calibrated on a bi-annual (every 2 seasons) basis.

Table 9.4 Field Equipment Maintenance, Testing, and Inspection Table.

Equipment	**Activity**	**Frequency**	**Acceptance Criteria**	**Corrective Action**	**SOP Reference**
Station Preparation	Clean, Paint, Test	Once before sampling season or as needed	Visibly free of debris, new hardware when necessary	Send to factory	S-6
Profile	Profile	Bi-monthly to monthly	Within 90% of field equipment	Data notation and flag if necessary	S-3
CHL and Nutrient Sampling	Filter Water Sample	Bi-monthly to monthly	Within 90% of field equipment	Data deletion/ notation	S-2

10.0 DATA MANAGEMENT, QA/QC, AND DOCUMENTATION

10.1 Data Management

Task 1 Calibration Protocols

All agencies will maintain records of calibration, deployment, and post-deployment readings to provide the necessary information for data QA/QC procedures and help identify faulty equipment. At the completion of sampling season, all log sheets, files, and notebooks will be made available to the project manager upon request.

Specifically, protocols will follow the **National Estuarine Research Reserve System-Wide Monitoring Program (SWMP) and/or the YSI EXO/6-Series Multi-Parameter Water Quality Monitor Standard Operating Procedures (V6.6, 2015)** in conjunction with all appropriate manufacturer equipment manuals. These manuals are included in this document (see B and C) or through request to the quality assurance officer.

Task 2 Field Protocols

These procedures consist of assessment of the station; sonde swap, water column profiling, and collecting grab water samples. All technicians must record field notes every time a station is visited. Field notes at a minimum should include date, time, visit reason, what was conducted, weather condition, problems, and resolutions. The SOP for this task may vary from site to site based on site setup (e.g. real-time, data loggers, etc.). Therefore, the SOP-3 is to be used as a guide. Weather conditions and time constraints may require field protocols to be modified. If modified, any changes will be documented in the field notes.

Task 2A Chlorophyll Collection and Analysis Protocols

At all locations, chlorophyll readings will be taken on a continuous basis using the YSI EXO/6-Series sondes. In addition, water samples will be collected for chlorophyll analysis whenever possible. Ideally, the water samples will be taken on the same interval as the sonde swaps for quality assurance purposes. The field technician will collect water and filter within a 4-hour holding time limit in accordance to standard operation procedures (SOP-2).

Chlorophyll and other nutrient samples will be collected throughout the field season as determined by the NBFSMN. The chlorophyll field sample filters can be frozen and processed during the end of the year review. The designated labs are to report the results to the respective site managers before or during the year-end review period.

Task 3 Nitrate Sampling Collection, Grab samples, and Analysis Protocols

The sites with Seabird (*Satlantic*) SUNA V2 nitrate sensors will take readings on an hourly basis continuously during site operations. Each SUNA V2 will be serviced twice a month. The instrument will be examined and cleaned during the service. Wipers will be cleaned and replaced as necessary. On a monthly minimum, instruments will be checked against deionized water sample (SOP-7) in the field for calibration integrity. If over calibration threshold (+/- 2 µmol), an instrument calibration will be conducted as described in the SUNA manual (Seabird). Field notes will be taken to document changes to calibration files on the instrument and field samples will be taken. All notes will be provided to QA officer annually.

Field samples for QA/QC will be collected at the same depth as the SUNAV2 sensor twice a month. The field technician will collect water and filter within a 4-hour holding time limit in accordance to standard operation procedures (SOP-2). The samples will be frozen until processed by the MERL.

10.2 Verification

Task 1 QA/QC Measures

The QA/QC management of water quality data consists of the following components:

(1) Data acquisition and visual inspection of the data in compatible programs.
(2) Pre-processing of the raw file into Excel. Insert station code columns, correct the time format, verify the units and format the headers. The file configuration verifies values using *R*, *Streamline*, a CDMO developed Excel macro or EQWinformat.xls (these are all network approved data processing software).
(3) Data validation of the file in EQWin or Excel using data checks, queries, reports and graphs.
(4) Data archival on a separate computer, hard drive, and to the local network.
(5) Data editing to remove errors, outliers, out of water data, pre- and post-deployment data in Excel.
(6) Data correcting to replace calibration errors, fouling, and outliers with linearly calculated values.
(7) Data documentation (metadata) to explain all suspect, deleted, calculated, and missing data.
(8) Data submission to the project manager of the yearly data.

Data editing and review procedure will follow the **YSI 6-Series Data Review and Editing Protocol** (Appendix C of the NERRS CDMO Operations Manual, see attached).

10.3 Documentation

Task 1 Metadata Documentation

Metadata explains all aspects of the data from the research objectives to the data QA/QC and should be created as each dataset is processed. The metadata documentation is based on Chapter 6 of the NERRS CDMO manual (see Appendix C).

Each site manager is responsible for including the following sections in each station's metadata document:

1) Associated researchers and projects (link to other products or programs) **-** Describe briefly other research (data collection) that highlights the NBFSMN.
2) Data collection period - Include each YSI deployment and retrieval date and time (**first** and **last** readings in the water) for each monitoring site for the year.
3) Coded variable definitions – Explain the five-letter sampling site code.
4) Anomalous/Suspect Data - This section should explain in detail all data that were retained but are considered suspect or anomalous. List the exact dates, times, and variables that are considered suspect and why. Anomalous data should be left in the data file when you have no factual reason to delete them (even though the data look suspicious) and note them as suspect data in this section. These data will be highlighted in light yellow in edited and corrected files only.
5) Deleted Data – Data are deleted in the edited and corrected files only. This section should explain in detail all data that were collected but deleted from the record. List the exact dates, times, and variables that were removed and justification for deletion. Deleted data will be in edited and corrected files (if applicable) only.
6) Corrected Data. This section should explain in detail all data that were corrected from the raw data file record. Corrected data will only be in the corrected file. In the metadata, all calculated data will be listed with an explanation of calculation method used. All calculated data are in bold and highlighted in the corrected file. The metadata will list the dates, times, time periods and variables that were

adjusted and how. This section should include data correction methods used (e.g. calibration error corrections, linear calculations, and/or fouling correction applied to data).
7) Missing data - This section will incorporate the use of a blanket statement for data that were never collected (missing data).
8) Time adjustments-This section is to include any variation to the sampling schedule (every 15 minutes on the quarter hour using local standard time, LST).
9) Post deployment information - Use this section for documentation of post calibration information for instruments deployed at each site.
10) Other remarks/field notes - Use this section for further documentation of the research data set. Include information on localized weather events (dates and amounts of rain, major storms or weather patterns affecting the area, etc.) that may have affected data recorded at the sites.

The QA officer is responsible for providing a comprehensive metadata document including all agency contacts, data referencing/ownership, distribution, sensor specifications, site descriptions, research methods, and research objectives. All metadata documentation will be distributed with the annual data report file through the NBFSMN network (http://www.dem.ri.gov/programs/emergencyresponse/bart/stations.php).

Task 2 Raw Files

Raw files are the data without any QA/QC requirements applied (no edits, deletions, or corrections applied). These are the direct files from the instruments and are generally in a comma separated values (csv) format. The raw data will be included in each site's final annual report. The raw files are formatted according to the **YSI 6- and EXO Series Data Reporting.** The raw files will contain all field data collected by each parameter during each deployment and will be labelled according to agency, site, and deployment date. For further details on formatting see Appendix C.

SUNA raw data files will be unaltered data from the real-time data reporting and saved as a comma separated values (csv) file.

Task 3 Edited files

Edited files will be included in each site's final report. The edited files are formatted according to the **Data Review and Editing Protocol.** The edited files will contain the QA data including data deletions. The edited dataset will be labeled according to station code and year collected. Edited data are in seasonal/annual format using Excel. For further details on formatting see Appendix C.

All SUNA data that are considered erroneous or suspect will be deleted and documented in the metadata document. The edited files will contain only the QA data. All time stamps will be accounted for, therefore deleted data will have blanks during the appropriate time stamp. Edited data are in seasonal/annual format using Excel. The edited SUNA data will be a worksheet within the edited Excel file for the instrument's site (GB, GD, TR, and CR).

Task 4 Corrected files

Corrected files will be included in each site's final report. The corrected files are formatted according to the **Data Review and Editing Protocol.** The corrected files will contain the QA data including data calculations and a column for combined date and time. The corrected dataset will be labeled according to station code and year collected. Corrected data are in a seasonal/annual format using Excel including graphics. For further details on formatting see Appendix C.

All SUNA data that are considered erroneous will be deleted, corrected where applicable, and documented in the metadata document. The corrected files will contain only the QA data and calculated values. All calculated values will be in bold and highlighted. All time stamps will be accounted for, therefore deleted data will have calculated values during the appropriate time stamp. Corrected data are in seasonal/annual format using Excel. The corrected SUNA data will be a worksheet within the corrected excel file for the instrument's site (GB, GD, TR, and CR).

11.0 Fixed Laboratory Analytical Method Requirements

Chlorophyll *a* (CHL*a*) samples will be taken from each water quality monitoring station at every sonde swap, if possible. If not taken, it will be documented why sampling was missed. Nutrients (Dissolved inorganic nutrients (NO3+NO2, PO4, NH3, SiO2, NO2), Total Nitrogen, Total Phosphate) samples are taken at select stations (GB, GD, TR, CR) where nutrient sensors are used. Nutrients are taken at a one-meter depth, so it can be used as quality assurance measurement against the SUNA nitrate sensor that is also mounted at 1 meter below the surface. Sampling schedule is based on the maintenance schedule for each station (generally, bi-monthly to monthly). All samples, CHL*a*, TN, TP and DIN, will be frozen until analysis can be conducted.

The samples will be analyzed at MERL at URI/GSO in Narragansett, Rhode Island or other certified laboratories, such as NBC or MassDEP. These samples will be analyzed using the referenced methods. The data from the chlorophyll analysis are to be used as a quality assurance/correlation measure for the YSI total chlorophyll sensor. The data from the nutrient analyses will be used as a quality assurance measurement against the SUNA nitrate sensor. SOP 2 and SOP 8 describes the standard operating procedures for MERL Laboratory for both chlorophyll *a* and nutrients, respectively. NBC conducts their own laboratory analysis. The SOP for chlorophyll *a* is described in S-2B.

Table 11.1 Fixed Laboratory Analytical Method/SOP Reference Table.

Reference Number	Fixed Laboratory Performing Analysis	Title	Definitive or Screening Data	Analytical Parameter	Instrument	Modified for Work Project
S-2	MERL	MERL Laboratory CHL-*a* Method for Detection of CHL-*a*	Definitive	CHL-*a*	NA	N
S-2B	NBC	Narragansett Bay Commission (NBC) Standard Operating Procedures for Nutrients, Chlorophyll, and Total Suspended Solids Sample Collection in the Bay and Freshwater Rivers	Definitive	CHL-*a*	NA	N
S-8	MERL	Nutrient Sampling MERL Methods QA/QC	Definitive	NO3+NO2, PO4, SiO2, NH3, NO2, TN, TP	NA	N

12.0 Quality Control Requirements

Table 12.1 Field Sampling QC: Sonde Swap.

Sampling SOP	S-1, S-1B					
Medium/ Matrix	Surface Water					
Analytical Parameter	Temp, Sal, DO, pH, CHL					
Analytical Method/ SOP Reference	S-4					
QC	**Frequency/ Number**					
	15-min sampling	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
		L-1	Discuss any problems in the field with sampler.	Site Manager	Precision	Within 95% confidence interval or 1 std. dev. between sondes at swap

Table 12.2 Fixed Laboratories Analytical QC: Chlorophyll *a* at MERL Laboratory and NBC Laboratory

Sampling SOP	S-2, S-2B					
Medium/ Matrix	Surface Water					
Analytical Parameter	CHL *a* (µg/L)					
Analytical Method/ SOP Reference	Reference Method					
QC	**Frequency/ Number**					
Method Blank	1 Per Batch	**Method/SOP QC Acceptance**	**Corrective Action**	**Person Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Reagent Blank	1 Per Batch	L-1	Re-prepare Batch	MERL/NBC Staff	Bias- Contamination	RPD exceeds 15% for samples

Table 12.3 Fixed Laboratories Analytical QC: Nutrients at MERL Laboratory and NBC Laboratory

Sampling SOP	S-2B, S-8
Medium/ Matrix	Surface Water
Analytical Parameter	TN, TP, Dissolved Inorganic Nutrients (NO3+NO2, PO4, NH3, SiO2, NO2)
Analytical Method/ SOP Reference	Reference Method
QC	**Frequency/ Number**

Method Blank	4-6 per analysis day	**Method/ SOP QC Acceptance Limits**	**Corrective Action**	**Person Responsible for Corrective**	**Data Quality Indicator**	**Measurement Performance Criteria**
Reagent Blank	4-6 per analysis day	L-1	Re-prepare Batch	MERL Staff	Bias-Contamination	Within +/- 10% of sample duplicates

Table 12.4 Data QA/QC Measures

Sampling SOP	QA/QC				
Medium/Matrix	Sensor performance				
Parameter	**SOP Reference**	**Resolution Reported**	**Operational and Normal Range**	**Acceptance Criteria**	**QA/QC Flag Criteria**
Temperature (º C)	YSI 6-Series Manual EXO 2-Series Manual	0.01 °C EXO 0.001 °C	-5 to 45 °C Normal Range in Narragansett Bay: -5-30 °C	Within confidence interval of 1 std. dev. between sondes at swap	Surface temp below bottom temperature, outside the normal range
Salinity (ppt), Specific Conductivity (mS/cm)	YSI 6-Series Manual EXO 2-Series Manual	6-Series 0.01ppt EXO 0.01 ppt	0-70 ppt Normal range in Narragansett Bay 0-34 ppt	Cond Constant: Within 95% confidence interval or 1 std. dev. between sondes at swap	Bottom salinity below surface salinity Surface salinity above the bottom salinity
Depth (m)	YSI 6-Series Manual EXO 2-Series Manual	0.001 ft (0.001 m)	0-100 ft (0 Max depth at stations (14m)	Within 1 std. dev.between sondes at swap	Graphic interpretation not following cyclical pattern, Any depth at/or near 0
Dissolved Oxygen (%, mg/L)	YSI 6-Series Manual EXO 2-Series Manual	0.1% air saturation	A0-500% Normal Range in Narragansett Bay 0-300%	1 std. dev. between sondes at swap	Data spikes/drift not followed by other parameters
Chlorophyll (µg/L)	YSI 6-Series Manual/ MERL CHL analysis /	0.1 ug/L; 0.1% FS	Full scale: 0-500 µg/L	Within 1 std. dev. between sondes at swap	Nearest neighbor rule: 2 std. dev. flag
Turbidity EXO – FSU	EXO 2-Series Manual	EXO 0.1 FNU	EXO 0-4000 FNU 0-50 normal range	Within 1 std. dev. between sondes at swap	Nearest neighbor rule: 2 std. dev. flag
pH	YSI 6-Series Manual EXO 2-Series Manual	0.01 units	0 to 14 units 6.5-9.5 normal range	Within 1 std. dev. between sondes at swap	Data spikes/drift not followed by other parameters

13.0 Data Acquisition Requirements

Narragansett Bay watershed has been studied over the past decade by NBFSMN. This information can be used to better understand weather and circulation factors related to low dissolved oxygen. Table A.1 contains information about the stations monitored throughout the bay. These data are used in analysis only and are not required to be part of the annual data report.

In addition, NBFSMN will use other information to support the study's findings. Weather, tides, and flow data are among the some of the continuous data collected. Rainfall and other weather information are from the National Weather Service. The Providence station is located at T.F. Green Airport in Warwick, Rhode Island. The airport is located within both the Greenwich Bay and Pawtuxet River watersheds. Table 14.1 summarizes non-direct measurements used by NBFSMN.

Table 13.1 Non-Direct Measurements Information and Limitations.

Non-Direct Measurement (Secondary Data)	Data Source	Data Generator	How Data Will Be Used	Limitations on Data Use
Rainfall	http://water.weather.gov/precip/	National Weather Service (NWS)	Quantify amount of rainfall received in watershed.	N/A
Flow Data	http://waterdata.usgs.gov/nwis/rt	Unites States Geological Survey (USGS)	Quantify amount of flow entering selected rivers (e.g., Providence River)	N/A
Tidal Data, Weather Data	www.http://tidesandcurrents.noaa.gov/	National Ocean and Atmospheric Association (NOAA)	Supplemental information for data interpretation	N/A

14.0 Documentation, Records, and Data Management

The Project Manager is responsible for the storage of all project files. RIDEM-OWR has a central filing system at its Providence Office where a copy of all documents will be kept. Each site manager can store original files at their discretion. A copy of all data will be kept indefinitely by each agency.

Table 14.1 Project Documentation and Records.

Sample Collection Records	Analysis Records	Data Assessment Records
Field Notes/Cal Sheets	Field Notes/Cal Sheets	Status Reports
Website Updates	Metadata	Annual Data Report

15.0 Assessments and Response Actions

The Project Manager or designee will be responsible for each of the project tasks and their associated quality assurance and quality control procedures. The Site Managers and QA officer will oversee consistency between sampling events and sampling teams. Continual reports to the QA Officer about the status of sampling, quality assurance, and quality control will highlight any problems that are encountered during sampling. If needed, the QA Officer and Project Manager will halt sampling until problems are remedied.

16.0 QA Management Reports

Table 17.1 lists the QA Management Reports that will be generated throughout this study.

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

Each week, the QA Officers will generate a general water quality status report. This status report will be posted on the RIDEM-BART website (http://www.dem.ri.gov/programs/emergencyresponse/bart/latest.php). The report will include a summary of the data interpretation of the critical stations. The QA Officers will also post graphics of the raw data from the critical stations to the RIDEM-BART website for public use.

At the completion of the field season, the QA Officer will write a final report summarizing the sampling season. In addition, the raw, edited, and corrected data will be available for public and network member distribution through the RIDEM-OWR. Information in this final report will include the following information:

- Brief description of the findings during the sampling event
- Data tables of all data collected during the sampling season
- Website Annual Attachments:
  - Project and site description document
  - Metadata document for each station
  - Raw data files from each station (csv files)
  - Edited data files from each station (Excel with graphics)
  - Corrected data files from each station (Excel with graphics)

Table 16.1 QA Management Reports.

Type of Report	Frequency	Person(s) Responsible for	Report Recipient
Verbal Status Report	As needed	NBFSMN	Heather Stoffel RIDEM
Written Status Report	Weekly- (May-Oct)	Heather Stoffel RIDEM/URI-GSO	RIDEM-BART website
Web-site Graphic Reports	As needed	Heather Stoffel RIDEM/URI-GSO	RIDEM-BART website
Final Annual Data and Metadata Report	Annually	Heather Stoffel RIDEM	RIDEM-BART website
Final annual Data and Metadata Report (TR and CR only)	Annually	Heather Stoffel URI-GSO	Richard Chase, Richard Carey MassDEP

17.0 Verification and Validation Requirements

Both the Site Manager and the QA Officer will review all data collected during this study to determine if the data meet QAPP Objectives. Decisions to qualify or reject data will be made by the Site Manager and QA Officer. To ensure quality control, all data collected will be included in the final annual report. The report includes metadata of the network, individual site metadata, raw data collected by deployment by station, edited files, and corrected files by station. To ensure correct interpretation of the data, all problems encountered in the field will be included in an individual metadata site report and discussed in the general text of the final annual metadata report. To assist in data interpretation, statistical information on sampling events, including sampling size, sample mean, and sample variance, will be reported, where applicable.

18.0 Verification and Validation Procedures

Once the data have been collected, they will be entered into Microsoft Excel files (raw, edited, and corrected). The site manager will proofread the data entry for errors. All data will be documented through individual site metadata. Suspect and erroneous data and inconsistencies will be flagged and documented for further review with the QA Officer. The decision to discard data will be made by the site managers and QA Officer. Deletion and correction of data are conducted only in the edited and corrected files, respectively. All changes to original or raw dataset will be documented in the final annual site metadata report. Table 19.1 discusses the data verification process.

Table 18.1 Data Verification Process.

Verification Task	Description	I/E	Responsible for Verification
Field Notes	Field notes will be collected during each station maintenance procedure.	I/E	Site Field Technician
Post-calibration	Test the validity of the field data throughout the deployment period	I/E	Site Lab Technician
Laboratory Data	CHL data will be verified in accordance with SOP	E	MERL, NBC

Data validation will utilize the measurement performance criteria documented in Tables 7.1, 12.1, and 12.2 of this report.

19.0 Data Usability/Reconciliation with Project Quality Objectives

As soon as possible after each sampling season, calculations and determinations for precision, completeness, and accuracy will be made and corrective action implemented if needed. If data quality indicators meet those measurement performance criteria documented throughout this QA Plan, the project will be considered a success. If there are data that do not meet the measurement performance criteria established in this QA Plan, the data may be discarded in the edited files and corrected where possible in the corrected files, or the data may be used with stipulations written about its accuracy in the metadata. The cause of the error will be evaluated. Any limitations with the data will be documented in the final annual metadata report.

References

Bergondo, D., Kester, D.R., Stoffel, H.E., Woods, W.L., 2005. Time series observations during the low sub-surface oxygen events in Narragansett Bay during summer 2001, Marine Chemistry, 97: 90-103.

Codiga, D.L., H.E. Stoffel, C.F. Deacutis, S. Kiernan, Oviatt, C.A., 2009. Narragansett Bay hypoxic event characteristics based on fixed-site monitoring network time series: intermittency, geographic distribution, spatial synchronicity, and interannual variability. Estuaries and Coasts 32:621-641.

Colt, A., 2008. The Rhode Island Bays, Rivers, & Watersheds Coordination Team's Bays, Rivers, and Watersheds Systems-Level Plan: 2009-2013.

Deacutis, C.F., 1999. Nutrient Impacts and Signs of Problems in Narragansett Bay. p7-23. In: Kerr, M. (Ed.), 1999. Nutrients and Narragansett Bay: Proceedings of a Workshop on Nutrient Removal from Wastewater Treatment Facilities. Rhode Island Sea Grant. Narragansett, RI.
Deacutis, C.F., Murray, D., Warren, P., Saarman, E., Korhun, L., Cicchettii, G., 2003. Hypoxic Waters of Narragansett Bay. Northeast Naturalist.

Deacutis, C., 2005. Filling the Gap: Dissolved Oxygen Monitoring in Narragansett Bay. 10.13140/2.1.4367.0403.

Deacutis, C.F., Murray, D., Prell, W., Saarman, E., Korhun, L., 2006. Hypoxia in the Upper Half of Narragansett Bay, RI, During August 2001 and 2002, in Natural and Anthropogenic Influences on the Mount Hope Bay Ecosystem, Northeastern Naturalist 13(Special Issue 4):173-198.

Doering, P.H., Oviatt, C.A., Welsh, B.L., 1990. Characterizing Water Quality in the Seekonk River, Providence River, and Upper Narragansett Bay, Final Report.

MassDEP, 2013. 314 CMR 4: The Massachusetts Surface Water Quality Standards. MGL Chapter 21, Sections 26 through 53. https://www.sec.state.ma.us/spr/massreg.htm

NBEP, 2013. Watershed Counts 2013 Annual Report.

NBEP, 2017. State of Narragansett Bay & Its Watershed http://nbep.org/the-state-of-our-watershed/

NERACOOS, 2016. Integrated Sentinel Monitoring Network for Change in Northeast U.S. Ocean and Coastal Ecosystems: Science and Implementation Plan: Ed. I. NERACOOS/NROC Coastal Ocean and Ecosystem Health Committee., Runge, J.A., Coté, M., & Thompson, B. (cochairs). Retrieved from: www.neracoos.org/sentinelmonitoring.

NOAA National Estuarine Research Reserve (NERRS), 2015. System-wide Monitoring Program Data Management Manual, v6.6. Centralized Data Management Office: www.nerrsdata.org. 221pp.

Oviatt, C.A., 2008 Chapter 18 Impacts of Nutrients on Narragansett Bay Productivity: A Gradient Approach in A. Desbonnet, B. A. Costa-Pierce (eds.), Science for Ecosystem-based Management, Springer 2008.

RIDEM, NBEP, NBNERR, 2000. Narragansett Bay Water Quality: Status and Trends 2000 A Summary of Water Quality Information http://www.dem.ri.gov/programs/benviron/water/quality/pdf/narbq00.pdf

RIDEM-OWR, 2003. The Greenwich Bay Fish Kill – August 2003 Causes, Impacts and Responses, RIDEM, Providence, RI.

RIDEM-OWR, 2005. State of Rhode Island and Providence Plantations Water Quality Monitoring Strategy 2005-2010, RIDEM, Providence, RI.

RIDEM-OWR, 2010. WATER QUALITY REGULATIONS
http://www.dem.ri.gov/pubs/regs/regs/water/h2oq10.pdf

RIDEM-OWR, 2010. Total Maximum Daily Load Study for Bacteria Mount Hope Bay and the Kickemuit River Estuary http://www.dem.ri.gov/programs/benviron/water/quality/rest/pdfs/mthope.pdf

Saarman, E., Prell, W., Murray, D.W., Deacutis, C., 2008. Chapter 11: Summer bottom water dissolved oxygen in Upper Narragansett Bay. In: Science for Ecosystem-based Estuarine Management: Narragansett Bay in the 21st Century, Desbonnet & Costa-Pierce (eds.), Springer Series In Environmental Management, 325-347.

USEPA, 2000. Ambient Aquatic Life Water Quality Criteria for Dissolved Oxygen (Saltwater): Cape Cod to Cape Hatteras. United States Environmental Protection Agency Office of Water 4304. EPA-822-R-00-012, Nov. 2000.

YSI, Inc., 2011. YSI 6-Series Installation and Operations Manual, Yellow Springs, OH

YSI, Inc., 2019. YSI EXO User Manual ADVANCED WATER QUALITY MONITORING PLATFORM reversion H. https://www.ysi.com/File%20Library/Documents/Manuals/EXO-User-Manual-Web.pdf

Vadeboncoeur, A., Hamburg, S.P., and Pryor, D. 2010. Modeled Nitrogen Loading to Narragansett Bay: 1850 to 2015. Estuaries and Coasts. 33:1113-1127.

Appendix A Sampling Station Information

Field samples are taken at each site during the time periods of each station as described above. Sampling seasons may be extended, but these are the minimum requirements for each station for mandatory data collection

Table A.1 Monitoring Schedule for Narragansett Bay Stations.

				Monitoring Protocol											
				Time of Sample											
ID	**Agency**	**Location**	**Class**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**
		Providence/Seekonk Rivers:													
NBCPS	NBC	Phillipsdale Surface*	SA	x	x	x	x	x	x	x	x	x	x	x	x
NBCPB	NBC	Phillipsdale Bottom*	SA	x	x	x	x	x	x	x	x	x	x	x	x
NBCBS	NBC	Bullock's Reach Surface	SA					x	x	x	x	x	x		
NBCBM	NBC	Bullock's Reach Mid-depth	SA					x	x	x	x	x	x		
NBCBB	NBC	Bullock's Reach Bottom	SA					x	x	x	x	x	x		
		West Passage:													
GSOCS	URI/GSO	Conimicut Point-Surface	SA					x	x	x	x	x	x		
GSOCB	URI/GSO	Conimicut Point-Bottom	SA					x	x	x	x	x	x		
GSOUB	URI/GSO	Upper Bay Winter Station-Surface	SA	x	x	x	x	x					x	x	x
GSONS	URI/GSO	North Prudence-Surface	SA					x	x	x	x	x	x		
GSONB	URI/GSO	North Prudence-Bottom	SA					x	x	x	x	x	x		
GSOGS	URI/GSO	Greenwich Bay Marina-Surface*	SB1	x	x	x	x	x	x	x	x	x	x	x	x
GSOGB	URI/GSO	Greenwich Bay Marina-Bottom*	SB1	x	x	x	x	x	x	x	x	x	x	x	x
GSORS	URI/GSO	Sally Rock Surface	SB1					x	x	x	x	x	x		
GSORB	URI/GSO	Sally Rock Bottom	SB1					x	x	x	x	x	x		
GSOMS	URI/GSO	Mount View-Surface	SB					x	x	x	x	x	x		
GSOMB	URI/GSO	Mount View-Bottom	SA					x	x	x	x	x	x		
GSOQS	URI/GSO	Quonset Pt-Surface	SB					x	x	x	x	x	x		
GSOQB	URI/GSO	Quonset Pt-Bottom	SA					x	x	x	x	x	x		
GSOGD	URI/GSO	GSO Dock-Mid Water depth	SA	x	x	x	x	x	x	x	x	x	x	x	x
		East Passage:													
GSOPS	URI/GSO	Poppasquash Point-Surface						x	x	x	x	x	x		
GSOPB	URI/GSO	Poppasquash Point-Bottom						x	x	x	x	x	x		
DEPTS	URI/GSO	Taunton River-Surface (MassDEP owned)						x	x	x	x	x	x		
DEPTB	URI/GSO	Taunton River-Bottom (MassDEP owned)						x	x	x	x	x	x		
DEPCS	URI/GSO	Cole River-Surface (MassDEP owned)						x	x	x	x	x	x		
DEPCB	URI/GSO	Cole River-Bottom (MassDEP owned)						x	x	x	x	x	x		
GSOHS	URI/GSO	Mt. Hope Bay-Surface						x	x	x	x	x	x		
GSOHB	NBNERR	Mt. Hope Bay-Bottom						x	x	x	x	x	x		
NARTS	NBNERR	T-Wharf- Surface	SA	x	x	x	x	x	x	x	x	x	x	x	x
NARTB	NBNERR	T-Wharf-Bottom	SB	x	x	x	x	x	x	x	x	x	x	x	x

*year –round station is weather dependent (icing in the bay occasionally occurs)

.

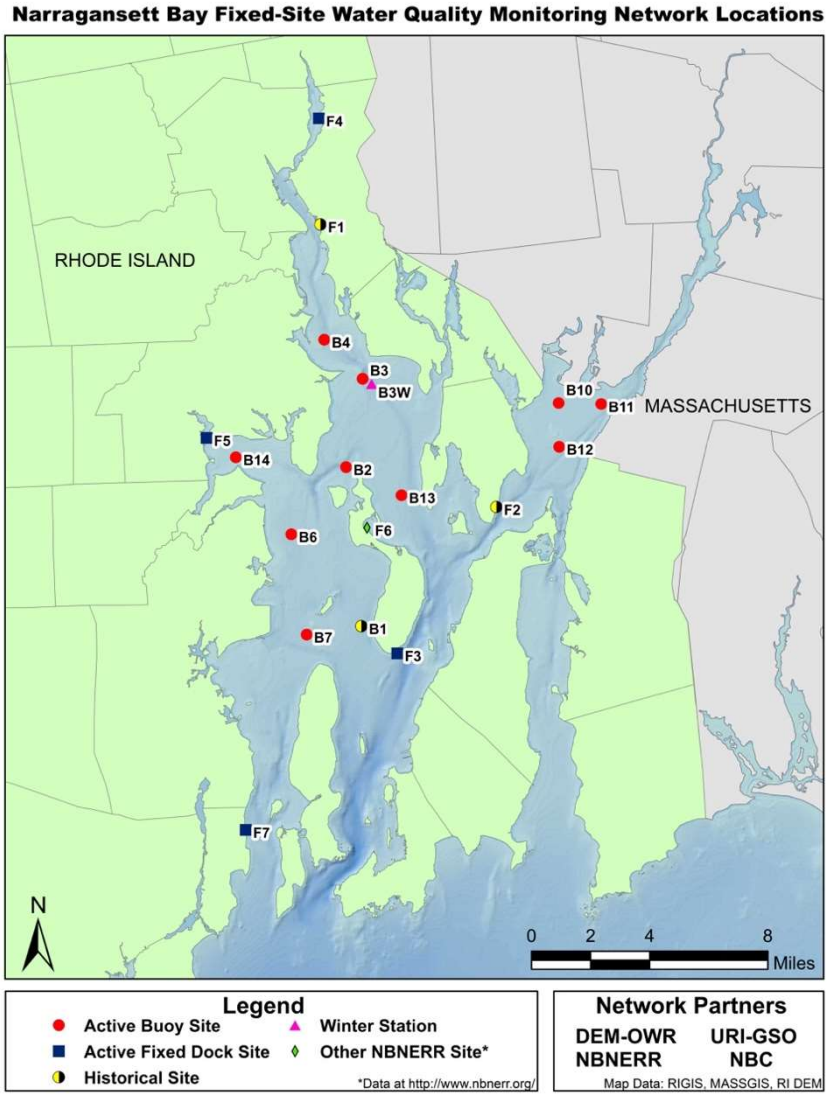


Figure A.1 Narragansett Bay Fixed-Site Water Quality Monitoring Sampling Stations (Historical and Active)

Group	Station	Latitude N	Longitude W	Water Depth (m)	Agency	Year Sites Operational
Upper Bay	Phillipsdale (PD-F4)	41 50.517'	71 22.305'	3	NBC	2004-Present
	Bullock's Reach (BR-B4)	41 43.958'	71 22.196'	6	NBC	2001-Present
	Conimicut Point (CP-B3)	41 42.828'	71 20.628'	7	GSO/RI DEM	2003, 2005-Present
	Upper Bay Winter Station (B3w)	41 42.689'	71 20.276'	13	GSO/RI DEM	2008-present (winter only)
	North Prudence (NP-B2)	41 40.224'	71 21.283'	11	GSO/RI DEM	2001-Present
West Passage	Mount View (MV-B6)	41 38.304'	71 23.621	7	GSO/RI DEM	2004-Present
	Quonset Point (QP-B7)	41 35.288'	71 22.839'	7	GSO/RI DEM	2005-Present
	GSO Dock (GD-F7)	42 29.535'	71 25.137'	2	GSO/RI DEM	1993-Present
East Passage	Poppasquash Point (PP-B13)	41 38.907'	71 19.207'	8	GSO/RI DEM	2004-Present
	T-Wharf (TW-F3)	41 34.731'	71 19.287'	6	NBNERR	2003-Present
Embay-ments	Greenwich Bay Marina (GB-F5)	41 41.090'	71 26.762'	3	GSO/RI DEM	2003-Present
	Sally Rock (SR-B14)	41 40.518'	71 25.437'	4	GSO/RI DEM	2008-Present
Mount Hope Bay	Mt. Hope Bay (MH-B12)	41 40.808'	71 12.913'	5	GSO/RI DEM	2005-Present
	Cole River (CR-B10)	41 42.079'	71 12.908'	5	GSO/MASSDEP	2016-Present
	Taunton River (TR-B11)	41 42.049'	71 11.262'	5	GSO/MASSDEP	2016-Present

Table A.2 **Active Stations**. Only the active stations are listed in this table. Dock stations are indicated by an F before the number location and buoy stations are indicated with a B. The buoy stations (B#) move slightly each year since buoys are retrieved and redeployed each year. The coordinates in this table are the overall average (all years) coordinated for each station. These are approximate locations since buoy locations move slightly from year to year. The yearly NBFSMN metadata document will record the actual coordinated for a given year.

Table A.3. Site Parameters and Sonde Equipment Used. Each Site is based on location and depth (S&B).

Site	**Sonde Type**	**Temp/Sal**	**Optical DO**	**Depth**	**pH**	**CHL**	**BGA**	**Turbidity**	**Nitrate**	**Year Started Use**
Phillipsdale-Surface (PS)	EXO	X	X	X	X	X	X			2010 (2004-2010 Membrane DO)
Phillipsdale-Bottom (PB)	EXO	X	X	X	X	X	X			2010 (2004-2010 Membrane DO)
Bullock's Reach-Surface (BS)	EXO	X	X	X	X	X	X			2018 (2001-2010 Membrane DO)
Bullock's Reach-Mid depth (BM)	EXO	X	X	X	X	X	X			2018(2001-2010 Membrane DO)
Bullock's Reach-Bottom (BB)	EXO	X	X	X	X	X	X	X		2018(2001-2010 Membrane DO)
Conimicut Pt- Surface (CS)	EXO	X	X	X	X	X	X			2019 (2001-2018 6series)
Conimicut Pt- Bottom (CB)	EXO	X	X	X	X	X	X			2019 (2001-2018 6series)
Upper Bay Winter-Surface (UB)	YSI 6-series	X	X	X	X	X				2008
North Prudence-Surface (NS)	EXO	X	X	X	X	X	X			2019 (2001-2018 6series)
North Prudence - Bottom (NB)	EXO	X	X	X	X	X	X			2019 (2001-2018 6series)
Mount View - Surface (VS)	YSI 6-series	X	X	X	X	X				2014 (2004-2014 Membrane DO)
Mount View - Surface (VB)	YSI 6-series	X	X	X	X	X				2014 (2004-2014 Membrane DO)

Site	Sonde Type	Temp/Sal	Optical DO	Depth	pH	CHL	BGA	Turbidity	Nitrate	Year Started Use
Quonset Point - Surface (QS)	YSI 6-series	X	X	X	X	X	X			2014 (2004-2014 Membrane DO)
Quonset Point - Bottom (QB)	YSI 6-series	X	X	X	X					2014 (2004-2014 Membrane DO)
GSO Dock (GD)	YSI 6-Series	X	X	X	X	X	X		X	2018
Poppasquash Point – Surface (PS)	EXO	X	X	X	X	X	X			2019
Poppasquash Point – Bottom (PB)	EXO	X	X	X	X	X	X			2019
Mount Hope Bay – Surface (MS)	YSI 6-Series	X	X	X	X	X	X			2014 Optical DO
Mount Hope Bay – Bottom (MB)	YSI 6-Series	X	X	X	X					2014 Optical DO
Taunton River – Surface (TRS)	EXO	X	X	X	X	X	X		X	2016
Taunton River - Bottom (TRB)	EXO	X	X	X	X	X	X		X	2016
Cole River Surface (CRS)	EXO	X	X	X	X	X	X		X	2016
Cole River Bottom - (CRB)	EXO	X	X	X	X	X	X		X	2016
T Wharf - Surface (TS)	EXO	X	X	X	X	X	X	X		2016
T Wharf - Bottom - (TB)	EXO	X	X	X	X	X	X	X		2018

Site	Sonde Type	Temp/Sal	Optical DO	Depth	pH	CHL	BGA	Turbidity	Nitrate	Year Started Use
Greenwich Bay – Surface (GS)	YSI 6-series	X	X	X	X	X	X		X	2016 optical DO 2018 SUNA
Greenwich Bay – Bottom (GB)	YSI 6-series	X	X	X	X	X	X		X	2016 optical DO
Sally Rock – Surface (SS)	YSI 6-Series	X	X	X	X	X	X			2008 2018 optical DO
Sally Rock – Bottom (SB)	YSI 6-Series	X	X	X	X					2008 2018 optical DO

Appendix B Field Sampling and Lab Calibration Manual

YSI Incorporated. (2011). 6-Series Multiparameter Water Quality Sondes User Manual (https://www.fieldenvironmental.com/assets/files/Manuals/YSI%206-Series%20Manual.pdf)

YSI Incorporated. (2017). EXO Advanced Water Quality Monitoring Platform User Manual (https://www.ysi.com/File%20Library/Documents/Manuals/EXO-User-Manual-Web.pdf)

Sea-Bird Scientific. (2017). Submersible Ultraviolet Nitrate Analyzer (SUNA) User Manual (https://www.ott.com/download/sbc-suna-manual/)

Appendix C Data Review and Editing Manuals and SOPs

Data formatting, editing and review procedures were adapted from **Water Quality Data Review and Editing Protocol** (Chapter 5 of the NERRS CDMO Operations Manual).

This protocol was adapted for the NBFSMN using National Estuarine Research Reserve System-Wide Monitoring Program (SWMP) format as its main guide using Excel instead of CDMO software.

Use the following links to view CDMO NERRS Operations Manual and SOPs:
http://cdmo.baruch.sc.edu/request-manuals-admin/pdfs/CDMOManualv6.6.pdf

http://cdmo.baruch.sc.edu/request-manuals-admin/pdfs/NUTCHLA_SOPv1.8.pdf

Attachment A. Field Sampling Standard Operating Procedures

Calibration QC SOP 1 (S-1): Calibration Procedures:

These procedures should be conducted on a regular maintenance schedule. They should be conducted in a controlled laboratory. These steps are recommended by the manufacturer of the product. The following calibration procedures are used according to the manual of the designated sonde. The manual procedures are based on instrumentation make and model (see below).

Parameter	YSI Instrument Type/Sensor	Calibration Procedure	Calibration Solutions	Frequency* Seasonally	SOP
DO	EXO Optical DO 6 series optical	ODO % Sat	Bubbling tap water at air saturation	Every 2 weeks	S-1, S-1B
Salinity	EXO Wiped C/T 6-series optical	SpC	50,000 µS/cm	Every 2 weeks	S-1, S-1B
pH	EXO Wiped pH 6 series pH (flat glass and guarded)	2 point	7 and 10 pH units	Every 2 weeks	S-1, S-1B
Total CHL	EXO TAL-PE (µg/L and RFU)	1 point 2 point*	DI water 0.625 mg/L Rhodamine	Every 2 weeks	S-1, S-1B
BGA (phycoerythrin)	EXO TAL-PE (µg/L and RFU)	1 point	DI water	Every 2 weeks	S-1, S-1B
Turbidity	EXO Optical turbidity	2 point	DI water and 126 NTU (124 FNU) solution	Every 2 weeks	S-1, S-1B
SUNA V2	SUNA V2 nitrate sensor	1 point	DI water	monthly	S-7

*NBNERR follows a 3-week seasonal calibration frequency

SOP 1. YSI 6-Series Manual.pdf
(https://www.fieldenvironmental.com/assets/files/Manuals/YSI%206-Series%20Manual.pdf)

SOP 1B. YSI EXO-Series Manual.pdf

(https://www.ysi.com/File%20Library/Documents/Manuals/EXO-User-Manual-Web.pdf)

Fixed Laboratory Analytical QC-SOP 2 (S-2): Chlorophyll Field Sampling Procedures:
This procedure is to be conducted when time, equipment, and field conditions permit. If samples are not taken the field notes should reflect why this procedure was omitted.

SOP 2. MERL Chlorophyll Sampling and Laboratory Procedures.doc
SOP 2B. Narragansett Bay Commission Sampling and Laboratory Procedures for Chlorophyll

Field Sampling SOP 3 (S-3): Field Maintenance Procedures:
This procedure is to be conducted when time, equipment, and field conditions permit. If a profile is not taken the field notes should reflect why this procedure was omitted.

SOP 3. Field Procedures.doc

Data QA/QC SOP 4 (S-4): QA/QC Procedures:
This procedure is to be conducted at the end of each field season at a minimum. These procedures are a guideline for how to manage datasets and QA/QC the data. These guidelines have been adapted from the NERRS Central Data Management Operations SOP for quality assurance.

SOP 4. NBFSMN Data Management for Corrections

Data Acquisition SOP 5 (S-5): Equipment Programming/Data Transfer:
Follow testing procedures prior to each seasonal deployment and operational test at the end of each season. They should be conducted in a controlled laboratory. The steps to follow are recommended by the manufacturer of the product used at each station with specifics on how each station was set up. Each station when purchased came with a site-specific manual. These are guidelines for operations since each data acquisition system is custom. Refer to the YSI 6200, Nexsen, or Campbell Scientific manual for further instructions on programming DCP equipment. No link is available for Campbell Scientific (These are custom by station, refer to site manager for manuals for each station).

Field Maintenance SOP 6 (S-6): Seasonal Preparation (station preparation):
Maintenance of buoys and equipment should be conducted on a regular maintenance schedule of a minimum of once a season. Since equipment is custom to each station, the procedures will vary. This SOP is to be used as a general guide to maintain and troubleshoot equipment.

SOP 6. Buoy Preparation and Storage.doc

Calibration QC SOP 7 (S-7): Calibration Procedures:
These procedures should be conducted on a regular maintenance schedule. They should be conducted in a controlled laboratory. These steps are recommended by the manufacturer of the product.

SOP 7. Sea-Bird Scientific. (2017). Submersible Ultraviolet Nitrate Analyzer (SUNA) User Manual

(https://www.ott.com/download/sbc-suna-manual/)

Calibration QC SOP 8 (S-8): MERL Nutrient Procedures:
These procedures should be conducted on a regular maintenance schedule. They should be conducted in a controlled laboratory. These steps are recommended by the manufacturer of the product.

SOP 8. Nutrient Sampling MERL Methods QA/QC

Revised June 2, 2003

SOP-2 MERL Chlorophyll Sampling and Laboratory Procedures

University Of Rhode Island
Marine Ecosystems Research Laboratory
Standard Operating Procedure

for

EXTRACTION AND ANALYSIS OF CHLOROPHYLL *a* AND PHAEOPHYTIN *a* IN SEAWATER USING A TURNER DESIGNS MODEL 700 FLUOROMETER

Summary of changes in this version: This SOP has been revised to reflect improvements to the method and to correct inadequacies in the previous versions.

1.1 OBJECTIVE

The purpose of this Standard Operating Procedure is to describe a fluorometric procedure for the analysis of chlorophyll *a* and phaeophytin *a* that can be performed in the laboratory or at sea. The methods follow those described by the U.S. Environmental Protection Agency (Arar and Collins, 1997)[1].

1.2 SUMMARY OF METHOD

Briefly, water samples are filtered through glass fiber filters (GF/F) by low-vacuum filtration, which are then allowed to steep in 90% acetone to extract the pigments. The extract is centrifuged, and the supernatant analyzed using a fluorometer to measure the fluorescence of chlorophyll and, after acidification, of phaeophytin. Fluorescence is then converted to concentration based on a 6 to 10-point linear regression calibration.

1.3 INTERFERENCES

Any substance extracted from the filtered sample that fluoresces in the red region of the spectrum may interfere with the measurements of chlorophyll *a* and phaeophytin *a*. The relative concentrations of chlorophylls *a*, *b*, and *c* will vary with the taxonomic composition of the phytoplankton. Depending on the concentrations (and the ratios of those concentrations) present in the samples, chlorophylls *b* and *c* may interfere significantly with chlorophyll *a* and phaeophytin *a* measurements due to spectral overlaps. Knowledge of the phytoplankton assemblage will aid the analyst in determining the need for additional (or alternative) analytical methods (e.g., spectrophotometric methods) described elsewhere.

2.1 PREPARATION

2.2 EQUIPMENT, GLASSWARE, MISCELLANEOUS SUPPLIES

- All apparatus must be clean and acid-free. Soak glassware in detergent (e.g., Joy, or similar dish washing or laboratory grade detergent) and water for 4 hours; rinse three times each with deionized water (DIW), and once with 90% acetone.
- Turner Designs Model 700 Series Fluorometer (or similarly equipped fluorometer) with the

[1]Arar, E.J., and G.B. Collins. 1997. *In Vitro* Determination of Chlorophyll *a* and Phaeophytin *a* in Marine and Freshwater Phytoplankton by Fluorescence. Method 445.0, Version 1.2 (September 1997). U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, OH

following lamp and filters:

- Light source: Daylight White Lamp (P/N 10-045)
- Excitation filter: 340 - 550 nm (P/N 10-050R)
- Emission filter: >665 nm (P/N 10-051R)
- Reference filter:400 - 700 nm (P/N 10-032)
- Photomultiplier tube: Red-sensitive 185-870 nm
- TD-700 Red PMT and 13 mm x 100 mm Round Test Tube Adaptor (P/N 7000-000)

- Turner Designs solid red secondary standards – 'high' and 'low'
- Centrifuge
- Lint-free laboratory wipes
- Glass fiber filters (GF/F), 47-mm diameter, nominal pore size 0.7 m
- Aluminum foil
- Graduated cylinders, 500mL and 1-L capacities
- Class A calibrated volumetric flasks, 25mL, 50mL, 100mL, and 1L capacities
- Polypropylene or glass centrifuge tubes, 50 mL capacity, nonpigmented screw caps
- Dropper bottle, 50mL capacity
- Polyethylene squirt bottles
- Gas Tight Syringes
- Flat-tipped forceps
- Vacuum pump capable of maintaining a vacuum up to 6-in. Hg.
- Filtration apparatus (1-to 2-L filtration flask, 47-mm fritted disk base, filter tower)
- Stainless Steel Spatulas

2.3 REAGENTS AND STANDARDS

- Spectrophotometric-grade acetone (CASRN 67-64-1)
- Concentrated hydrochloric acid (HCl) (sp. gr. 1.19) (CASRN 7647-01-0)
- Magnesium carbonate ($MgCO_3$), light powder (CASRN 39409-82-0)
- Chlorophyll *a* free of chlorophyll *b* calibration standard (Sigma Chemical C5753)
- Turner Designs certified chlorophyll *a* standard – nominally 20 and 200 g/L (P/N 10-850)
- Deionized water (DI water)

2.4 REAGENT SOLUTIONS

2.4.1 10% HCl solution

1. Place 90 mL DI water into a 100 mL volumetric flask.
2. Add 10 mL of concentrated HCl and mix well.
3. Transfer to a clearly labeled plastic storage container.

Storage: This solution is stable at room temperature for up to 3 months.

2.4.2 Saturated magnesium carbonate solution (1% solution)

1. Dissolve 1g $MgCO_3$ + 3g NaCl in 100 mL of DI water in a clear plastic storage container.
2. Mix well before each use.

Storage: This solution is stable at room temperature for up to 3 months.

2.4.3 Aqueous buffered acetone solution (90% acetone)

1. Measure 100 mL of DI water using a 1L graduated cylinder and transfer to a storage container.
2. Measure 900 mL of acetone using a 1L graduated cylinder, transfer to the container, and mix.
3. Add 10 drops (using an eye dropper) of 1N $NaHCO_3$ buffer solution to assure an alkaline solution. (Sodium bicarbonate solution: 8.4g $NaHCO_3$ dissolved in 100 mL DI water mixed well.)

Storage: Store at room temperature for up to 3 months.

2.5 STANDARD SOLUTIONS

All standard solutions prepared in volumetric flasks are prepared by adding the material of interest, a small amount of solvent, mixed to dissolved, and then brought to volume. All materials of interest and solvents must be at room temperature prior to preparation of standards.

2.5.1 Chlorophyll a Primary Stock Solution (~20 mg/L)

1. The chlorophyll *a* dry standard will be shipped in a flame-sealed amber glass ampoule; the standard must be stored in the dark and at -20□C until just prior to use.
2. Tap the ampoule until all of the dried chlorophyll is in the bottom of the ampoule. In subdued light, carefully break the tip of the ampoule to open, and completely transfer the contents into a 1000 mL volumetric flask.
3. Dilute the chlorophyll to volume with 90% buffered acetone. (For example: If a nominal weight of 1 mg chlorophyll is added to a 500 mL volumetric flask, then the primary stock solution will be 2000 □g/L chlorophyll). Label the flask and wrap with aluminum foil to protect from light.

Storage: Store at -20□C and in the dark; minimize time between preparation of primary standard, spectrophotometric determination of primary standard concentration, and calibration of fluorometer with secondary standards. A 24-hr period is optimal although the solution is stable for > 6 months (Arar and Collins, 1997).

2.5.2 Determination of Primary Chlorophyll a Standard Concentration

The concentration of the primary chlorophyll *a* standard must be determined spectrophotometrically using a multiwavelength spectrophotometer. There are a number of valid spectrophotometric methods and equations available for determination of chlorophyll concentration. The calculation method used at the Marine Ecological Research Laboratory multiplies the absorbance values at 664 nm and 647 nm by the constants 11.93 and 1.93 respectively, and takes the difference of the two values. The final equation is as follows:

$$Chla = (11.93 * \lambda_{664}) - (1.93 * \lambda_{647})$$

Where,

Chl*a* = concentration (mg/L) of chlorophyll *a* measured,

λ_{664} = sample absorbance at 664 nm, and

λ_{647} = sample absorbance at 665 nm

2.5.3 Chlorophyll a Intermediate Stock Solution (~1 mg/L)

1. Add 25 mL of the chlorophyll *a* primary stock solution (Section 2.4.1) to a clean 50mL volumetric flask.
2. Dilute to volume with 90% acetone solution. (If exactly 1 mg of pure chlorophyll *a* was used to prepare the primary stock, then the concentration measured by spectrophotometry would be ~2000 □g/L and the intermediate stock solution concentration ~1000 □g/L).

Storage: Prepare daily before each use. Standards must be used within two hours of preparation. Protect from light.

2.5.4 Calibration Standards (1 to 200 µg/L)

Calibration standards are prepared as dilutions of the intermediate stock solution. The actual concentration of the standards and the volumes required for the dilution may change based on the actual Chl *a* concentration measured by spectrophotometry for the primary stock solution. The table below presents an example of a 6-point calibration curve that is prepared from a 1 mg/L intermediate stock solution. At least five standards are prepared to bracket the expected sample concentration range as follows:

Concentration of Calibration Standard (µg/L)	mL of Intermediate Stock Solution at 1000	Final Volume (mL) of Standard
0	0	90%Acetone
1.0	0.1	100
5.0	0.5	100
20	0.5	25
50	5.0	100
100	5.0	50
200	5.0	25

Preparation/Storage: Prepare immediately before each use. Standards must be used within two hours of preparation. Protect from light.

2.5.5 Chlorophyll Standard Reference Material (SRM; nominally 20 and 200 µg/L)

Chlorophyll *a* certified standard from Turner Designs have one high-level and one low-level concentration. These SRMs are essentially free from chlorophyll *b* and are diluted with solvents that are free of contaminants that can cause background fluorescence (note that other independently spectrophotometrically verified chlorophyll *a* standards can be substituted as appropriate – must use same modified Lorenzen equations for calculation of concentration).

1. The Turner Designs certified standards will be shipped in two flame-sealed, foil wrapped glass ampoules; the standards must be stored in the dark and at -20°C until just prior to use.
2. SRM's are ready to run - break the ampoule, empty contents into 13 mm cuvette and analyze.

Storage: Store at -20°C and in the dark until just prior to use; minimize time between delivery and analysis of standard. A 24-hr period is optimal although the solution is stable for 2 months (Turner Designs specifications).

2.5.6 Solid Secondary or Check Standards (high and low)

The Turner Designs solid red secondary standards provide a simple and stable alternative to multiple calibrations with a primary standard and replace the use of coproporphyrin solutions as a check standard. Once the instrument is calibrated with a primary standard, the solid secondary standards can be used effectively to check the calibration, with only occasional verification with a primary standard (e.g. Turner Designs SRM). Thus, the solid secondary standards make it simple to check for instrument drift and to perform routine calibration checks. The Turner Designs solid secondary standards are sealed in a single holder that contains two fluorometric standard concentrations: one high-level and one low-level concentration equivalent. The solid secondary standards require no special storage conditions and can be stored in a drawer or on the benchtop. They are not photosensitive or temperature sensitive. Degradation is minimal after years of environmental exposure.

3.1 CALIBRATION

The Turner Designs 700 fluorometer is calibrated following a three-step process. First, the instrument sensitivity is set against a standard of ~80% full scale (200 µg/L). Then a 6-point linear regression calibration for calculating sample concentrations is performed by analyzing the calibration standards prepared in Section 2.4.4. The standards are analyzed using the same procedures used to analyze samples (Section 4.0). This is conducted to ensure the linearity in response of the instrument over the range of calibration that will be used to determine the concentration of actual samples. Once calibrated, the instrument calibration should be stable for at least a year. The stability of the calibration is monitored during the routine analysis of samples by comparing the analysis of the solid check standards to the results obtained for the solid check standards during the initial calibration. The calibration is also verified against a chlorophyll *a* SRM following calibration and then on an annual basis to ensure the instrument remains in calibration. If the instrument is out of calibration (see Section 3.2), a new 6-point linear regression calibration must be performed. If the instrument sensitivity settings are ever changed, it is recommended that the entire three-step calibration process be performed.

3.2 CALIBRATION OF TURNER 700 FLUOROMETER

The following 3-step process should be used for calibration of the TD-700 instrument initially and whenever instrument checks (solid standards) fail to meet the acceptance criteria defined in Section 6.0.

3.1.1 Setting the Instrument Sensitivity

The process of setting the instrument sensitivity is detailed in the Turner Designs Model 700 manual. It is recommended that the manual be consulted prior to conducting the steps that are listed below.

1. Turn on instrument using power button located on the right side of the front of the machine and allow the instrument to warm up for 60 minutes.
2. Press the <ENT> key to move the *Home* screen to the *Setup* menu.

3. Press the <1> to load the *Setup* menu, then <1> again for the *Mode* menu.
4. Choose the Multi-Optional Mode, and then press <2> to choose the calibration procedure. Choose <Raw Fluor> for the Raw Fluorescence calibration procedure, and then press <ESC> twice to return to the *Setup/Cal* menu.
5. Press <2> from the *Setup/Cal* menu to access the calibration sequence and the Multi- Optional-Raw Fluorescence calibration sequence will appear.
6. Fill a clean test tube with chlorophyll a standard solution with a concentration of ~80% of the maximum concentration (~200 µg/l – exact concentration is not necessary as the instrument will be calibrated following this step that merely sets the general sensitivity of the instrument). Wipe the test tube dry and insert it into the sample adaptor in the sample chamber. Press <ENT> to proceed to the next screen.
7. If the sample is 80% of the maximum concentration that will be read, accept the default value of 800 by pressing <1>. If a reading equal to 800 is not acceptable, press <9> to change the value. (Assigning a higher value decreases the maximum sample concentration that can be read and increases the instrument's sensitivity and resolution. A lower value will increase the maximum sample concentration that can be read and decrease instrument's sensitivity and resolution.) Key in the desired number and press <9>, then <1>.
8. The TD-700 will now set its sensitivity, as indicated by the SENS FACTOR, based on the final sample value accepted. Once set, press <1> to run a blank.
9. Fill a clean test tube with 90% buffered acetone, wipe the outside of the tube dry, insert it into the sample adaptor, and press <ENT>. Allow the reading to stabilize and press <0>. Once the blank is read, the instrument will automatically return to the *Home* screen.

3.1.2 Six-Point Calibration Curve Analysis

1. Measure the fluorescence of each of the calibration standards from section 2.4.4 both before and after acidification (see section 4.5.2). Record the results in the fluorometer logbook.
2. Perform the linear regression of response versus concentration and obtain the constants *m* (the slope) and *b* (*y*-intercept). Force the regression line through zero (so that the *y*-intercept = 0) and ensure that the correlation coefficient (r) $\geq$ 0.995.
3. Once linearity of the calibration curve has been determined perform an analysis on the SRM and solid check standards. Record the fluorescence results in the fluorometer logbook.
4. Daily solid red standard checks will also be recorded in the fluorometer logbook. The SRM results must be within 95% to 105% of nominal concentration.

3.3 CONTINUING CALIBRATION

Once the procedures in Section 3.1 are completed, sample analysis may continue on subsequent days using the same initial calibration curve as long as the instrument is still stable. Instrument stability is verified by analyzing a 90% acetone blank and the solid check standards at the beginning and end of each day of analysis. Results are recorded on the fluorometer logbook. Sample analysis may begin, and the established initial calibration curve applied to the data, if the solid check standards (high and low) fluorescence is $\leq$ 5% different than the reading taken in Section 3.1.3 (Initial Calibration). If the check standard value is greater than 5% different from the initial value, then the instrument must be recalibrated as described in Section 3.1. Thus, it is imperative that the percent difference be calculated prior to the analysis of samples. A 90% acetone blank and the solid check standards must be analyzed routinely

- prior to sample analysis,
- at the end of sample analysis, and
- to meet many specific project plan requirements (e.g. frequency of 1 per every 10-20 samples).

3.4 INSTRUMENT LINEAR DYNAMIC RANGE

A linearity standardization that verifies the working range of the instrument must be performed at least once per study, whenever the calibration check fails the acceptance criteria (Section 3.1), or for long-term studies, annually. If the linear dynamic range is not determined, the range will be assumed to include all concentrations up to the highest concentration used in the current 6-point calibration.

1. Perform a calibration using $\geq$ 5 calibration levels and calculate the regression as described in Section 3.1.
2. Incrementally analyze standards of higher concentration until the measured fluorescence response *(R)* of a standard no longer yields a calculated concentration (C_c, where $C_c = (R-b)/m$) that is 10% of the known concentration *(C)*. That concentration defines the upper limit of the linear dynamic range of the instrument.
3. Enter the instrument response of each standard vs. the calibration standard concentration on the calibration log form.

NOTE: Dilute and reanalyze each sample having a concentration that is 90% of the upper limit of the instrument linearity.

3.5 DETECTION LIMITS

Both instrument and estimated detection limits are established once annually.

3.4.1 Instrument Detection Limit (IDL)

1. Zero the fluorometer with a solution of 90% acetone.
2. Serially dilute a known concentration of pure chlorophyll *a* in 90% acetone until it is no longer detected by the fluorometer.

3.4.2 Method Detection Limit (MDL)

As noted in Arar and Collins (1997), an MDL determination is not possible nor practical for a natural water or pure species sample due to known spectral interferences and to the fact that it is impossible to prepare solutions of known concentrations that incorporate all sources of error (sample collection, filtration, processing, etc.). It is recommended that an estimated detection limit (EDL) be determined.

3.4.3 Estimated Detection Limit (EDL)

1. Process 7 blank filters according to procedures in Section 4.4 and analyze as described in Section 4.5. Calculate the mean fluorescence response for the filter blanks. This calculation uses the relative fluorescence values directly from the instrument (no need for chlorophyll concentration calculation).
2. Serially dilute a known concentration of pure chlorophyll *a* in 90% acetone until it yields a response that is 3 times the mean filter blank response. The resulting concentration is the EDL.

4.1 PROCEDURE

Personnel who have been trained by a qualified analyst may perform the following analytical procedures.

4.1 SAMPLE COLLECTION AND STORAGE

Collect whole water by using either a pumping system or a water sampling bottle (e.g., Niskin or similar bottle). If sample filtration cannot be performed immediately store samples on ice or at 4°C and protect from exposure to light.

4.2 SAMPLE FILTRATION

1. Rinse the filtration unit with DI water and place a 47-mm GF/F filter on the base of the unit.
2. Thoroughly mix the sample by gently inverting it three to five times. Measure a 10 to 200 mL subsample (depending on sample concentration and particulates) with a calibrated pipette or in a graduated cylinder. Rinse the pipette or cylinder between each use.
3. Pour the subsample into the reservoir of the filtration apparatus, add two to ten drops of the magnesium carbonate solution, and apply a vacuum (not to exceed 20 kPa).
4. **Do not filter until dry between measured aliquots**. NOTE: Final filtration volumes may be designated by the Project Manager or Chief Scientist and are often stipulated in project specific work plans. Filtration volume will depend on the phytoplankton density (and other suspended solids) in the water. In nearshore waters, filter in increments of 10 mL; in open waters, filter in increments of 200 mL.
   NOTE: Turn off the vacuum pump before filtering to dryness.
5. Fold filter in half using forceps (do not touch the center of the filter), wrap in aluminum foil, and store frozen (-20°C) until extracted.
   NOTE: Samples must be stored in the dark until analysis.
6. Record the volume filtered on the Sample Collection/Analysis datasheet or if a consistent volume is sampled for a program, the volume can be written directly on the sample label and only deviations from the standard volume recorded on sample or station logs.

Storage: (1) The sample filters can be stored frozen for up to 4 weeks without significant loss of chlorophyll *a.* (2) Samples must be stored in dark and store (-20°C) until analysis.

4.3 FIELD FILTER BLANK

Prepare a minimum of one blank filter each day that samples are filtered or approximately one (1) filter for every 20 samples processed, and whenever a new lot of filters are used. In the field, remove a glass fiber filter (GF/F) from the storage container, fold, wrap in aluminum foil, and store frozen at -20°C as if it contained a routine sample.

4.4 SAMPLE EXTRACTION

Perform the following operations in subdued light.

1. Remove filter from aluminum foil and place in numbered centrifuge tube. Record the sample code and the tube number on the data sheet.
2. Add 10 – 30 mL of 90% buffered acetone (depending on the estimated chlorophyll concentration and the filter volume) to each centrifuge tube, cap, and shake tube so that filters are completely submerged in the acetone solution.

3. Place all tubes in a light sealed container and store in freezer for 20 to 24 hours, avoiding exposure to light.
4. Field filter blanks are processed identically to the field samples.

4.5 SAMPLE ANALYSIS

4.5.1 Instrument Set-up

Perform the following in subdued light:

1. Turn on instrument and allow 30 to 60 minutes to warm up.
2. Fill a clean cuvette with the 90% acetone solvent solution that is used for sample extractions. Dry and place the cuvette into the fluorometer.
3. Press <*> to read value (this initiates the discrete sample analysis timer – set to have a 7 second delay and then a 12 second averaging period).
4. Record the meter reading in the fluorometer logbook.
5. Place the solid red check standard into the instrument with the letter "L" (etched on top of the solid standard holder) on the left-hand side. Make sure that the metal pin is completely seated in the notches of the 13 mm round cuvette holder. Press <*> to read the value.
6. Record the meter reading in the fluorometer logbook.
7. Pull solid standard out and rotate 180° and reinsert with the letter "H" on the left-hand side. Make sure that the metal pin is completely seated in the notches of the 13 mm round cuvette holder.
8. Press <*> to read value.
9. Record the meter reading on the Check Standard Calibration Log Form.
10. Repeat blank and solid check standard readings at the end of the day (additional readings may be required by individual projects, e.g. following every 10 or 20 samples).

4.5.2 Sample Analysis

Perform the following procedure in subdued light.

1. Centrifuge samples for 5 minutes (making sure centrifuge is balanced) at setting 5 in an International Equipment Company clinical centrifuge. Following centrifuging, allow samples to warm to room temperature (keep centrifuge tubes capped until analysis).
2. After centrifuging, decant supernatant into a clean large test tube, cover with Parafilm and invert 5 times.
3. Fill a smaller test tube with the extract, dry, and clean the test tube of all fingerprints, etc., and insert into instrument.
4. Press "*" once the reading has begun to stabilize (~ 30 seconds), this will initiate the discrete sample averaging sequence. During the delay period "DELAY" will appear in the upper right-hand corner of the display. This will change to "AVE" during the averaging period and then "DONE" when it is finished. The reading will freeze for 5 seconds once it is "DONE". Record the meter reading on the Sample Collection/Analysis Log Form.
5. All samples must be analyzed within the calibrated range of the instrument. If the relative fluorescence value for any sample is higher than the highest standard, then dilute the sample and reanalyze.
6. Add 1 drop of 0.6 N HCl acid. The instrument reading should drop rapidly after acidification wait until it stabilizes (~90 seconds) before hitting "*" to take the after acidification reading.

7. Record the instrument reading on the Sample Collection/Analysis Log Form.

5.1 CALCULATIONS

5.2 CALIBRATION FACTORS

The calibration factors (F_s and r) are calculated as the slopes of linear regressions between standard concentrations, fluorescence before acidification (R_b), and fluorescence after acidification (R_a). Load the standard concentrations, R_b, and R_a values into an Excel spreadsheet (a template has been developed) and calculate the calibration factors as:

F_s = response factor = slope of regression of concentrations versus R_b r = ratio of R_b and R_a = slope of regression of R_b versus R_a

This is similar to the method used to calibrate the older analog fluorometer, where shutter specific Fs and r would be calculated based on single calibration points (e.g. F_s=Concentration/R_b and r=R_b/R_a). The Turner Designs Model 700 is a digital fluorometer that allows for a wide-range of concentrations to be measured at one sensitivity setting (e.g. no changing shutters). This allows for the calculation of calibration factors based on a single point or multiple points. In order to increase confidence and accuracy of the calibration, it is recommended that a multiple point (6) regression be used to calculate the calibration factors as described herein.

5.3 CORRECTED CHLOROPHYLL a AND PHAEOPHYTIN a (□g/L)

Calculate the uncorrected chlorophyll *a* (chl a_e) and phaeophytin *a* (pha a_e) concentrations (□g/L) in the sample extract as follows:

$$\text{chl } a_e\ (\square\text{g/L}) = F_s\,(r / r\text{-}1)\,(R_b - R_a)$$

$$\text{pha } a_e\ (\square\text{g/L}) = F_s\,(r / r\text{-}1)\,(rR_a - R_b)$$

where,

F_s = response factor for the calibration standard used.
R_b = fluorescence of sample extract before acidification. R_a = fluorescence of sample extract after acidification.
r = before-to-after acidification ratio of pure chlorophyll *a* solution.

These calculations are performed in a spreadsheet once the raw data and new calibration data are entered. The spreadsheet also calculates the volume corrected chlorophyll *a* (chl a_e) and phaeophytin *a* (pha a_e) concentrations (□g/L) for the sample (e.g., concentration in nature) as follows:

$$\text{chl } a_e = (\text{chl } a_e \text{ X } e) / V$$

$$\text{pha } a_s = (\text{pha } a_e \text{ X } e) / V$$

where,

V = volume (mL) filtered
e = extraction volume (mL)

Perform all calculations values in a spreadsheet.

5.4 PERCENT DIFFERENCE

Calculate the percent difference between the initial and continuing readings of the solid check standards and SRM as follows:

$$\% \text{ Difference} = [(\text{Initial reading} - \text{continuing check reading}) / \text{Initial reading}] \times 100$$

6.1 QUALITY CONTROL

The project work plan will define the quality control requirements for specific projects. General guidance is provided in this section.

6.2 FIELD FILTER BLANKS (FFB)

1. Prepare a minimum of one blank filter each day that samples are filtered or approximately one (1) filtered for every 20 samples processed, and whenever a new lot of filters are used.
2. Calculate the average "concentration" of the filter blanks. If the blank average □10% of the sample values (batch average), measure ten additional filter blanks from a particular batch of filters.
3. The project work plan must define whether the filter blank value will be subtracted from the field sample data or only reported with the data.

6.3 LABORATORY ANALYSIS DUPLICATES

Laboratory analysis duplicates are prepared by splitting the extract from a single filter into separate aliquots and measuring response separately.

1. Analyze a minimum of one duplicate sample with every batch of □20 samples.
2. Calculate the relative percent difference (RPD) of uncorrected values of chlorophyll *a*.
3. Reanalyze the batch of samples if the chlorophyll RPD exceeds 15% for samples that are approximately 10X the instrument detection limit. (The RPD for phaeophytin *a* might typically range from 10% to 50%.)

$$RPD = [(C_1 - C_2) / (C_1 + C_2)]200$$

6.4 FIELD DUPLICATES

It is recommended that a minimum of one field duplicate is collected and processed in the field with every 20 samples. The RPD for field duplicates should be within 50%.

6.5 CHECK STANDARDS

The solid check standards must be analyzed at the start and end of each day of analysis (additional measurements may be required by individual project plans – e.g. once every 10 or 20 samples). For most projects, it is expected that both high and low solid check standards will be analyzed, but specific project requirements may use only one depending on the range of chlorophyll *a* concentrations that are analyzed (e.g. in oligotrophic waters the fluorometer may be calibrated at a higher sensitivity (lower concentrations) and the high solid check standard would not be applicable). The solid check standard (high and low)

fluorescence must be ≤ 5% RPD of the initial reading measured during instrument calibration. If a check standard value is greater than 5% different from the initial value, then the instrument must be recalibrated as described in Section 3.1.

6.6 STANDARD REFERENCE MATERIAL

It is also recommended that independently verified chlorophyll standards or standard reference material (SRM; e.g. Turner Designs certified standards) be analyzed at least once per year (more often if specified by project requirements) to ensure that the instrument is in calibration. The SRM (high and low) fluorescence must be ≤ 5% of the nominal concentrations. The SRM will be analyzed following calibration of the instrument as verification of the calibration, and then at least annually to check stability of the calibration. If the SRM value is greater than 5% different from nominal, then the instrument must be recalibrated as described in Section 3.1. Normally both the low and high SRM concentrations will be analyzed unless project specific chlorophyll a concentration ranges exclude the high SRM value (e.g. focused on lower concentration range).

7.0 INSTRUMENT MAINTENANCE

The Turner Designs Model 700 fluorometer is a durable instrument that requires minimal maintenance. However, in order to ensure the proper operation of the instrument, a few simple checks and cleaning procedures will be performed if the instrument fails to calibrate.

1. Remove the cover to the sample compartment and verify that the compartment is dry and all components, including the filters, lamp, and electronics, are clean.
2. If the compartment and components are not clean, perform the following procedures.
   a) Wash the filters with soap and water, rinse thoroughly with tap water followed by DI water, and dry using a lint-free wipe.
   b) Clean bulb using a lint-free wipe.
   c) Insert fresh desiccant packets to the filter chamber if necessary. This will minimize fogging of the filters and optics.
3. Replace lamps and filters as needed.
4. Check sample test tubes for scratches, dirt, etc., and determine if they match optically (e.g., giving the same fluorescence reading within □5%. If the cuvettes do not match, select only one and use it throughout the entire analytical process.

Record all maintenance activities on the Instrument History Record Form (Attachment 1) maintained in the instrument maintenance log. If any instrument optical components are cleaned or replaced the instrument must be recalibrated.

8.1 TRAINING

A Certificate of Training (Attachment 2) will be issued to the trainee once proficiency of this procedure is demonstrated. The original certificate will be maintained in Quality Assurance Unit.

Before beginning training on instrument operation and calibration and sample extraction and analysis, the trainee will read this SOP in entirety and several sections of the instrument manual that are essential for instrument operation.

8.2 INSTRUMENT OPERATION AND CALIBRATION

Individuals assigned to operate the Turner Designs Model 700 fluorometer must be supervised and trained in the procedures for calibrating and operating the instrument. Personnel performing these procedures must demonstrate proficiency in the following activities.

1. Preparing chlorophyll standards for the initial calibration ($\geq$ 5 levels).
2. Determining the linearity of the initial calibration.
3. Setting up the instrument.
4. Running calibration standards, check standards, and samples.

Personnel will be certified to operate the instrument without supervision when they have successfully performed the above operations three times without instruction. Training on calibrations should only be performed when a new calibration is necessary. Optional training on calibration of the instrument should include all aspects of calibration (making standards, running them on the instrument, calculating calibration factors, etc.), EXCEPT setting the instrument sensitivity and the initial two-point instrument calibration. These two steps should only be conducted when necessary (e.g. change optics components, replace lamp or photomultiplier tube, sensitivity adjustment changed for other methods).

8.3 EXTRACTION AND ANALYSIS

Individuals performing analyses according to this SOP must be supervised and trained by qualified technical staff. Personnel performing this method for the first time should demonstrate proficiency in the extraction of sample filters. (20 to 30 natural samples should be collected.) A set of 10 or more samples should be extracted and analyzed according to this procedure. The relative standard deviation (RSD) of uncorrected values of chlorophyll *a* should not exceed 15% for samples that are approximately 10X instrument detection limit. (The RSD for phaeophytin *a* might typically range from 10% to 50%.)

9.1 SAFETY

Safety considerations are noted throughout this SOP.

9.2 PERSONAL PROTECTION

Safety glasses, lab coats, and disposable polyethylene gloves must be worn during all laboratory operations (sample collection, filtration, extraction, and analysis).

9.3 SAMPLE STORAGE

1. Store sample filters at -20□C and in the dark as soon as possible after sample collection; short-term storage on ice is acceptable for no more than 4 h. Filters may be stored frozen for up to 4 weeks without significant loss of chlorophyll *a*.
2. Store extracted samples in the dark, or at a minimum in subdued light, until analyzed. Approximately 25 to 50 samples can be extracted and analyzed in an 8-hour day**. Once a sample is extracted, the extract must be analyzed within 24 hours.**

9.4 WASTE HANDLING AND DISPOSAL

All laboratory waste containing acetone or HCl must be handled and disposed of according to Safety and Risk Management guidelines.

ATTACHMENTS

1. Instrument History Record Form
2. Certificate of Training

APPROVALS

Author		
Technical Reviewer		
Quality Systems Manager	**Signature**	**Date**

ATTACHMENT 1

Instrument History Record Form

Turner Designs Model-10-AU

Fluorometer

Date of Action		Description of Maintenance Performed and Results	Performed by
Start	End		

ATTACHMENT 2

CERTIFICATE OF

TRAINING

SOP No. 5-265-05

SOP Title: Extraction and Analysis of Chlorophyll *a* and Phaeophytin *a* in Seawater Using a Turner Model 10-AU Fluorometer

Trainee:_____

Instructor:_____

Date Training Completed (Date/Instructor's

Initials): SOP Read:_____

Instrument Operation and Calibration:_____

Extraction and Analysis:_____

Comments:

The above mentioned trainee has satisfactorily completed the training requirements associated with this SOP. Supporting documentation (if needed) is attached.

Approved by:_____

Date:

SOP 2B: Narragansett Bay Commission (NBC) Standard Operating Procedures for Nutrients, Chlorophyll, and Total Suspended Solids Sample Collection in the Bay and Freshwater Rivers

TABLE OF CONTENTS

PRE-SAMPLING PREPARATIONS

A. Clean Filtration Equipment and Bottles

a. BE SURE TO USE GLOVES DURING ALL CLEANING PROCEDURES AND HANDLING OF EQUIPMENT.

b. All reusable sample collection bottles, syringes, and plastic filter pieces are washed with non-phosphate detergent, while suction and pump tubings are flushed with non-phosphate detergent. Following the initial wash, acid washing occurs per the procedures below.

c. All carboys and containers are acid-rinsed in 10% HCl – add acid to bottom of bottle, cap, and invert to mix. Rinse in deionized (DI) water three times. Test final DI water rinse in cap of bottle by using a pH strip; pH should be 7. Complete a final rinse of the bottle cap with DI water. Following pH check, invert bottles to dry.

d. Plastic chlorophyll filtering devices and syringes are soaked in 10% HCl for 24 to 48 hours, then rinsed with DI water three times.

e. Suction and pump tubings are flushed with 10% HCl and rinsed with DI water three times.

f. Be sure filtration equipment is stored in a manner that prevents contamination (bottles inverted or capped when not in use).

g. Please note, only the ammonia sample bottle is washed and re-used. All other sample bottles are new, sterile bottles.

B. Generate Sample Bottle Labels and Submission Sheets

a. Upon completion of the nutrient sampling schedule, ask the Environmental Monitoring (EM) Clerk to print out Laboratory Information Management System (LIMS) labels (which contain water quality analysis, sample location, sample point description, LIMS sample ID, and sample date) several days ahead of sampling for bottle preparation. In the field, monitors will record time of sampling and initials of sample collectors on the labels. Relevant field observations and other notes should be made on submission sheets.

b. Print out submission sheets the day before sampling.

C. Sample Bottle Preparation

a. Once bottle labels have been generated, pre-label all acid-washed sample bottles.

b. Bottles needed <u>per station</u>:

- 1 – 2-L bottle for initial sample collection
- 5 – 125-mL plastic amber bottles for dissolved nutrients
  - 1 – total dissolved nitrogen (TDN)
  - 1 – ammonia (NH_3)
  - 2 – nitrate (NO_3^-), nitrite (NO_2^-), orthophosphate (PO_4^{3-})
  - 1 – silicate (SiO_2)
- 1 – 500-mL bottle for total suspended solids (TSS) collection
- 1 – 250-mL bottle for non-filtered (NF) total nitrogen (TN) collection

c. 1 to 2 complete extra station sets of bottles in case of contamination or mishap.

d. Bottles needed for QA/QC procedures:

- *Field Blanks* – 5 – 125-mL plastic dissolved nutrient bottles, 1 – 250-mL TN bottle

- *Duplicates* – 5 – 125-mL plastic dissolved nutrient bottles, 1 – 250-mL TN bottle, 1 –500-mL TSS bottle
- *Equipment Blanks (conducted in controlled laboratory environment when determined necessary)* – 5 – 125-mL dissolved nutrient plastic bottles, 1 – 250-mL TN bottle

e. Make sure all bottles are kept closed until collection of sample.

D. Filters

a. Gather appropriate number of disposable 0.45-µm high capacity in-line groundwater sampling filter cartridges for dissolved nutrient filtering.

b. Gather appropriate number of 0.7-µm 47-mm diameter TCLP GF/F filters for chlorophyll filtering. Using gloves and clean tweezers, place one filter in the cleaned filter apparatus. There is one filter apparatus to use per site for chlorophyll; pre-package the filter apparatus and place in a Whirl-Pak bag. Prior to sample collection, the filter will be rinsed with DI water.

E. Deionized Water

a. Fill two 4-L acid-cleaned bottles with DI water and bring into field for collection of field blanks.

F. Field Supplies/Equipment Needed

a. Use prepared lists for River Nutrient Sampling (Attachment A) and Bay Nutrient Sampling (Attachment B).

G. Backup Field Sampling Equipment

a. Whenever feasible, backup equipment should be taken in the field for use in the event of problems with sampling gear, such as a water pump failure. The following is a list of suggested equipment that should be available if problems occur:

- Backup water pump system (if available)
- Backup filtration apparatuses
- Spare batteries to run pump unit

FIELD COLLECTIONS

It is important to remember to keep all containers closed until immediately before filling. Do not use any container that appears dirty, or appears to have been previously used. Be sure to place bottles and caps on a clean surface or hold with gloves. If sample bottles become contaminated during field collection or filtering procedures (e.g., caps fall into puddles on the ground, bottles fall on ground and get dirt inside), substitute one of the spare bottles to ensure the sample remains free of contamination. Contact of the inside of the bottle or bottle lids and necks with surfaces (bare fingers, the ground, the floor of the vehicle, etc.) can introduce contamination. Rinsing contaminated bottles/lids with DI water is not sufficient to remove contamination.

A. Stations:

RIVER STATIONS

River Stations	Latitude	Longitude
Blackstone River @ Bikepath Bridge	41.938	-71.434

Blackstone River @ Slater Mill	41.877	-71.382
Blackstone River @ Stateline	42.010	-71.529
Coles River @ Milford Rd.	41.750	-71.204
Moshassuck River @ Footbridge at Mill St.	41.834	-71.411
Moshassuck River @ Higginson Ave.	41.886	-71.408
Palmer River @ Rt. 6	41.775	-71.281
Pawtuxet River @ Broad St.	41.764	-71.391
Runnins River @ River Rd.	41.788	-71.329
Taunton River @ Berkley Bridge	41.835	-71.108
Ten Mile River @ Central Ave.	41.890	-71.340
Ten Mile River @ Omega Pond (through Nov. 2017)	41.839	-71.369
Ten Mile River @ Roger Williams Ave. (starting Aug. 2018)	41.834	-71.361
Warren Reservoir/Kickemuit River	41.739	-71.260
Woonasquatucket River @ Manton Ave. Bridge	41.833	-71.471
Woonasquatucket River @ Valley St.	41.823	-71.440

BAY STATIONS

Bay Stations	Latitude	Longitude
Phillipsdale Landing	41.842	-71.372
India Point Park	41.816	-71.396
Edgewood Shoal	41.782	-71.386
Edgewood Yacht Club	41.777	-71.384
Pomham Rocks	41.775	-71.373
Pawtuxet Cove	41.760	-71.386
Bullock Reach Buoy	41.733	-71.370
Conimicut Point	41.722	-71.355

B. Collection of Whole Sample Volume

Remember to wear clean gloves during all handling of equipment and sample collection. If gloves come into contact with potential sources of contamination (e.g., concrete, the ground, soil, railings, your face or hair, etc.), replace gloves.

a. Rivers

- Position sampling equipment as close to mid-stream (thalweg) as possible. Using the peristaltic pump and clean tubing, lower suction tube to proper depth, just below surface for rivers, and pump forward for at least 30 seconds to flush tubing with river water. Refer to Attachment C, "Hose Clearing Times" when conducting the pre-sampling tube flushing.
- Lower the sonde profiler to the same depth as the pump tubing. Record temperature, pH, depth, and salinity.
- Following complete flushing of tubing, pump a small amount of water into the 2-L sample bottle and shake and pour out, repeating this step a total of three times. Once the sample bottle is adequately rinsed, fill the 2-L bottle with sample. Make sure to move the tip of the pump tubing upwards as sample the

bottle is filling, so that tip does not contaminate the sample. Cap bottle when full.

- Raise suction tubing immediately after the whole sample bottle has been filled and capped.
- Turn off pump. Attach tubing ends to each other to complete closed circuit, wrap, and place suction tube in clean bag until next site.
- Bring sample bottle to work bench area for filtration.

b. Bays

- At each sampling site, place the horizontal water sampler into the water and "rinse" the sampler by moving it *gently* back and forth a few times to let water flow through the body.
- For all Bay surface samples, record temperature, pH, depth, and salinity from the data flow 6600 YSI sonde readings from the on-board computer, which runs continuously during monitoring.
- Lower the sampler 0.5-1 meter below the water surface for Bay surface collections and approximately 1 meter above bottom for Bay bottom collections. Once the sampler is at the correct depth, send the messenger down the line to close the ends to collect a sample inside the body and then bring up to boat.
- Fill TSS and TN bottles first (see details below in "Sample Bottle Handling, Field Filtration, and Preservation Procedures").
- Put a small amount of water from the water sampler into the 2-L sample bottle and shake and pour out, repeating this step a total of three times. Once the sample bottle is rinsed, fill the 2-L bottle with sample from the water sampler. Cap bottle and bring to work bench area.

C. Sample Bottle Handling, Field Filtration, and Preservation Procedures

a. Chemical Handling - *Review the dangers and take all necessary safety precautions in order to use the needed preservatives for chlorophyll and ammonia samples in the laboratory. In both cases, minimum volumes (i.e., drops) will be added to particulate matter for chlorophyll and filtrate for ammonium. Use syringes or pipettes, in both cases, to apply the solutions. The ammonia chloroform needs to be added after the bottle is rinsed with filtrate, which the general sampling SOP requires.*

b. Sample Bottle Handling – Non-Filtered Samples

- ### Total Suspended Solids

1. Pour a small amount of sample water into the TSS 500- mL bottle from 2-L collection bottle (stream) or sampler (Bay). Ensure correct label is applied to bottle and label contains time of collection and collector's initials. Place in cooler with ice.

- ### Total Nitrogen

1. Pour a small amount of sample water into TN NF 250-mL bottle from 2-L collection bottle (stream) or sampler (Bay). Cap bottle, shake, and pour liquid out. Repeat this two more times.
2. Fill 250-mL plastic bottle about ¾ full with stream or Bay water. Label bottle correctly and place in cooler with ice.

c. Sample Bottle Handling – Filtered Samples

Chlorophyll (for Bay samples only)

This process involves using a syringe to push sample water through a filter. The substance to be analyzed is then left on the filter and the remaining filtered water can be discarded. The only thing needed for this analysis is the glass fiber filter.

1. Prepare cleaned filter apparatus in holder set-up with chlorophyll GF/F, 0.7-um, 47-mm diameter TCLP filter.
    a. Filter and inside of filter apparatus should not be touched. Tweezers should be used in ALL handling of filters.
2. After gently inverting the water to mix, pull up about 20 mL sample water into disposable plastic 60 mL syringe from initial sample water container. Rinse syringe by shaking water inside it and then dispensing water into "waste" container. Repeat this two times.
3. Pull up exactly 60 mL of sample water into syringe. Attach syringe to filtration apparatus. Slowly push water through filter and into the extra bottle. If water passes through the filter relatively easily, filter another 40 mL of sample water through, without pushing water too hard. Stop if filtering becomes too difficult.
4. If filtered volume is different than 100 mL, record volume filtered onto label and submission sheet along with other needed information.
5. Gently agitate Magnesium Carbonate ($MgCO_3$) solution in small amber bottle. Fill small plastic disposable pipette with a small amount of the $MgCO_3$ solution.
6. Remove 60 mL syringe from filter apparatus and take off top of filter apparatus so filter is exposed. Place 3-4 drops of $MgCO_3$ around filter. Rinse pipette with small amount of DI water and place in plastic bag for reuse.
7. Using two pairs of tweezers, carefully fold filter in half and place into plastic Petri dish. Label dish with any needed info with sharpie (i.e., if volume is different than 100 mL). Wrap in aluminum foil and place in Whirl-Pak bag with LIMS label and then into a dark jar/bag in cooler.
8. Rinse syringe and filter apparatus with DI water between samples, if reusing.

Dissolved Nutrients

Remaining water in original sample bottle will be used for filtration into 125-mL bottles for dissolved nutrients. The filter cartridge must be discarded after filtration of each sample.

1. Remove the filter cartridge from the protective bag. Attach peristaltic pump tubing to the inlet connector of the filter unit.
2. Pump DI water through the filter unit in sufficient quantity to flush the filtration apparatus. Discharge the rinse water into an empty bottle, to be discarded.
3. Cap bottle of sample water and slowly invert bottle a couple of times. This is to keep water mixed before drawing water with pump.
4. Uncap dissolved nutrients bottles and arrange in a row.
5. Place rinsed tubing into center of sample collection bottle and begin pumping a small amount of sample water from original sample container into each dissolved nutrients bottle.

6. Cap each bottle, shake, and empty contents out to rinse the bottle with sample water. Repeat two times.
7. Fill bottles approximately ¾ full with filtered sample water.
8. Bottles will be pre-labeled; record date, time, and collector's initials.
9. **FOR BAY SAMPLES ONLY**: Place approximately 3 drops of chloroform into ammonia bottle, cap, and invert for preservation.
10. Make sure LIMS numbers correlate correctly from submission sheet to bottle and sufficient field observations are recorded on field sheet.
11. Place all bottles in cooler with several ice packs.
12. Run DI water through the filtration tubing to rinse tubing between samples.
13. Replace filter cartridge for each new sample (e.g., a new filter will be used for surface and bottom samples taken from the same Bay sampling point) and run DI water through filter cartridge.
14. Store filtration tubing in clean plastic bag to prevent contamination between sites.

D.QA/QC Sampling

a. Field Blanks

- The procedure for collecting a field blank consists of transporting sufficient DI water into the field and collecting a sample using identical sampling, filtering, and preservation procedures (if applicable) as described under sampling procedures above. Collect the blank as the last sample of the day, preferably, but never before the first sample of the day.

    1. Use the DI water as if it were the sample water from another location by filling the collection bottle with DI water, using whatever method is used at the regular sites (i.e., if pump and tubing are used to fill the sample containers, then use pump and tubing to pump DI water into the same kind of sample container for the field blank).
    2. This water will then be processed according to normal sample handling and filtering procedures.

b. Duplicates

- Duplicate samples shall be collected as determined by the project managers. Approximately 10 percent of all samples collected shall be quality control samples. Duplicate samples will be collected from at least one site per field crew.

    1. Duplicate sampling consists of collecting double the amount of sample water (4-L) and following the procedures twice that are outlined above in Step C: "Field Filtering & Preserving Procedures," therefore processing two sets of samples for one sample location. Invert bottle before filtering second set of samples to ensure adequate mixing occurs.

c. Equipment Blanks (in EM lab)

- Equipment Blank samples shall be collected as determined by the project managers.

1. Equipment blank sampling consists of filling sample bottles (prepared as for field samples above) with DI water.
2. Additional tests may be requested based on information needed for Quality Assurance Protocol Development.

POST-SAMPLING ACTIVITIES

A. Sample Bottle Handling and Equipment Return

a. Once all sample bottles are brought back to the NBC, TSS samples should be brought to the NBC laboratory for processing *immediately* if laboratory personnel are still available. If all labeling and submission sheets have been double checked, then bring all samples including nutrient bottles to the laboratory for analyses. If there is a need to store samples in the EM laboratory overnight, all samples will be frozen except TSS samples and ammonia samples (see refrigeration guide below):

- **FROZEN SAMPLES**
  1. 1 – 125-mL filtered TN (Total Dissolved Nitrogen)
  2. 1 – 250-mL NF TN (Total Nitrogen)
  3. 2 – 125-mL filtered nitrite, nitrate, orthophosphate
  4. 1 – 125-mL filtered silicate
- **REFRIGERATED SAMPLES**
  1. 1 – 125-mL filtered ammonia (add chloroform preservative for BAY samples; in amber bottle)
  2. 1 – 500-mL NF TSS

b. Place all equipment/boxes in the Nutrient Sampling area in the back of the EM laboratory in the proper place.

c. Begin the washing/rinsing process with all bottles and equipment needed for future nutrient, TSS, and chlorophyll sampling, if time allows.

Attachment A

River Sampling Supply List

Sonde Equipment

- ☐ Capped profiling sonde with wire zip-tied to sonde harness
- ☐ Sonde handheld computer and cable
- ☐ Bucket
- ☐ Toolbox (contained in field truck)

Deionized water

- ☐ Appropriate amount for field blank(s) and rinsing between samples/stations
- ☐ 1-2 clean squirt bottles

Nutrients

- ☐ 125-mL plastic amber bottles
- ☐ 250-mL plastic bottles
- ☐ High capacity filters, in bags (plastic filter holder, plus filter)
- ☐ Yellow peristaltic pump and tubing for filtration
- ☐ Small "bench" workstation for back of truck
- ☐ Absorbent padding material for filtering surface

TSS

- ☐ 500-mL bottles

Coolers & Ice

- ☐ 1 – Large cooler
- ☐ 1- Smaller cooler
- ☐ Enough ice packs/ice to keep samples cold

Sample water bottles

- ☐ 2-Liter Bottles for initial filling of sample water
- ☐ 2-Liter Bottles for DI rinsing of equipment

Pump

- ☐ Gray peristaltic pump
- ☐ Tygon tubing

Other

- ☐ Labels (contained on bottles)
- ☐ Gloves (various sizes)
- ☐ Tape
- ☐ Scissors
- ☐ Sharpies
- ☐ Pens and Pencils
- ☐ Tweezers
- ☐ Plastic trash bags and 1-gallon bags for clean sample equipment and trash, etc.

- ☐ Kimwipes
- ☐ Clipboard
- ☐ Field iPad

Attachment B

Bay Sampling Supply List

Deionized water

- ☐ Appropriate amount for field blank(s) and rinsing between samples/stations
- ☐ 1-2 clean squirt bottles

Nutrients

- ☐ 125 mL plastic amber bottles
- ☐ 250 mL plastic bottles
- ☐ High capacity filters, in bags (plastic filter holder, plus filter)
- ☐ Bottle (in aluminum foil) of Chloroform
- ☐ Yellow peristaltic pump and tubing for filtration
- ☐ Absorbent padding material for filtering surface

Chlorophyll

- ☐ White GF/F 0.7 um, 47 mm diameter TCLP filters
- ☐ 2 pairs of tweezers
- ☐ Bottle of $MgCO_3$ (in small brown HDPE bottle in drawer)
- ☐ Plastic disposable pipettes
- ☐ Small plastic Petri dishes
- ☐ Plastic 60 mL syringes
- ☐ Aluminum foil (for wrapping Petri dishes)
- ☐ Whirl-Pak bags (for putting Petri dishes into)

TSS

- ☐ 500-mL plastic bottles

Coolers & Ice

- ☐ 1 – Large cooler
- ☐ 1 – Smaller cooler (for chlorophyll samples, unless have dark bag/bottle to put them in with other samples in large cooler)
- ☐ Enough ice packs to keep cold

Sample water bottles

- ☐ 1 – 2-Liter Bottle for initial filling of sample water
- ☐ 1 – 2-Liter Bottle for DI rinsing of equipment

Sampling Equipment

- ☐ Niskin sampler bottle and messenger
- ☐ Tygon tubing

Other

- ☐ Labels (contained on bottles)
- ☐ Gloves (medium and large)
- ☐ Tape
- ☐ Scissors

- ☐ Sharpies
- ☐ Pens and Pencils
- ☐ Extra rolls of aluminum foil
- ☐ Plastic trash bags and 1-gallon bags for clean sample equipment and trash, etc.
- ☐ Kimwipes
- ☐ Absorbent padding material for table surface (12 large square pieces-*2/station*)
- ☐ Field clipboard
- ☐ Field iPad
- ☐ Toolbox (contained on boat)

Attachment C

Sampling Hose Clearing Times

It is imperative that sufficient hose clearing time be allowed to ensure the hose is fully flushed and the water being sampled is obtained from the intended depth. There are two ways to determine how much water must pass through the hose:

- *Air Plug method (most commonly used in NBC sampling):*
  - Turn the pump on with the draw end of the hose above the water surface to place air into the hose.
  - Turn off the pump and lower the hose to the sample depth.
  - Turn on the pump and watch for the air to completely exit the hose then begin sampling.

- *Calculated clearing times:*
  - Each time a new hose or pump is installed, a clearing time can be calculated in the following manner to ensure there is sufficient waiting time to clear the hose:

    a. Calculate the volume of the hose in gallons: $(r/12)^2 * 3.14 * L * 7.48 = V$, Where
    r = radius (inches) of hose inner diameter
    L = length (feet) of hose
    V = volume (gallons)

    b. Determine pump capacity (gallons per minute pumped) from the pump specifications.

    c. Calculate time to flush hose: V/(gpm) = time, where
    Gpm = gallons per minute pumped
    Time = minutes to flush hose

    d. Multiply the time by 1.25 as a minimum clearing time for the hose.

SOP-3

Field Procedures

Profiling

DCP/ Buoy Maintenance **Sonde Swap**

Field Notes **Toolbox & Field box Setup**

DCP & Buoy Field Procedures

Day Prior to Field Maintenance:

1. Back up latest version of configuration file to take in field.
2. Check battery power on field laptop and marine field battery.
3. Make sure direct connect cable, battery power adapter cable, DCP manual, and antenna testing cable are in field laptop case.

Day of Field Maintenance Prior to Departure:

1. Double checks to make sure the latest files were transmitted to the receiving computer.
2. Check data for any malfunctions
3. Double check weather (winds < 15kt for sonde swap only. If direct connection to DCP is required for troubleshooting problems or data download, then winds should be < 10kt) Must have no precipitation to direct connect to DCP or break DCP seal for troubleshooting problems.
4. Double check field laptop case for direct connect cable, battery power adapter cable, and antenna testing cable.
5. Be sure to grab back up marine field battery to power laptop and/or boat.
6. Bring a towel or cloth to cover screen of laptop. Plastic bags are also handy to keep connections dry.
7. Pack new desiccant, rubbing alcohol, and vacuum grease in field gear. Just in case seal of DCP canister needs to be broken and resealed in the field (troubleshooting problems only).

Field Maintenance at Buoy Site:

1. Tie up to site using eyebolts. Tie up on the down current side it makes it easier to work and causes less potential damage to the buoy.
2. Document tie up time in field notebook. Notes on GPS location weather tides, technicians, etc.
3. Check buoy for any visible damage or vandalism. Check for excessive rust around connectors. Beacon must be flashing. Inspect solar panels for any damage. Make sure all connectors are free of ice and snow. If water is on the surface of buoy, make sure no bubbles are coming from DCP canister seal.
4. Check connection. Make sure all connections are tight and free of debris. Document and clean any corrosion.

   ****If no damage is visible and no direct connection or troubleshooting is necessary then move on to sonde field procedures**.

Direct Connect for downloading files:

1. Make sure DCP cover is dry. Use towels to keep direct connect port on DCP dry from splashing and mist.
2. Setup laptop with direct connect cable to computer and DCP. Make sure appropriate COM port is chosen. (Generally just COM Port 1 on laptops). Cover connections in plastic if possible. Use dry towel to cover laptop screen to protect it from sun damage.
3. Open program and download latest data
4. Data will appear on the screen. Check each window to make sure data is being logged.
5. Conduct troubleshooting if data does not transfer
6. At the bottom of the window it will say interrogating until data retrieval is complete.
7. Make sure settings are set for appropriate unattended sampling (cell, radio, direct connect, etc). Then close window and disconnect cable and shut down laptop.

***Tip- keep direct connect and integration window open until after sonde swap. This allows for potential data problems or communication problems to be identified.*

Field Profiling Procedures

Day Prior to Field Maintenance:

1. Check battery power on field handheld (YSI 650) and memory. Pack in waterproof and shockproof container for storage and transport.
2. Make sure direct connect cable, weight for profiling sonde, and cover for YSI 650 screen are packed in field supplies.
   *** YSI 100ft. Field cable (sonde connection & military clip connection for YSI 650) coiled in a round tote with hole cut in for YSI 650 end to pass through. This minimizes kinking of cable and maximizes cable life*.
3. Pack calibrated profiling sonde and sonde guard.
   (*See Calibration section for calibrating sonde prior to use*)
4. Connect profiling sonde to field profiling cable. Be sure to seal with silica grease and cable guard clip is attached to sonde handle. Weight can be tied to guard clip at this point.

Seabird or other profiling devices may be used instead of YSI 650 and sonde. Make sure to have equipment (batteries and cleaning devices) to troubleshoot equipment in field

Day of Field Maintenance in Route to Site:

1. Place sonde guard on sonde. BE SURE NOT TO HIT SENSORS! May need to bring weights if current or wave action is strong.
2. Wrap sonde in wet white towels. The towel keeps sensors cool and wet for air saturation reading before deployment.
3. Turn on YSI 650. Let instrument warm up for 10 min if YSI before sampling.
4. Check data to make sure all parameters are reading properly before profiling.
5. Log sampling if possible, for later use in QA/QC process.
6. Good idea to bring a cover for display unit to prevent damage from waves and sun.

Field Sampling at Buoy Site:

1. Record readings at air saturation (recording while sonde wrapped in wet towel).
2. Make sure cable and weight are secure. Then place sonde overboard. Make sure sonde is at the surface (water level should be about halfway up the sonde).
3. Wait 2 minutes and record readings at the surface. Make sure instrument is working properly before conducting profile. Note variability in the readings.
4. Carefully lower sonde to bottom. Let weight hit the bottom. Pull up a little on cable. You want to position the sonde so that it is about 1 foot from the bottom. Let sonde stabilize for 2 minutes then record readings.
5. After readings recorded raise sonde 1 meter until back at surface.
6. Take sonde out of the water. Rinse with tap water. Put sonde cap over guard or wet towel. Let stabilize to record air saturation reading for QA/QC purposes. Then, highlight **stop logging** and hit **enter**. Then hit escape to disconnect from the sonde.
7. At the end of sampling, be sure to put cap with a little tap water back on sensors for storage.

Once back in Lab:

1. Download data if logged to instrument
2. Label file with site and date name.
3. Store data files so they can be used in the QA/QC process
4. Do a post cal check on sonde to make sure it was working properly the whole sampling time period.

5. Field Notes Suggestions

Day Prior to Field Maintenance:

1. Be sure to use a weatherproof notebook.
2. Make sure to pack back up writing utensils (pens, permanent markers, and pencils).
3. Prep field notebook by setting it up with the following headings:

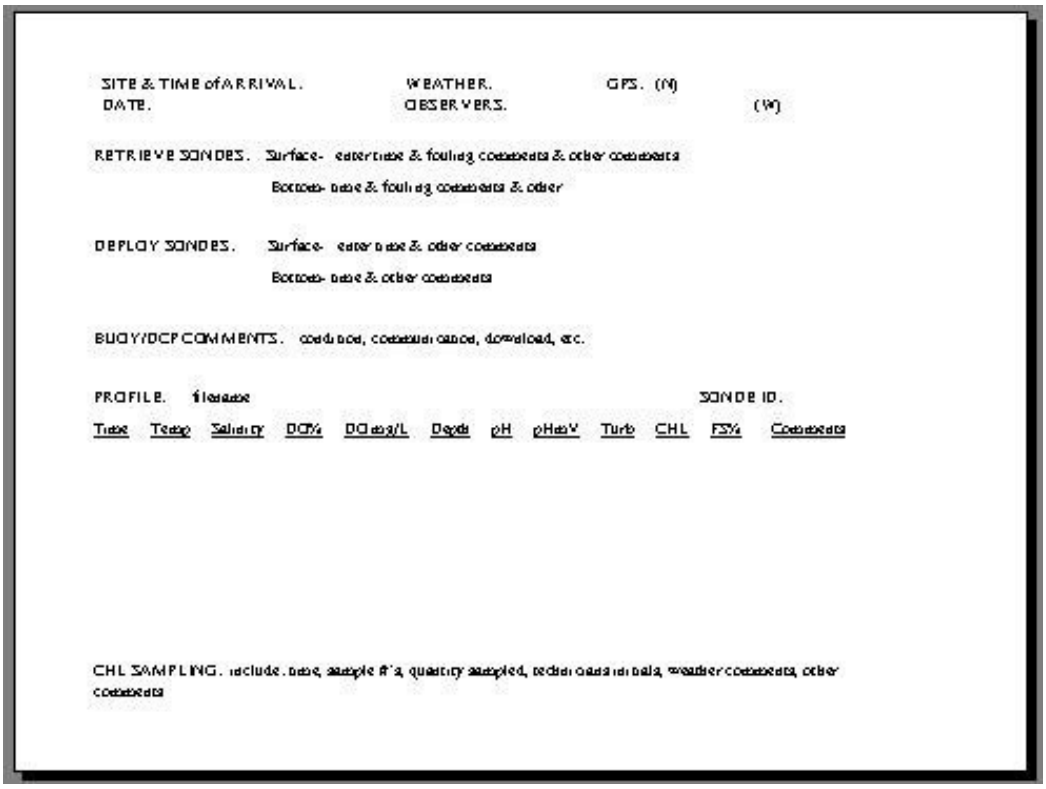


Figure 5-2. Field Notes.

Field Sampling At Buoy Site:

1. Fill in every section by following all field procedures.
2. If for some reason a field procedure is skipped be sure to note why.
3. Always a good idea to have one person to record field notes.
4. In buoy comment section, if nothing is to report be sure to note: *everything is operational.*
5. **REMEMBER MORE INFO IS ALWAYS BETTER THAN NOT ENOUGH!! GOOD FIELD NOTES ARE FUNDIMENTAL TO GOOD DATA!!**

Sonde Swap Field Procedures

Day Prior to Field Maintenance:

1. Pack calibrated sondes with guard (including freshly rinsed with tap water sponge) in a carrying bucket. Make sure large enough for all to fit upright and sturdy enough to handle the weight.
2. Label all sondes to prevent confusion in field. Example: S=Surface, B=Bottom, Site name, SDI address and date calibrated (S111, SDI=0, 5/10/03). If more than one technician is calibrating it might be a good idea to put their initials on the label. The best label is electrical tape.
   ***Recommended: different color electrical tape for surface & bottom sondes*
3. Pack towels, rags, soft cloth, toothbrushes, sponges, *Kimwipes*, Q-tips (cosmetic ones are best), O-ring grease, extra sonde caps, 2 spare buckets, and other cleaning brushes.
4. Make sure your toolbox has all the tools to troubleshoot buoy problems and do the sonde swap.
5. Toolbox needs for sonde swap: zip ties, sockets 7/16" depending on brackets holding sondes, spare brackets and nuts and bolts, snips, small adjustable wrench, large adjustable wrench/pliers, extra caps, spare shackles, spare bracket holder, electrical tape, ss hose claps, screwdrivers, and WD-40. (see toolbox setup for more info)

Sonde Swap at Buoy Site:

1. It is always a good idea to travel to the site with two technicians. You can divide up the field procedures to reduce time at each site. Weather should be < 15 knots to swap sondes safely.
2. First step is to record the time, tide and weather conditions. Pull sonde. Keep cables attached to instruments.
3. Make notes of the status of sondes and cable. Pictures are always a good idea. Clean brackets and cables first. The green scrubby is ideal for cleaning cables.
4. Be sure to make notes of fouling and other conditions (e.g., wear & tear on cables, brackets, and sonde).
5. Then wiper clean sonde (NOT SENSORS). Just use clothes to clean of growth.
6. Finally, clean then dry cable connection area. Toothbrush and *Kimwipes* are ideal for this task. Release safety clip, then cable to sonde connector. IMMEDIATELY, dry with *Kimwipes* and place caps on both ends.
7. Have newly calibrated and labeled sonde handy. Remove cap. Clean, dry, and apply new O-ring grease to top of new sonde, if necessary. Make notes of any cable damage. Then connect cable to new surface sonde. Fasten clip to sonde handle.
8. Put new sonde in and re-secure to buoy.
9. Put surface sonde in guard cup and place in transport bucket.
10. BE SURE TO NEVER PUT AN UNSECURED SONDE OVER THE SIDE OF THE BOAT!
11. Bottom or other depth sondes require cleaning as rope and cable are being raised. Green scrubby is ideal for the task and insulated gloves. The cable should be secured to weighted rope that allows for slack on cable and tension on rope. Be sure to bring cable and rope in boat. If left in the water, it can get tangled with counterweight.
12. Lift the sonde and anchor on board in one motion. This will prevent any damage.
13. Follow same instructions for sonde cleaning. Slowly lower cleaned sonde, cable, and rope into water. Feel for the anchor hitting the bottom before releasing.
    ***Bottom sonde deployed on West Side. DONOT TANGLE with mooring ropes.*

Toolbox & Field Box Suggestions

Toolbox Contents:

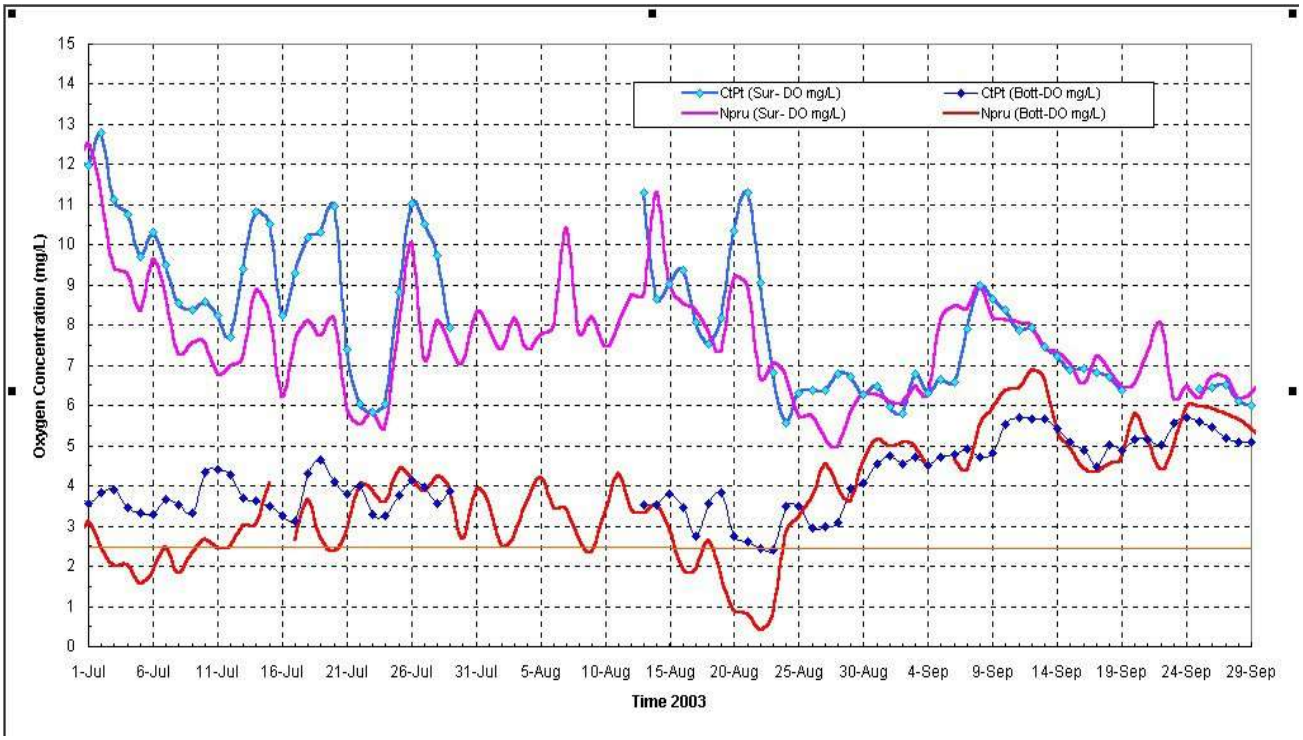
- Snips, screwdrivers, WD-40, vacuum tester, sockets (7/16, ½), Allen wrench, Allen head bolts for DCP can/ss bucket, bolts for antenna, zip ties, O-ring grease, caps, o- rings, DO changing supplies (membranes, KCL solution, utility knife), adjustable wrenches (2 sizes), pliers (2 sizes), seizing wire, bracket fixtures, shackles, electrical tape, duct tape, and lock de-icier.

Field Box Contents:

- GPS, charts, Kimwipes, Q-tips, field notebook, pens, back-up batteries (AA & C), battery tester, back-up configuration discs, *Ziplock* bags, YSI 650, flashlight, back-up beacon flasher, operation manuals, field checklist, cell phone, and float plan w/ contact info.

SOP-4

NBFSMN Data Management for Corrections



Raw Files

Working Files

Data

Management

Data management is used as a quality control measure for the data collected by a continuous water-quality monitoring program. To ensure the highest quality data, the data must be triple checked and be well documented. The data is triple checked by using the calibration/post-calibration information, the sonde swap information, and the spot check or profile information. All of these steps require accurate documentation to be meaningful in the data management process.

The data management process consists of downloading and formatting the raw files, examining the data for sensor operation outliers, checking for subtle instrumentation variability, possible data correction alternatives, and formatting the final data files. All of these steps need to be processed and archived uniformly.

Raw Files:

Data are downloaded using three main pathways: (1) directly from the sonde, (2) from the YSI handheld logger (YSI 650), and (3) transferred to a base station computer. All use YSI compatible software. Therefore, all files are downloadable. For the purposes of this manual, we will just discuss downloading for the sonde and transferred data from the DCP to the base station computer. The YSI 650 downloading procedures are available in the appendices of this manual or from the *YSI 650 Operations Manual*.

The software allows for two types of downloads: a dat format or a comma delimited format, producing txt or csv files. From there, the data parameters can be formatted for consistency and then be exported into a csv or txt file for further QA/QC using a number of software packages. Some of these software packages are *MS Excel*, *MS Access*, and *Matlab*. For the purposes of this manual the data will be exported into *MS Excel* to explain some of the QA/QC procedures.

Downloading from the Files-

The sonde will need to be downloaded only when it has been programmed to log internally. The downloading procedures are described in the YSI manual. When data are not available through the sonde, the files from the DCP or datalogger can be used. Files should be in text format and stored by deployment date.

Files are formatted by parameters using the following formatting from the YSI manual:

Parameter	Short Name	Units	Format
a. Date	**Date**	**mm/dd/yyyy**	**mm/dd/yyyy**
b. Time	**Time**	**hh:mm:ss**	**hh:mm:ss**
c. Date & Time	**C**	**mm/dd/yyyy hh:mm**	
d. Water Temperature	**Temp**	**°C**	**00.00**
e. Specific Conductivity	**SpCond**	**mS/cm**	**00.00**
f. Salinity	**Sal**	**ppt**	**00.00**
g. Dissolved Oxygen	**DO**	**%**	**000.0**
h. Dissolved Oxygen	**DO_mgl**	**mg/L**	**00.00**
i. DO Charge	**DO c**	**units**	**00.0**
j. Depth	**Depth**	**m**	**0.000**
k. pH	**pH**	**units**	**00.00**
l. pH mV	**pH**	**mV**	**00.0**
m. Chlorophyll	**CHL**	**µg/L**	**00.0**
n. Total Fluorescence	**FS**	**%**	**00.0**
o. Turbidity	**Turb**	**NTU**	**00.0**

The data order and measurement units of the YSI data logger output can be changed, if need be.

See the YSI and/or software manuals for these features.

Working Files (Setting Up Files in Excel for QA/QC) :

1. If the site has surface and bottom readings, it is best to set up a file with both readings in the same spreadsheet. It will add important insight into the review and editing process. Copy and paste in the template.

Mount View Water Column Time-Series 2004: These data are preliminary; they are subject to corrections after post-c
For information on use of these data please contact Candace Oviatt (401-874-6661; coviatt @gso.uri.edu
Graduate School of Oceanography, University of Rhode Island

	Surface Sonde						Bottom Sonde					
Date & Time	Temp C	Salinity ppt	DO% %	DO Co mg/L	Chl ug/L	FS %	Date & Time	Temp C	Salinity ppt	DO% %	DO Conc mg/L	Depth m
8/5/2004 0:02	24.15	30.25	98.2	6.93	12.2	2.9	8/5/2004 0:02	22.51	30.99	73.3	5.30	6.370
8/5/2004 0:17	24.13	30.12	97.8	6.92	12.5	2.9	8/5/2004 0:17	22.49	30.99	72.5	5.24	6.310
8/5/2004 0:32	24.23	30.18	101.4	7.16	11.8	2.8	8/5/2004 0:32	22.62	30.96	75.1	5.42	6.240

Figure 6-5. Excel Headings for working file

2. Save the file according to the map code, agency, site, and year. Use the extension working.xls. This will become your working file. There is no need to use abbreviations for names in Excel.
   Example: B5.GSOmv2004.working.xls

3. Now graph the parameters. Use the column D date and time for the *X*-axis on all graphs. Use the following template as a guide. Feel free to add other graphs. This template only offers the minimum to guide the review and editing process. Simply copy and paste the data from the **txt** files into this template. Make adjustments based on the parameters measured. **The working files are f o r internal use only by the data reviewer. Only the final formatted files are to be used for data distribution.**

   graphing template for surface and bottom sondes.xls

4. Other programs such as *Matlab*, *Streamline* and CDMO can also be used for review. The corrections are completed in Excel and edited and corrected files are distributed in Excel for the most universal user format.

5. In the end, each station will post a raw, edited, and corrected versions of the dataset on a yearly basis. These datasets are posted to the RIDEM-OWR BART webpage. (www.ridem.gov/BART**).**

Once formatted properly and graphed, the working file is ready for data review and editing. The working file is used to create the review file, editing file, and final formatted file. The next section will explain the principles behind editing the raw data and general guidelines for deleting data. These guidelines come directly from the CDMO manual and were adopted in 2004. There may be adjustments made in future sampling seasons.

Data Management QA/QC and Correction Protocols:

After the completion of the QA/QC process two data files are generated for the NBFSMN annual dataset report. The edited file will contain only QA/QC data. When data is deleted it will have a blank for the time stamp, but all time stamps will be accounted for. The second file is a corrected dataset file. It is designed to minimized data gaps by applying correction factors if justifiable. All calculated data are in bold and highlighted in bright yellow. If there are suspect data that could not be justified but fall under discretionary deletion they will be highlighted in light yellow only.

This section will cover the general philosophies for data acceptance and rejection. These protocols come directly from the CDMO manual (http://cdmo.baruch.sc.edu/documents/manual.pdf).

Introduction-

The following document has been prepared to aid users of the YSI products in ascertaining the reliability of the data from their deployments. This document is clearly not designed to be the final word on the data review and editing issue, but instead to simply be a starting point for consideration, rejection, and modification by the NERR System-wide Monitoring Program as more experience is acquired and more data are generated and processed.

The general philosophy for data acceptance or rejection will be based on absolute and discretionary factors.

Absolute: In the first phase of data review and editing, values sometimes can be rejected on the basis of absolute factors via software statements with no detailed analysis of the study by the Data Manager or reviewer at each site.

Discretionary: These are other instances in which the data must be examined after absolute rejection. In the second phase, we are recommending that the data reviewer evaluate each deployment study.
These anomalies can be somewhat subjective. Discretionary anomalies are based on pre- and post- calibration information, field information, profiling data, etc.

Absolute data rejections-

Following the absolute data rejection criteria begin the data review process. All data that is rejected is to be deleted only during the data review process. Document all deletions. Leave the data cells blank. Save the file using the same format as the master file with ***data review.xls*** as the extension instead of *masterfile.xls.*

The Value Recorded in the Sonde Memory is Outside the Listed Range Specifications of the Instrument: The following criteria are based on the latest YSI 6-Series Environmental Monitoring Systems
Operating Manual sensor specifications and are what the NERR CDMO error checking criteria are based on. The Narragansett Bay Water Quality Monitoring Network has adopted the follow criteria, as well.

Temperature: -5 to 45 °C
Specific Conductivity: 0 to 100 mS/cm
Salinity: 0 to 70 ppt
Dissolved Oxygen (% Saturation): 0 to 200 and 200 to 500 % air saturation
Dissolved Oxygen (mg/L): 0 to 20 and 20 to 50 mg/L
Shallow Depth: 0 to 9.1m
pH: 2 to 14 units
Chlorophyll: 0 to 500 ug/L
Turbidity: 0 to 1000 NTU

Always reject data that are outside of the range of the probes. The only exceptions to the absolute data rejection for out-of-range values are for the shallow depth, chlorophyll, and turbidity probes. These exceptions are explained under their respective headings in this document.

An Unexpected Tidal Fluctuation or an Improperly Deployed Sonde:

Usually a very low (near zero) or a very sharp decline in conductivity readings will indicate these situations even when the unit is known to be at a site characterized by brackish water. This effect

is demonstrated in Figure 6-6A where it is evident that the water level has dropped below the conductivity sensor on several occasions. In the study associated with Figure 6-6B, the sonde seemingly came out of the water midway through the study and remained there.

Reject all of the data in these areas of the data record, not just conductivity/salinity because it is impossible to tell whether the other sensors were in the water at the time of measurement. Remember to leave the time stamp within the dataset during the data review process.

Times of pre- and post-deployment when transporting the sonde:

Figure 6-7 and the beginning of Figure 6-9 show that the beginning and end (tails) of data (pre- and post- deployment) are not in range of the other readings. Note that the time on the sonde is not always the same as what is on your watch, especially during daylight savings. Remember that any data collection including that of the data sondes should be recorded in standard time only NOT daylight savings time.

All data should be examined for these types of data, and **the tails should be rejected and deleted** from the deployment record.

In DCP setup, the DCP will record –1000000 or NaN when the sonde is not connected or is having difficulty communicating with the sondes. Reasons for the DCP to record –1000000 or NaN are as follows:

- Cable communication errors. Examples are leaking cable, broken cable, pins bent, etc.

- Internal codes of the sonde. Generally, this occurs when the sonde has not been updated. The sonde and DCP codes don't match up. Examples are a newly repaired DCP trying to communicate with older sondes. To prevent this from happening, keep track of the software version the sonde is using. This is found under the **status menu** of the sonde. The DCP will have trouble communicating with versions older than 2.16 and will not communicate with the YSI 6000.

- During the sonde swap, when the sonde has been disconnected from the cable.

All –1000000 or NaN are to be deleted from the data set. Document the reason for the recorded –100000 in the metadata. DO NOT DELETE THE TIME STAMP! ALL TIME STAMPS ARE TO REMAIN IN THE DATA SET.

No sensor installed Values:

All probes will register a value even if there is no sensor installed on the sonde. This is a situation that cannot be replicated (for example, the motherboard does not always register the same values when the sensors are missing)!

Always delete data for sensors that have not been installed. Always document when you are missing a sensor for each deployment.

In time, experience may indicate other absolute data rejection criteria. At this time, the Narragansett Bay Water Quality Monitoring Network has agreed upon all of the above absolute data rejection criteria.

Discretionary data rejection-

In this part of the procedure, data analysis of all recorded parameters should be carried out by or under

t h e supervision of the site Data Manager. If anomalies are observed, the anomalous data may be marked as an anomaly, left in the data set and documented, or rejected and removed at the discretion of the data reviewer or data manager in the final format for distribution. **Data rejection, anomaly documentation, and data deletions are done during the data review process.**

Data review and editing should take place as soon as possible after sonde recovery so that the details of the deployment will be fresh in the minds of the site personnel and if anomalies are found, corrective action can be attempted prior to the next deployment. Immediately after recovery of the sonde, both YSI and the CDMO recommend an upload of the data file in the PC6000 format followed by cursory analysis of the data using the plotting function of the YSI-supplied *Streamline, EcoWatch, or* other compatible programs. The DCP transferred data should be reviewed on a daily to weekly basis. This action will provide insight into whether problems occurred with any of the sensors during deployment, which might be grounds for rejection of portions of the data. It also helps to reduce erroneous data by providing an opportunity to troubleshoot problems as soon as possible.

All files should be archived at the individual sites (AKA base station computer). These are the true raw files. Therefore, all data records (good and suspect) will be present. Also, PC6000 (.dat) files can always be used to export comma-delimited files using *EcoWatch,* Streamline, or other compatible programs.

In the discretionary evaluation of the data, each sensor should be evaluated individually. Usually the data manager should be looking for a discontinuity (sudden jumps high or low - to out of range values or other anomalies) in the data, which indicates a sensor has failed catastrophically during the deployment. This type of failure can be either reversible (wiper covering Chlorophyll sensor) or irreversible (broken pH probe, for example).

In general, all data resulting from a known failure of a sensor within a particular deployment should be rejected. However, an exception to this general rule may apply in some turbidity studies as discussed below. A listing of possible failure mechanisms for each sensor is provided below. In some cases, a figure documenting a data discontinuity, which appears to be associated with the failure mechanism, is also provided.

REMEMBER TO DOCUMENT ALL ANOMOLIES IN THE METADATA WHETHER DELETED OR NOT!

It is a good idea, if using Excel for the data review process, to **highlight** all suspect data. It will make the data reviewer's job easier to review these anomalies in more detail later, if they are highlighted.

Once the review of data is completed, the corrected file will have highlighted a bold for any calculated values, raw data will be in normal cell formatting, suspect data will be highlighted only, and deleted values will be empty cells in the excel file.

Time:

On occasion, time jumps (from seconds to minutes) can occur in the data logger file for no apparent reason. There are two explanations for this. First, the data logger could have been interrupted by an uploading session while the sensors were trying to record water quality data or the contacts between the batteries and the sonde (the metal coil) had gotten damp and needed cleaning.

It is important to document in the metadata when the time was off. The CDMO pre-processing Excel macro will correct all times for you to the nearest half or quarter-hour. **All time stamps must be accounted for.**

Time Gaps in the data file & Internal Device Error statement-

If time gaps are observed in the uploaded data file or if a time gap is suspected, then you may have an Internal Device Error problem with the sonde. This is an indication of a handshaking problem between the internal boards of the instrument. When the board that runs the sensors transfers the sensors' signal to another internal board, there occasionally can be a communication problem. When a communication problem does occur, an Internal Device Error statement appears and there is a statement on a timeline that the error has occurred INSTEAD of the data. Thus, when an Internal Device Error occurs there are no data at all at for that time. The message indicates that a sample is missing. It does not mean that the data before or after the error message is bad. In the file report, the only evidence of an internal device error is a time gap in the data.

Note: An internal device error statement is only visible in the "viewed data" and not in an "uploaded data" PC6000 formatted file. View the data on the screen using the View command from the sonde and look for the internal device error log.

Any data that is recorded in the memory is probably okay since internal device errors do not affect sensor performance, only internal communication. Contact YSI to determine how to recover your data.

All data collection including that of the data sondes should be recorded in Eastern Standard Time (EST) only, NOT daylight savings time.

Temperature:

The temperature sensor on the YSI 6030 probe rarely fails. If it does fail, the malfunction is inevitably irreversible due to leakage of environmental water into the thermistor container. Although we have only very limited experience, the failure of the temperature sensor is usually signaled by jumpy and/or clearly incorrect readings. If a problem is suspected, the accuracy of the thermistor can be checked on return vs. another Model 6000 or a mercury-in-glass thermometer.

If a clear point of temperature discontinuity is present in a data record, all temperature readings from that point on should be eliminated from the final format to be used for distribution. This point might be signaled by a sharp jump in temperature to an unexpected value or an overall drift that seems unreasonable.

Since the data from most all other sensors (salinity, specific conductivity, depth, dissolved oxygen mg/L, pH, turbidity and chlorophyll-a) is temperature compensated using the values from the thermistor, all values for all logged parameters after a temperature probe failure should be viewed as suspect and eliminated from the official record. Thus, because of the ubiquity of temperature compensation, failure of the temperature sensor is particularly serious for the overall data record. This is demonstrated in Figure 6-8 where the temperature sensor failed during the study. However, remember that temperature probe failure is extremely rare. All suspect and erroneous data should be documented.

Conductivity/Salinity:

The conductivity sensor of the YSI 6030 probe seldom shows catastrophic failure. If an error occurs, the symptom is usually a drift of the overall conductivity output due to a changing of the cell constant during deployment. This cell constant change is, in turn, usually due to the presence of fouling in the cell compartment that causes a change in the effective volume. If the perturbation only involves the coating of the cell and electrodes with a layer of fouling, the change in cell constant is usually not significant. However, the formation of barnacles in the cell constant will result in readings that are in error.

A post deployment check of the sensor in a solution of known conductivity (not necessarily a primary standard) will allow the data reviewer to assess the extent of the drift. Cleaning of the sensor as described in the manual almost always reverses the drift caused by significant change in the cell volume. **If a reversible drift is suspected, a linear compensation based on quality assurance data (pre-, mid-, and post-deployment) is possible using an appropriate calculation**. YSI recommends that the decision as to whether to employ this (or any) compensation be left in the hands of the data reviewer. Any data compensation calculations will occur during the data editing process. If a drift has occurred, only highlight and document the extent of the drift during the data review process. **Discretionary compensation calculations and data removal calculations are used by the Narragansett Bay Water Quality Monitoring Network and only present in the corrected version of the data.**

In the unlikely event of a total sensor failure, a sharp discontinuity will usually appear in the output. All readings (salinity, specific conductivity, dissolved oxygen mg/L and depth) after this type of failure should be eliminated from the final format for distribution.

Remember though that sharp discontinuities in conductivity can also be due to the sonde being out of the water, as is described in the Absolute Data Rejection section above or as a result of an incorrect calibration. The BEST indicator of determining whether a sonde was out of the water is to use the Conductivity data. See figure 6- 6A and 6-6B. Use the conductivity data in conjunction with depth values to help with decision-making. In addition, it is recommended to use other salinity information, the profile data, rainfall data, and flow data when available.

If the sonde was determined to be out of the water, reject ALL YSI data in these areas of the data record because it is impossible to tell whether the other sensors were in the water at the time of measurement.

Occasional Low Salinity/Conductivity Spikes-

Occasional low value spikes that are not consistent with the overall data record may be real (Figure 6- 12). Generally, these spikes are caused by organisms getting stuck within the sensor opening or from sediment build-up. Reject or accept spikes in conductivity and salinity values at the site's discretion.

The best way to visually examine these types of spikes is to plot surface and bottom salinity readings for each site together on the same y-axis. In addition, plot the salinity readings with rainfall or flow data on a secondary y-axis. The spikes are easily highlighted by plotting the x-axis using the date and time (use the date and time formatted in the same column).

To automate data screening for low salinity spikes, agencies have adopted different methods. Since 2004, the data manager used a 95-percental rejection method based on a seasonal basis.
Generally, there are two comparable methods used to screen for data spikes:

i. Since not all parameters are normally distributed, such as conductivity, a 95% rejection method can be applied. Any value that is outside the 95% range around the median (median based on seasonal averages). This method is applied when there is an offset at the sonde swap. See data manager for more info.

ii. Another method used by NBFSMN, incorporates overall max and min data observed at the site and rate of change between each data point. The rate of change is based upon the 95%, 2 times the standard deviation or 2 times the nearest neighbor rule. This is applied to individual readings

iii. If surface & bottom salinity are available for the station, then plot together and delete salinity values from the bottom that are significantly less than surface. In addition, plot with river flow data to determine if spikes are real or erroneous.

However, do not reject or delete the data, unless you are absolutely sure that they are erroneous data.

If you do not reject the data, leave the data in the file and document them as anomalous in the metadata. If you do reject them, delete and document them in the metadata.

pH:

Like the conductivity sensor, the pH probe seldom shows catastrophic failure. However, the probes only have about a two-year life span. If an error does occur, the symptom is usually an offset of the overall pH output due to a perturbation of the reference electrode during deployment. A post deployment check of the sensor in a solution of known pH (usually pH 7 & pH 10buffers) will allow for assessment of the extent of the drift. The drift is usually confined to the sensor offset, not the sensitivity, and while not reversible *per se*, can normally be "calibrated out" prior to the next deployment. A decision to employ this (or any) compensation should be left in the hands of the data reviewer.

In the event of a complete sensor failure (most likely due to breakage of the glass bulb),

a. a sharp discontinuity may appear in the output,
b. the readings may either be totally unreasonable,
c. the ISE1 mV output in the Diagnostics submenu may be exactly 0 mV no matter what solution the sensor is immersed in, and/or
d. readings will show a great deal of noise.

All readings after this type of failure should be eliminated from the final data set for distribution.

A more subtle clue to a near sensor failure (due to probe age or due to the gel drying up) indicates that the sensor will read from 5 to 6 units no matter what calibration solution it is in. The probe will not calibrate to any calibration standard. All readings from this type of failure should be eliminated from the final format.

Another clue to a near sensor failure due to probe age is that the pH sensor appears to be working fine when the probe is submerged in a particular pH standard (for example, if the standard is a pH of10, the probe's readings will be near 10), and it appears to track changes in pH; but when you try to calibrate the probe, the calibration is not accepted. After soaking the probe to restore it, it may appear to work properly and accept calibration. However, within a few weeks the message "calibration not accepted" may again be generated during calibration.

YSI technical support stated that this problem might also indicate that the internal coefficients for the pH calculations are incorrect (which will be the case for a newly installed pH probe). Corrective action in this case includes clearing the internal coefficient values and re-calibrating with a 2-point calibration. Contact YSI for specific procedures to check, clear, and reset the sonde internal coefficients. All readings from this type of failure should be examined carefully before being submitted to the final format for distribution.

If an offset has been documented throughout the whole deployment (figure 6-9), NBFSMN applies a correction constant (using the offset value between deployments) to adjust data to line up overall dataset. This sometime can occur when sensors are aging or when there is a slight calibration offset between sensors. The offset correction is only applied when there are inconsistencies among sensors and no other parameters. The corrections are only applied to the corrected files, highlighted in dataset, and documented in metadata.

Dissolved Oxygen:

The oxygen sensor of the YSI 6030 probe is susceptible to both drift and catastrophic failure during deployment. Optical DO sensors dramatically reduce this because of the wiper and structure of sensor. The most common error found with optical sensors are based on sensor operation (negative readings) and out of the water readings of the sensor. The negative values and/or out of the water readings are deleted for the edited file and corrected files. Where applicable, data is calculated using the average of adjacent sensor readings.

Optical sensors have minimized drift in sensors. Drift is usually caused by deposition of a layer of biological fouling on the sensor membrane. The puncturing of this membrane by biological fouling usually causes catastrophic failure. A post-deployment check of the sensor in a medium of known DO content (usually water-saturated air or air-saturated water) will allow the reviewer to assess the extent of the drift. If a reversible drift is suspected, the suspect data is graphed to determine the beginning of the offset. Once the beginning is determined, the erroneous data is deleted for the edited file. In the corrected file, a linear compensation based on quality assurance data (pre, mid-, and/or post deployment) is applied to correct for the sensor drift. YSI recommends that the decision as to whether to employ this (or any) compensation be left in the hands of the data reviewer. NBFSMN applies this principle to the corrected dataset.

Membrane Fouling-

As of 2018, all stations do NOT use membrane sensors unless an optical sensor/sonde is broken. Membrane sensors are only used as a backup method. Membrane sensors are prone to puncture, drift/DO tarnish, and failure. If the membrane is improperly installed or is punctured during the deployment, the sensor output is generally characterized by a large discontinuity. Figures 6-10 and 6-11A-C demonstrate this effect that is suspected to be due to membrane holes. Figure 6-10 shows DO failure at the beginning of the deployment and could well be due to improper membrane installation. Figures 6-11A-C shows failures during the deployment that are likely due to a membrane puncture from debris or animal activity. In most cases, the DO readings become unreasonably high very quickly and then drift off to varying extents. In Figure 6-11C however, the readings simply rise precipitously at the suspected point of puncture and then become noisy. For both symptoms, YSI suspects that the cause of the error is "cross talk" through the membrane hole between the DO and conductivity sensors in the conductive brackish water medium.

In all cases, all percent saturation and dissolved oxygen mg/L readings after the discontinuity should be eliminated from the final data set for that deployment record. Note, however, that sensor malfunctions from membrane punctures usually affect only the DO data of the deployment in question -- reconditioning and re- membrane the probe correctly prior to the next deployment will likely return the sensor to its proper operating condition.

The dissolved oxygen sensor can occasionally fail during a deployment due to electrochemical or materials failure (fouling of the anode, internal short in the probe, etc.). These problems are usually characterized by a discontinuity in the data record and can usually be confirmed by the presence of high DO charge and/or noisy or negative readings during the post deployment check of the DO sensor. As for membrane punctures, the sensor is not likely to recover function during a deployment once these events have occurred and therefore, all DO readings associated with this deployment after the discontinuity should probably be eliminated. Some of the latter symptoms (internal shorts, material breakdown from age) are irreversible and will require probe replacement. For fouling of the electrodes, however, probe function can usually be restored by reconditioning the probe face with the fine sandpaper found in the 6035 kit.

A post deployment check of the sensor in a wet towel or aerated bath (100% air saturation) will allow the data reviewer to assess the extent of the drift. Cleaning of the sensor as described in the manual almost always reverses the drift caused by significant change in the cell volume. **If a reversible drift is suspected, a linear compensation based on quality assurance data (pre-, mid-, and post-deployment) is possible by calculating it linearly in Excel**. YSI recommends that the decision as to whether to employ this (or any) compensation be left in the hands of the data reviewer. Any data compensation calculations will occur during the data editing process. If a drift has occurred, only highlight and document the extent of the drift during the data review process. **Discretionary compensation calculations and data removal calculations are still under review by the Narragansett Bay Water Quality Monitoring Network.**

Depth[1]:

The shallow depth sensors used within the NBFSMN are a non-vented probe that is very susceptible to changes in barometric pressure. Negative depth values are a possibility when the sondes are deployed in shallow estuaries, as shown in Figure C-7. Do not reject the depth values or the data for the other probes based on **negative** depth readings alone. Examine the other probe's readings (primarily specific conductivity) to determine whether or not the sonde was actually out of the water. (See the information about how the specific conductivity (4.8) can be used as an indicator of the instrument being out of the water).

Make sure that the probe was out of the water before rejecting and deleting the negative depth and other sensor values! If the depth probe was out of the water, the depth reading(s) will be negative and the other probe reading(s) (especially specific conductivity and salinity) will also be bad (Figure C-1A and C-1B). Reject, delete, and document all data after it has been determined that the sonde was out of the water.

If the depth probe was not out of the water and the depth readings are negative, the other probe readings will be in line with the previous data (Figure C-7). Do not reject the data but mark the negative depth data as anomalous and document it in the metadata.

From discussions with YSI's John McDonald (January 1997), it was determined that with the non- vented level probe, measurements could be as much as 0.39m (1.3 feet) off with an intense low-pressure hurricane event. Keep this in mind when evaluating these data.

Note: The outlier programs (r, Streamline, Excel macros) will still flag negative depth values (anything < zero), but this is done on purpose to warn you that the data may be erroneous and that the data need to be examined and evaluated.

[1] Even though the depth probe is not supposed to measure below zero, it was agreed at the NERRS meeting at St. Simons Island, GA (November 1996) that negative depth would be allowed (and categorized as anomalous) due to the way the sensor could be influenced by low pressure weather systems.

Turbidity:

The 6026-turbidity sensor associated with the YSI 6000 is usually not susceptible to drift *per se*. Since turbidity is not consistent parameter collected by every station within the NBFSMN, it is up to the site manager to include this parameter in the final annual reporting. This means that there will generally be little need for manual compensation of readings during a deployment due to the fouling or sensor drift that may affect the conductivity, pH, and dissolved oxygen sensors. The turbidity sensor can, however, produce erroneous readings for reasons other than drift such as mechanical failures. Examples of these are leakage of water into the sensor housing and scratches on the optics caused by an improperly installed wiper. The sensor can fail completely during deployment as shown in Figure 6-13 where the flat readings are almost certainly due to complete loss of probe sensitivity. Clearly, turbidity readings after this type of discontinuity should be rejected (Figure 6-13).

High Positive (>1000) and Large Negative Values-

Sometimes turbidity readings can be erroneously high (>1000 NTU) and then erroneously large negative readings. Or sometimes turbidity readings will be in the normal range of the instrument (0 to 1000 NTU) and then become large negative values. The most common problems associated with turbidity data like what is described above are likely due to one of the following:

(1) The presence of a large quantity of debris such as algae or *Spartina*,
(2) animals in the probe compartment,
(3) the wiper parking over the optics, or
(4) when there are actual turbidity values that the sensor is experiencing that are > 1000 NTU (greater than the range the probe can measure). This is a real event that the probe is experiencing and is not an error! Figure 9 shows that after a failure of a water control structure (see water level values before 14/07/96 0:00) which released a huge volume of water into the system that Delaware NERR was measuring, turbidity was increased beyond 1000 NTU which caused the turbidity sensor to "roll over" (see next paragraph).

In 1-3 above, the sensor is affected by a direct interference from a foreign body or the wiper. Sometimes the wiper can be jammed over the optics by debris or the wiper will park over the optics due to a dirty wiper blade. Note, in some cases you will need to replace the wiper and recalibrate the probe. All scenarios listed above can cause very high and large negative readings. Before the release of Version 3.10 sonde software for the YSI 6000UPG in January 1997, there was a "rollover" problem with the turbidity probe. When the A/D converter of the turbidity probe senses a very high reading, it "rolls over" and the output of the system becomes large and then negative. Thus, wiper malfunctions, direct interference in the optics, or turbidity values >1000 during a reading are usually characterized by very large, negative NTU data points as shown in Figures 6-15 and 6-16. The distribution of new sonde software (Version 3.10 and higher) from YSI corrected this problem.

The turbidity probe is an optical probe, which causes it to behave very differently that the rest of the probes. However, as opposed to the other sensors, if there is a malfunction it can be completely reversed within a given deployment. Thus, if the impediment is removed from the optics via natural causes in subsequent readings, there is no reason to suspect their validity.

If it is determined that there was an animal living in the YSI instrument, or debris was seen attached to the wiper area, or the wiper was stuck in the middle of the turbidity window, then reject and delete the data. This is where deployment notes are important to note any unusual circumstances regarding the instrument deployment. Make sure to review the turbidity data from each deployment and make a judgment as to the possible reliability of the data if large negative spikes occur and whether this data should be included in the SWMP data logger database.

However, since, in most cases, it cannot be determined whether or not the anomalous value is due to animal, debris, wiper, or natural causes, it is recommended that all anomalous data remain in the database. The values should be documented as anomalous in the metadata and left in the data file.

TIP: Small meshed netting over the sensor guard secured with cable tires can protect the probes from debris and animals taking up residence in the probe area. Contact YSI for the suggested mesh size and type.

Small Negative Values-

Just a small amount of water left on the probes (from the cup that the probes are stored in) can contaminate the zero-turbidity standard when calibrating the turbidity probe. Contamination can cause the zero calibration to be off by +5 to +8 NTUs. So, when the probe really experiences zero turbidity, the values are -5 to -8 NTU. Therefore, shake or dry off the instrument and probes thoroughly before continuing with calibration.

Due to this small calibration error possibility, small negative turbidity values should be kept in the data file and documented as anomalous due to this small calibration error.

Occasional High Positive Turbidity Spikes-

Occasional high positive spikes that are not consistent with the overall data record may be real (Figure 6- 17). Reject or accept spikes in turbidity values at the site's discretion.

However, do not reject or delete the data, unless you are absolutely sure that they are erroneous data. If you do not reject the data, leave the data in the file and document them as anomalous in the metadata. If you do reject them, delete and document them in the metadata.

Total Chlorophyll and TAL:

The YSI 6025/EXO sensor is designed to estimate the phytoplankton content of study site water. One key factor to consider with the YSI 6025 chlorophyll sensor is that it has significant limitations associated with its use that the user should appreciate fully before using. For more detail information on the 6025 sensor, refer to **Appendix I in the YSI 6-Series/EXO Environmental Monitoring Systems: YSI Environmental Operations Manual**.

The 6025-chlorophyll sensor associated with the YSI 6600, 6600EDS, 6820, 6920 and 600OMS is usually not susceptible to drift *per se*. This means that there will generally be little need for manual compensation of readings during a deployment due to the fouling or sensor drift that may affect the conductivity, pH, and dissolved oxygen sensors. The chlorophyll sensor can, however, produce erroneous readings for reasons other than drift such as mechanical failures. Examples of these are leakage of water into the sensor housing and scratches on the optics caused by an improperly installed wiper. The sensor can fail completely during deployment as shown in Figure 6-13 where the flat readings are almost certainly due to complete loss of probe sensitivity. Clearly, chlorophyll readings after this type of discontinuity should be rejected (Figure 6-13).

High Positive (>500) and Large Negative Values-

Sometimes chlorophyll readings can be erroneously high (>500µg/L) and then record normal readings. The most common problems associated with chlorophyll data like what is described above are likely due to one of the following:

1. The presence of a large quantity of debris such as algae
2. animals in the probe compartment,
3. the wiper parking over the optics, or
4. When there are actual chlorophyll values that the sensor is experiencing that are > 500µg/L (greater than the range the probe can measure). This is a real event that the probe is experiencing and is not an error! However, it is reading the fluorescence for a piece of macroalgae. This is not representative of the phytoplankton in the water column.

In 1-3 above, the sensor is affected by a direct interference from a foreign body or the wiper. Sometimes the wiper can be jammed over the optics by debris or the wiper will park over the optics due to a dirty wiper blade. Note, in some cases you will need to replace the wiper and recalibrate the probe. All scenarios listed above can cause very high and large negative readings.

The chlorophyll probe is an optical probe, which causes it to behave very differently that the rest of the probes. It has a tendency to produce a lot of "noise" or highly variable readings. However, as opposed to the other sensors, if there is a malfunction it can be completely reversed within a given deployment. Thus, if the impediment is removed from the optics via natural causes in subsequent readings, there is no reason to suspect their validity.

If it is determined that there was an animal living in the YSI instrument, or debris was seen attached to the wiper area, or the wiper was stuck on top of the chlorophyll probe, then reject and delete the data. This is where deployment notes are important to note any unusual circumstances regarding the instrument deployment. Make sure to review the chlorophyll data from each deployment and make a judgment as to the possible reliability of the data if large spikes occur and whether this data should be included in the final formatted data set.

However, since, in most cases, it cannot be determined whether or not the anomalous value is due to animal, debris, wiper, or natural causes, it is recommended that all anomalous data remain in the database. The values should be documented as anomalous in the metadata and left in the data file.

Using the data screening designed by NBNERR or URI/GSO, as mentioned above in the Conductivity/Salinity section, can help provide insight into determining real values from suspect data.

TIP: Small meshed netting over the sensor guard secured with cable tires can protect the probes from debris and animals taking up residence in the probe area. Contact YSI for the suggested mesh size and type.

Small Negative Values-

Just a small amount of water left on the probes (from the cup that the probes are stored in) can contaminate the zero-chlorophyll standard (DI water) when calibrating the chlorophyll probe. Contamination can cause the zero calibration to be off by +5 to +8 ug/L. So, when the probe really experiences zero chlorophyll, the values are -5 to -8 ug/L. Therefore, shake or dry off the instrument and probes thoroughly before continuing with calibration.

Due to this small calibration error possibility, small negative chlorophyll values can be kept the raw file only and documented as anomalous due to this small calibration error. This error can be adjusted based on pre- and post-calibration info at the decision of the data manager. The corrected and edited files will not contain any negative values. They will be documented, deleted, and calculated for the corrected file where possible. All calculated data will be in bold. The metadata document will track these changes.

Occasional High Positive Chlorophyll Spikes-

Occasional high positive spikes that are not consistent with the overall data record may be real (Figure 6- 17). Reject or accept spikes in chlorophyll values at the site's discretion.

However, do not reject or delete the data, unless you are absolutely sure that they are erroneous data. If you do not reject the data, leave the data in the file and document them as anomalous in the metadata. If you do reject them, delete and document them in the metadata.

All data review is done with calibration, post calibration, sonde swap, profiling, weather, flow, and other sensor information to make the best judgment possible and preserve or correct data when possible for the purposes of the NBFSMN.

Once all parameters are reviewed, raw files by deployment are kept for achieves, edited files (QA/QCd) by site and year (no corrections applied to this dataset), and the corrected dataset are made available through the DEM-OWR BART webpage on an annual basis by QA officer. All documented metadata are also available with annual dataset.

Other Notes about the Blue Green Algae Sensor (BGA):

As of 2017, the blue green algae sensor is a new sensor only available through the EXO sondes. Blue green algae basic QA/QC measures follows the same as chlorophyll sensor. Other validation of the data is not available at this time. This data information will be released at the site manager's request. This sensor is only reported on the EXO instruments; not all stations report BGA. The network also does not have field methodology available to validate readings from the sensor in an estuarine environment. Since it is not reported consistently through the network, it will not be included in the NBFSMN annual datasets. This data may be requested through the site manager.

SUNA Nitrate Sensor (Seabird):

Most stations use the SUNA V2 with wiper. The SUNA reports several variables for QA/QC assistance and instrument operations. NBFSMN will report data and time, sample number, nitrate umol, nitrate, µg/L, light, dark in the raw, edited and corrected formats. The raw files will be annual csv files, edited will be reported within the sites edited file, and the corrected will be reported within the site's corrected file. SUNA data will only be reported from GB, GD, TR, CR. Since, the data are not available at all stations it is up to the site manager if the data will be available through the NBFSMN annual dataset.

Data will be QA/QCd using methods highlighted in the SUNA manual. The SUNA manual recommends using the light readings, relative humidity, and the RMSE reading for the data verification process. Data flags will be applied to the data that do not meet light, relative humidity, RMSE and negative values thresholds. In addition, graphing the data against key parameters (grab samples, flow, salinity, depth, and chlorophyll) will be used to determine data offsets during deployments/station servicing. There are specific offsets that can be documented and corrected for. They include calibration offsets, negative values, and slight drift (negative) (figure 6-18).

Calibration offsets-During the sampling season, field checks are required to see if the instrument is working properly. If the offset is greater than 2-4 µmol, a re-calibration is suggested. Since this calibration is done in the field with a parafilm method, described in manual and Youtube video (https://video.search.yahoo.com/search/video?fr=mcafee&p=SUNA+V2+field+calibration+you+tube#id=1&vid=e61f788e18fa1d0f7b2360c743f50a27&action=click), offset errors can occur. These offsets are generally caused by a bubble in the parafilm or debris in DI solution. It this case, data is evaluated using a graphic display of the data. If the offset is consistent throughout the deployment a correction using the post deployment and next deployment information to create a constant correction value to be applied to the erroneous data.

Negative Values-Negative values can occur when the sensor is close to zero and the detection limit, random negative values can be reported occasionally. This data is deleted for the edited file and calculated using the mean of the adjacent values for the corrected data file. All negative values and time periods are documented in the metadata document. Time stamps can also be missed. This will remain blank in the edited dataset and calculated the same way using the mean of the adjacent values for the corrected file.

Fouling/Sensor Drift-When sensor drift occurs causing the readings to go slightly negative during a deployment, graphic interpretation with other parameters are used to determine the beginning of the offset. In the corrected dataset, a linear correction was applied to minimize the negative readings using the corrected offset as the end member for this correction.

There are fouling that can cause the sensor to go erroneously high. When this occurs the same graph interpretation method is applied to determine the beginning of the offset. In addition, light levels and RMSE values can be useful at determining the validity of the data, if available. All available data including the grab samples will be used to provide the most accurate determination for where the offset began. Since, a linear correction may not generate better quality data, corrections are not applied. In positive drifts of the sensor, the data is deleted in both the edited and corrected data files.

Grab Samples- Grab samples are used to validate the data throughout the sampling period. Since, both methods can have error, the NBFSMN will report both values (grab sample results with date and time collected and SUNA data. It is up to the end user to determine if a regression should be applied to the overall SUNA values to adjust to grab samples.

Figure 6-6A. Out of Water during Deployment

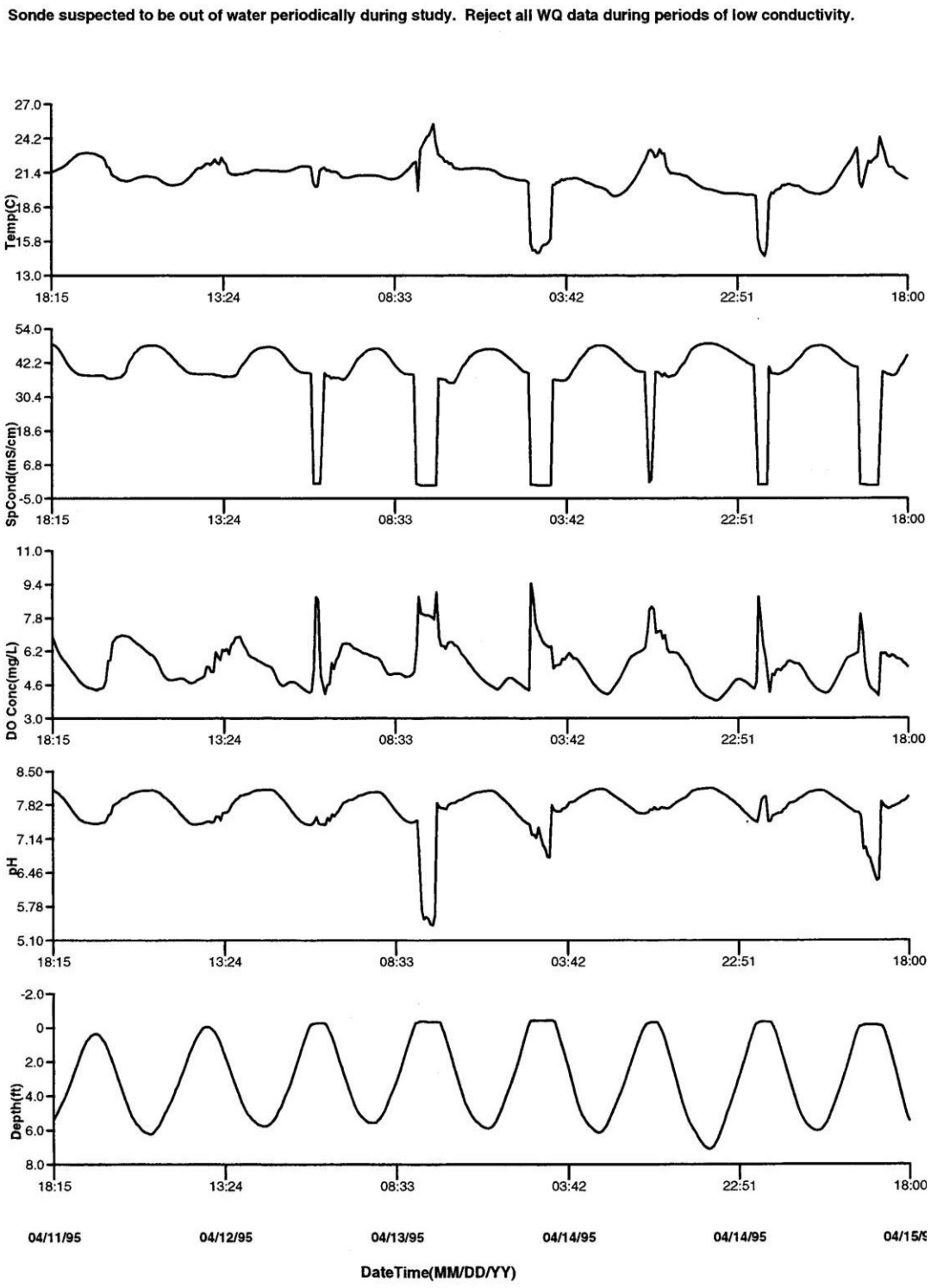


Figure 6-6B. Out of Water during Deployment.

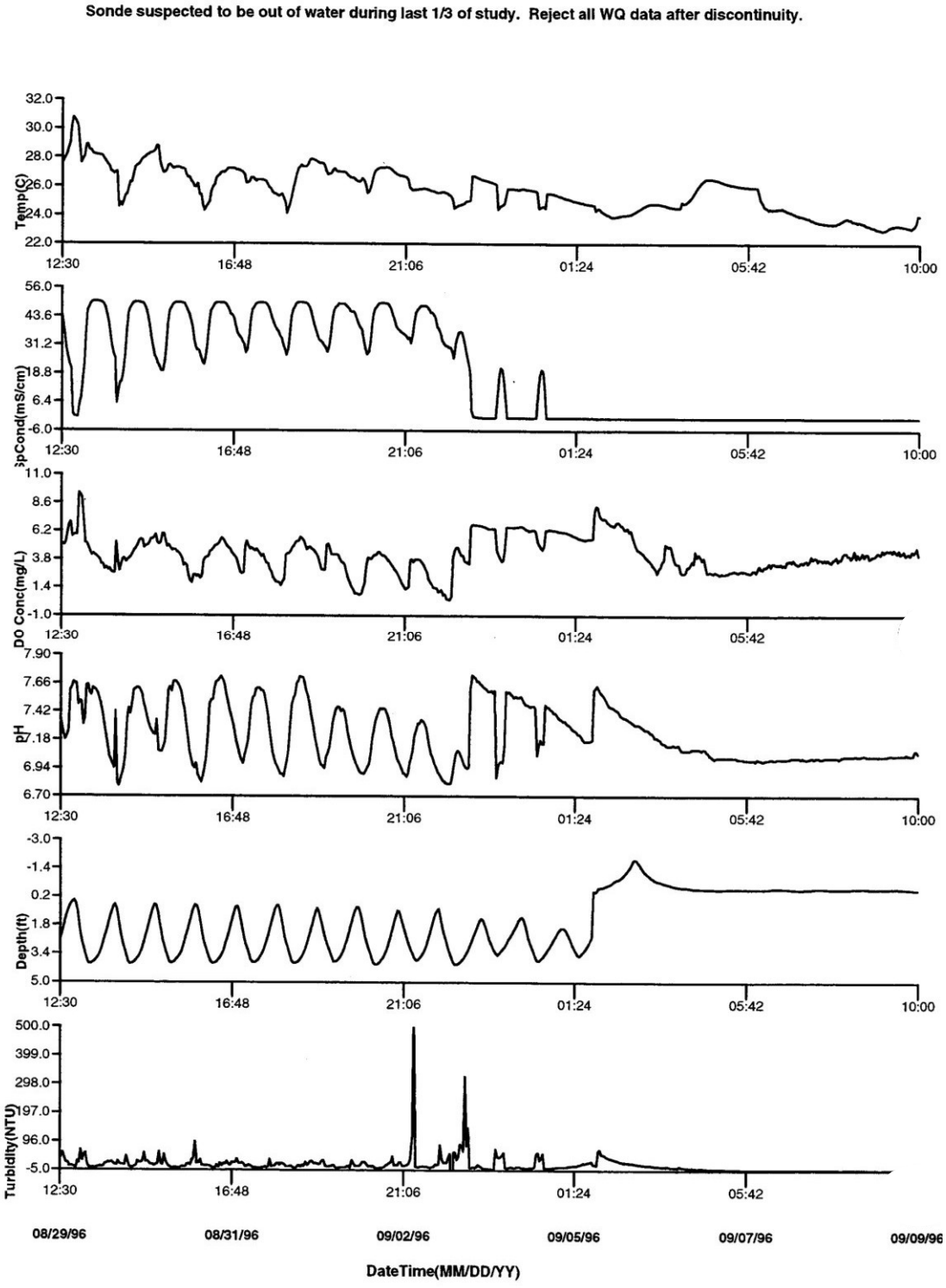


Figure 6-7. Sonde Swap/Data "Tails."

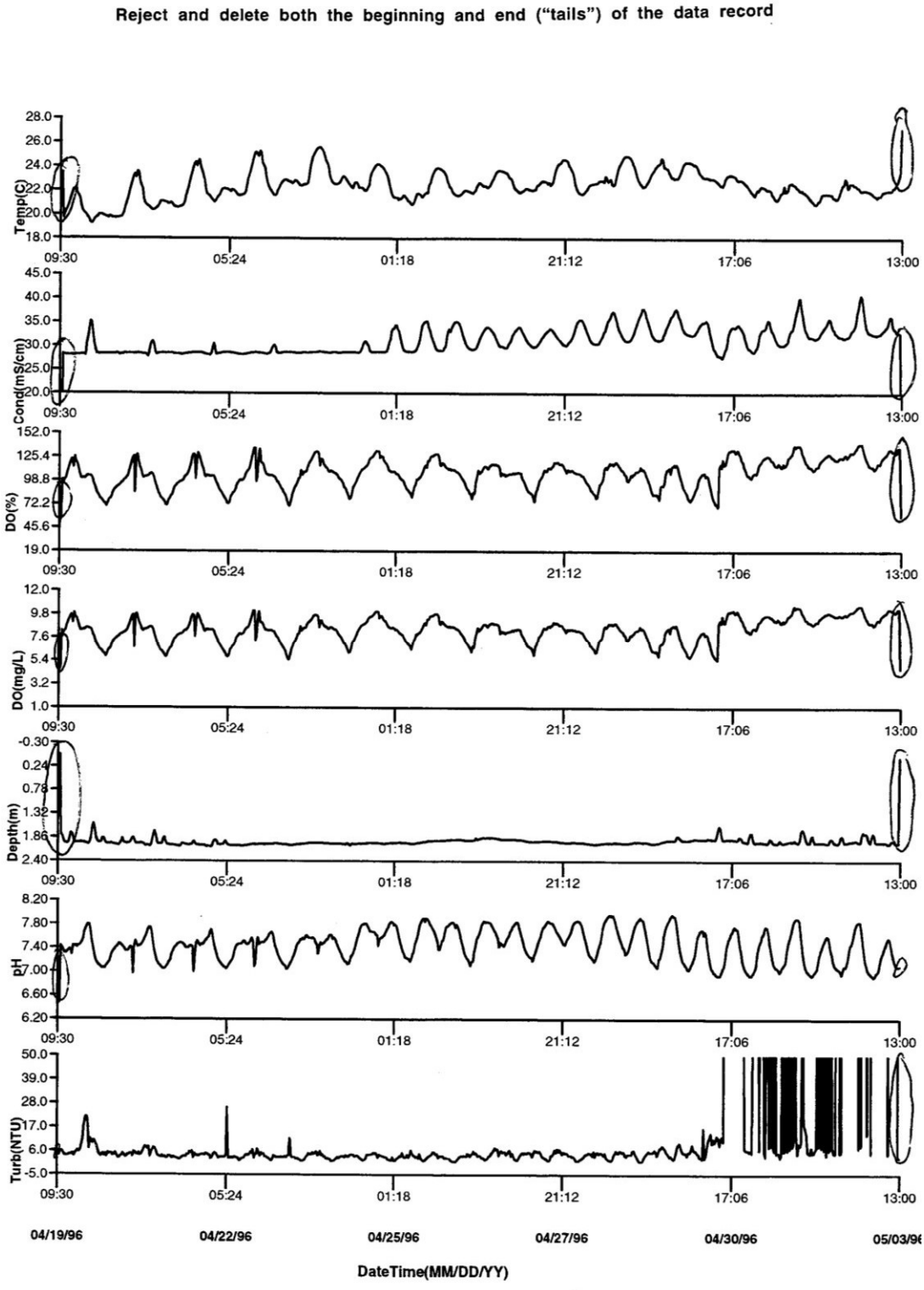


Figure 6-8. Temperature Probe Failure.

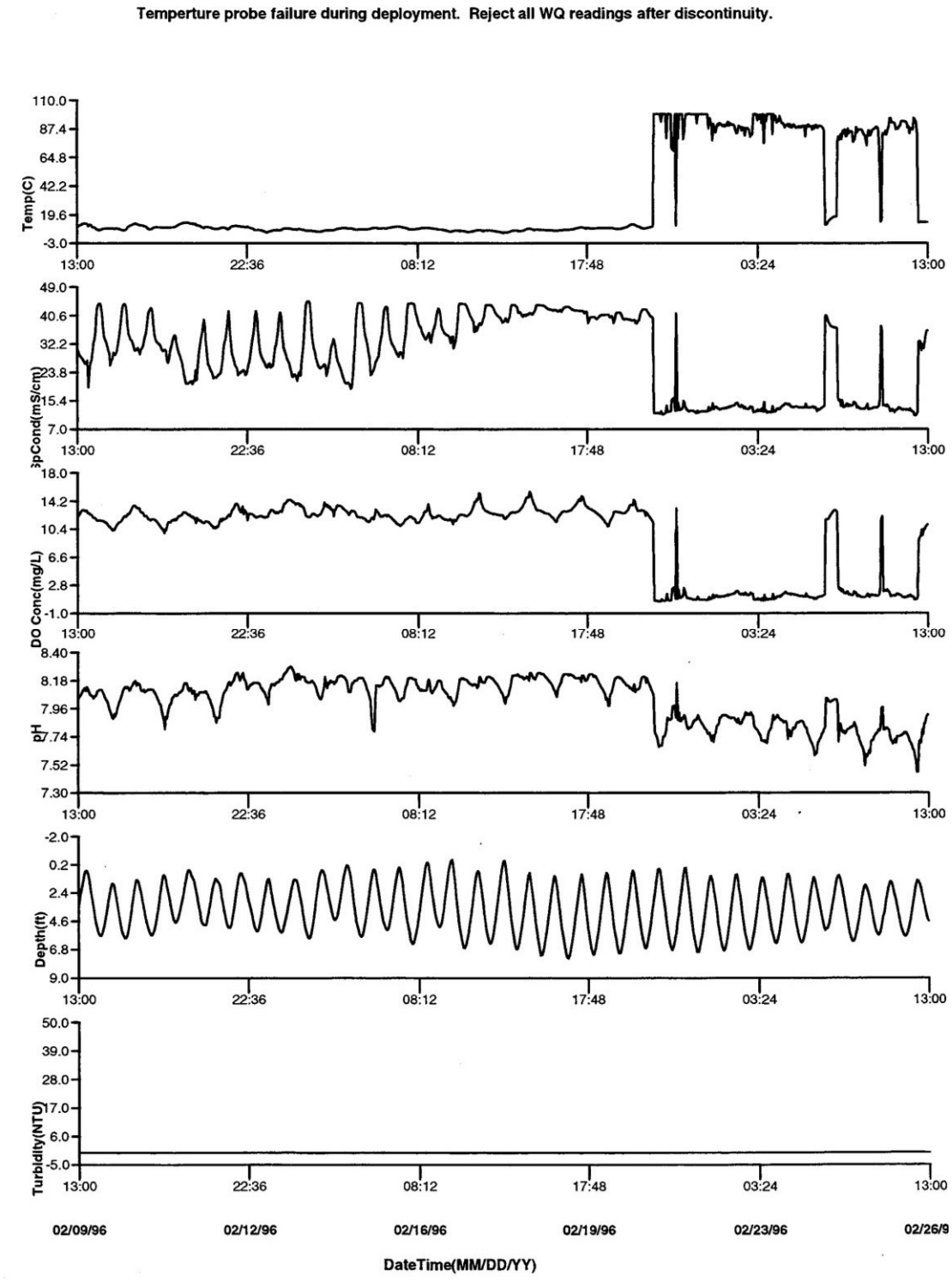
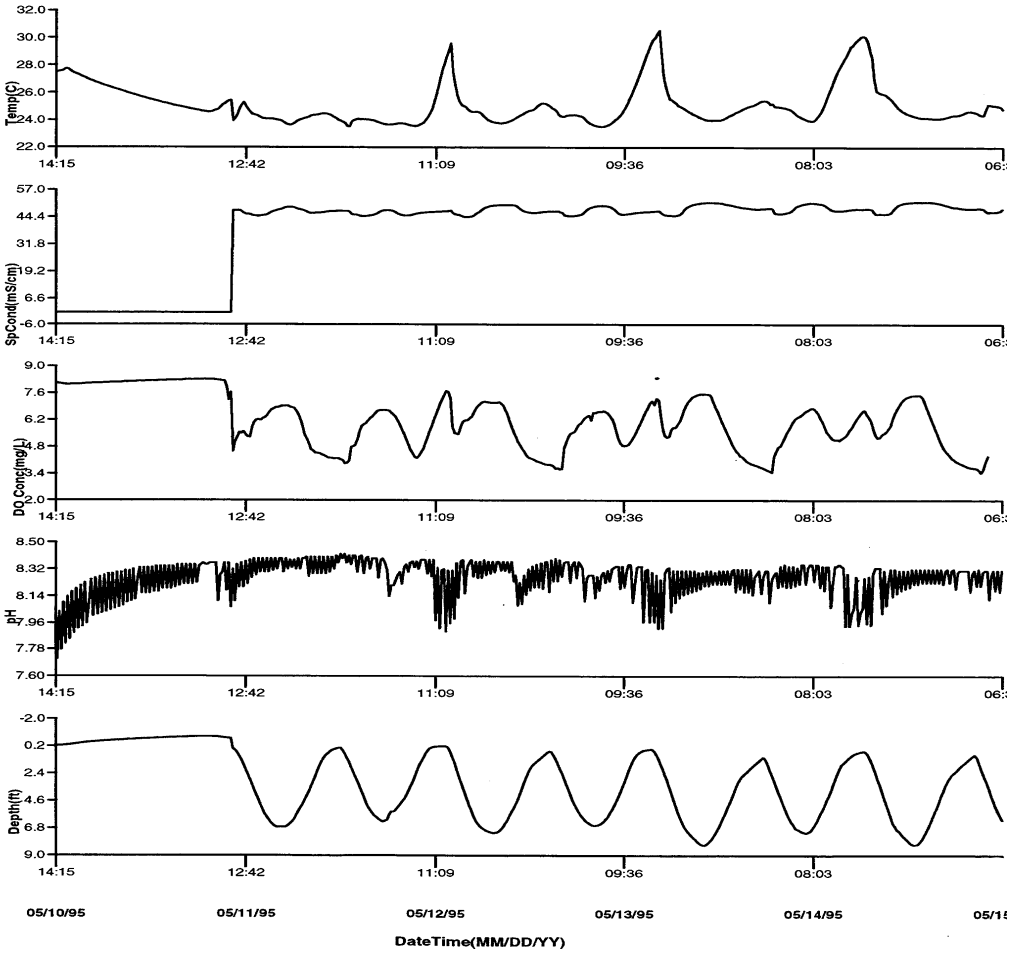


Figure 6-9. pH Malfunction and offsets.



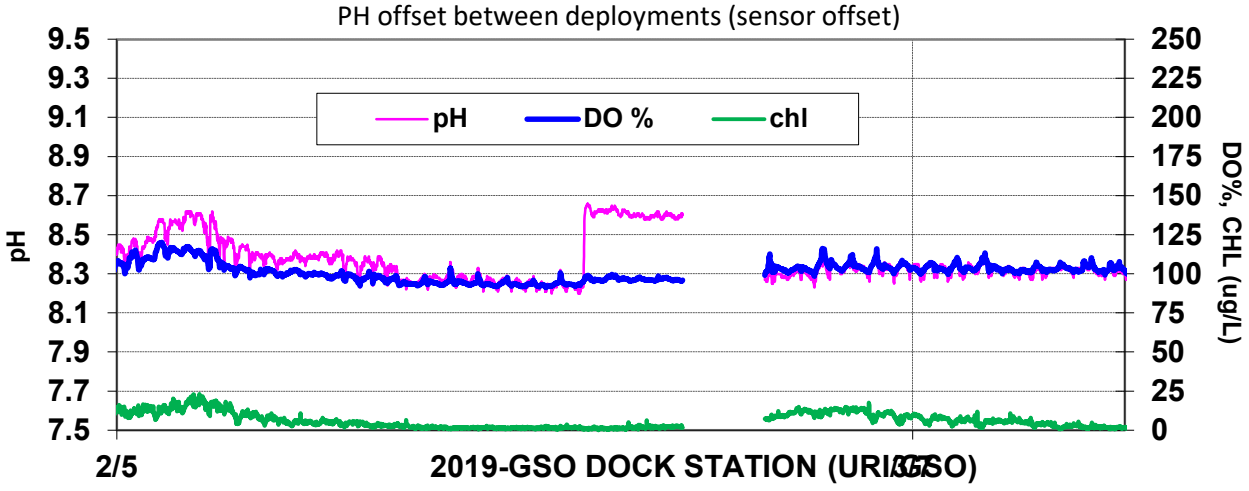


Figure 6-10. DO Membrane Problem.

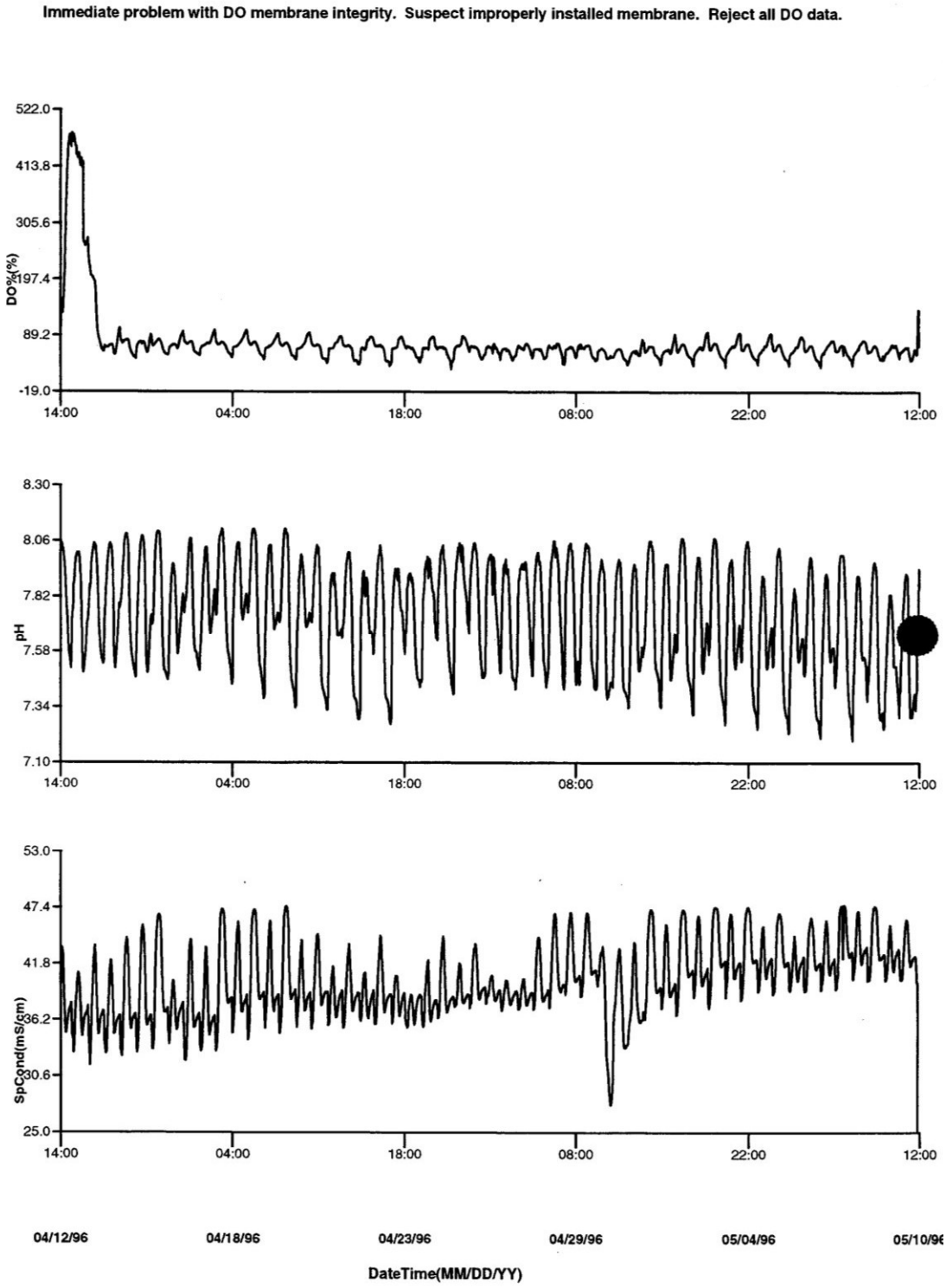


Figure 6-11A. Suspect DO Data.

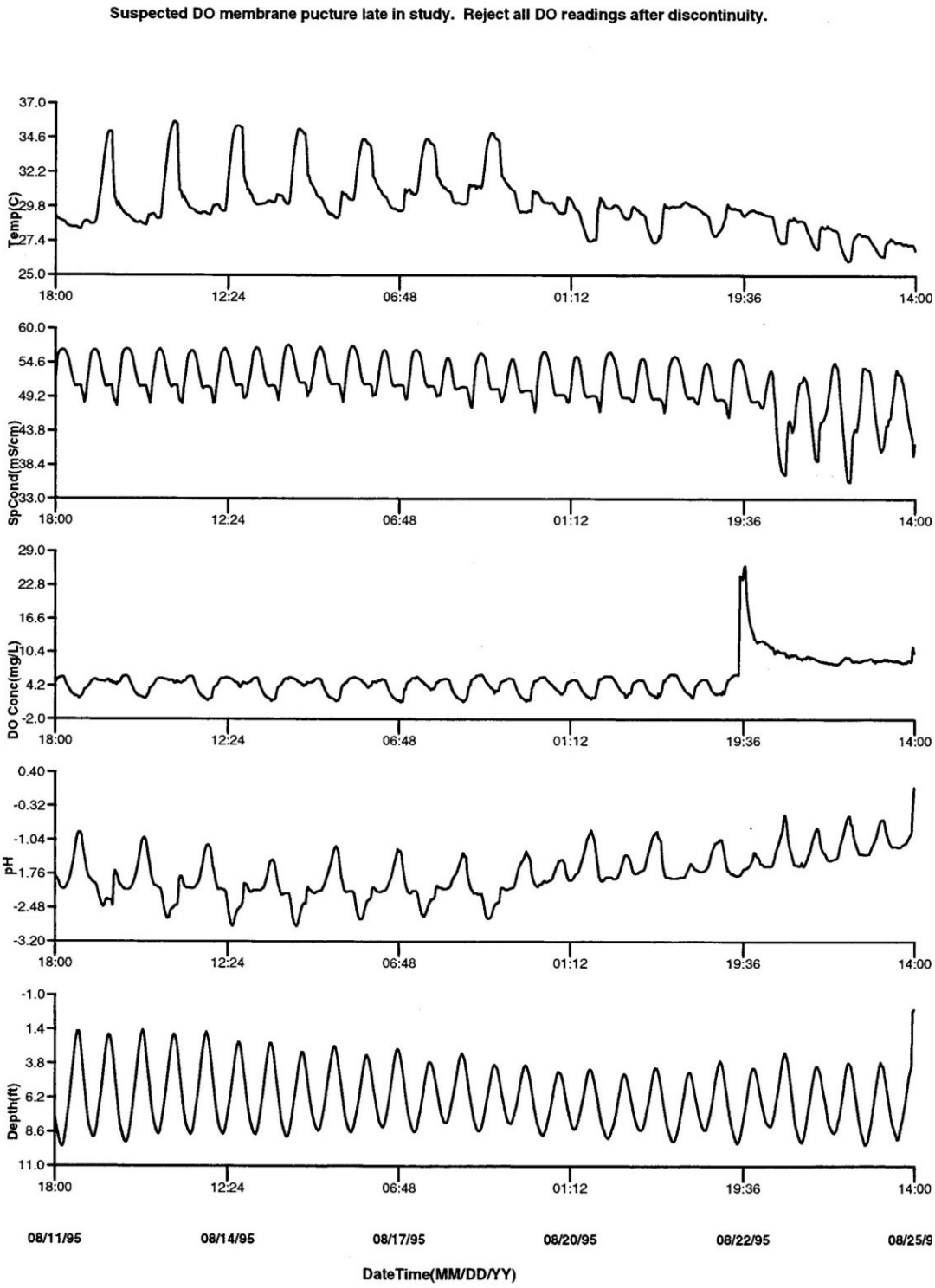


Figure 6-11B. Suspect DO Data.

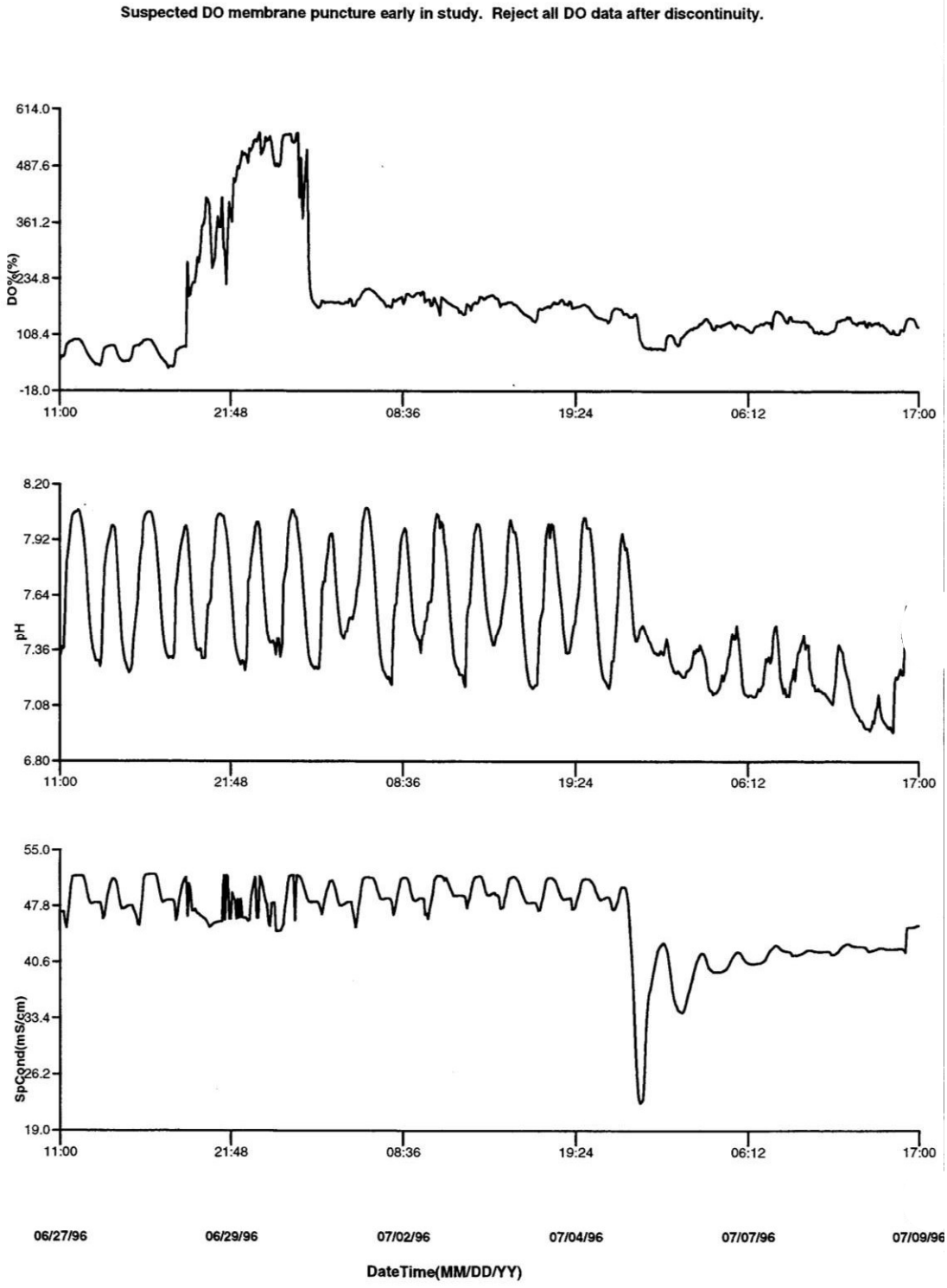


Figure 6-11C. Suspect DO
& Salinity Drift (salinity drifting from 7/13/96 on)

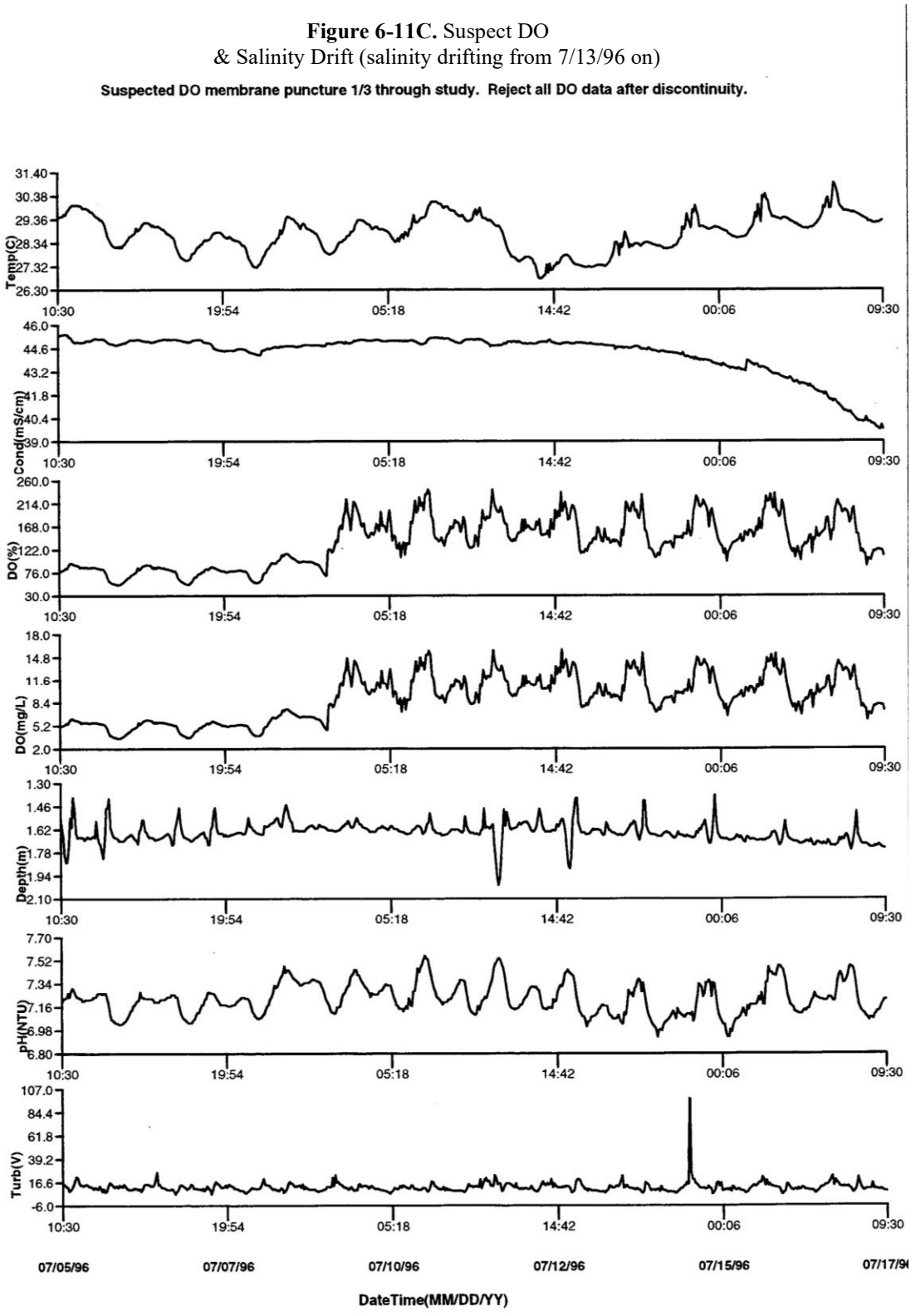


Figure 6-12. Turbidity & Chlorophyll Noise.

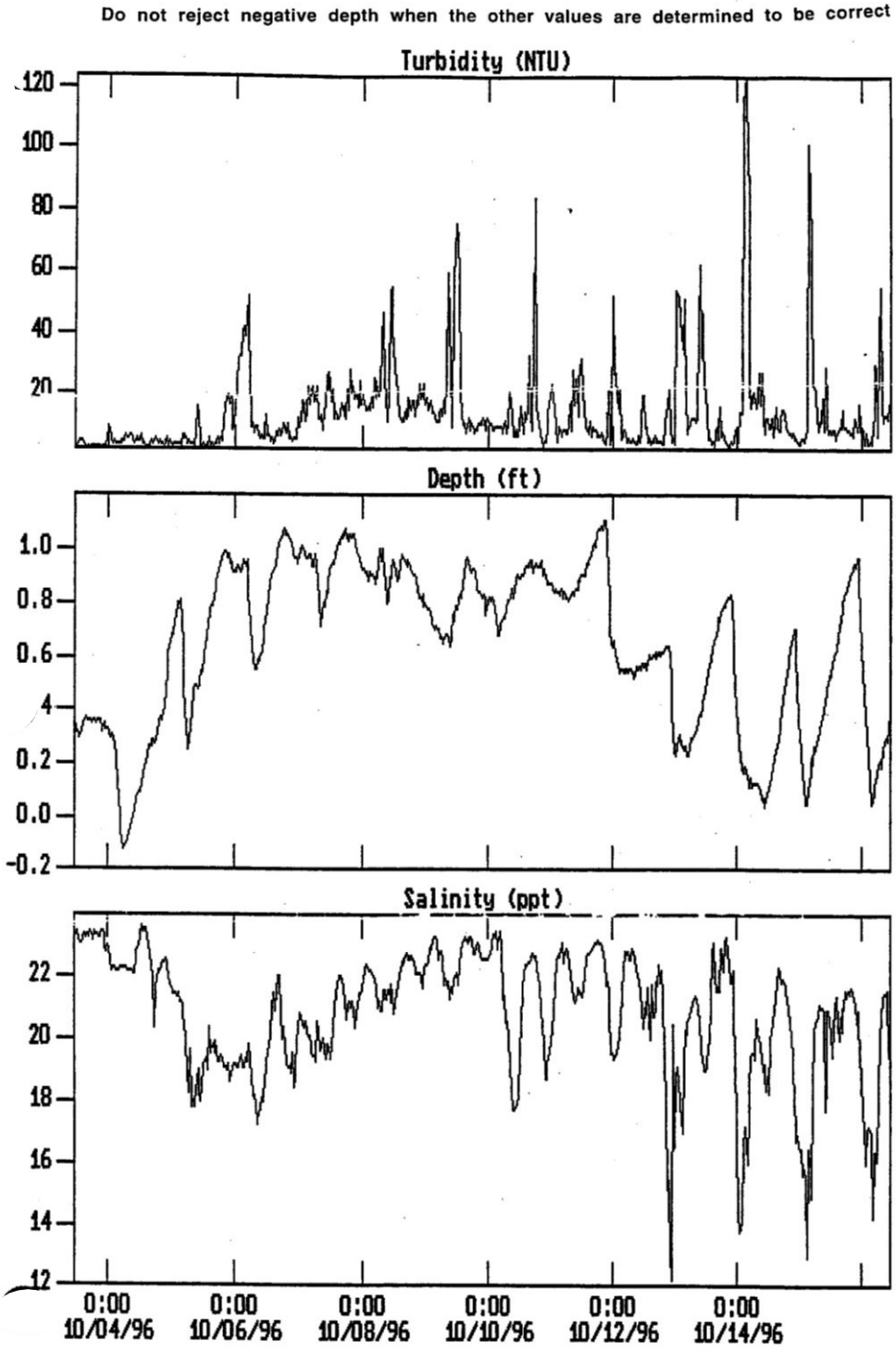


Figure 6-13. Turbidity Probe Failure and Ph Drift.

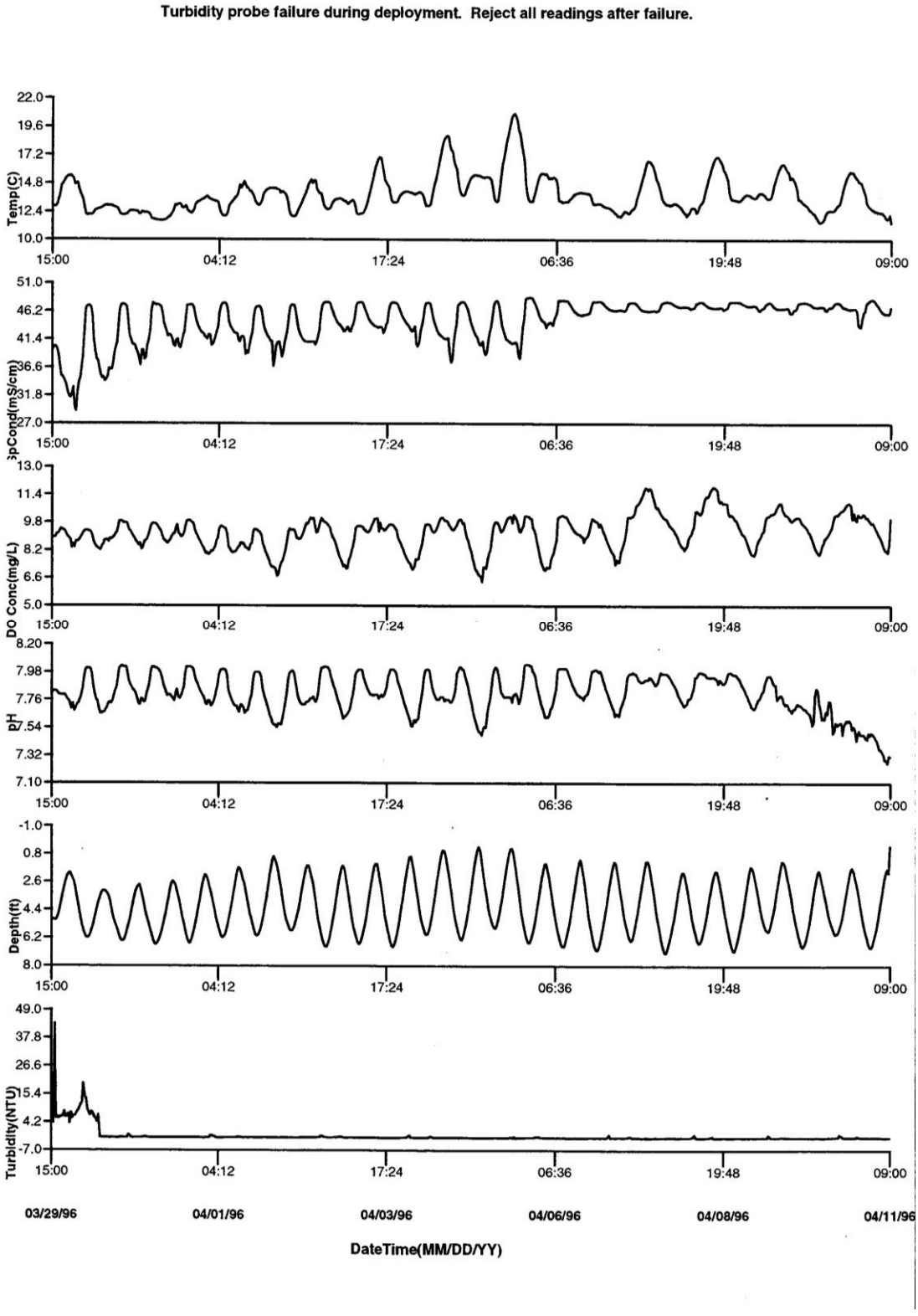


Figure 6-14. Negative turbidity Values.

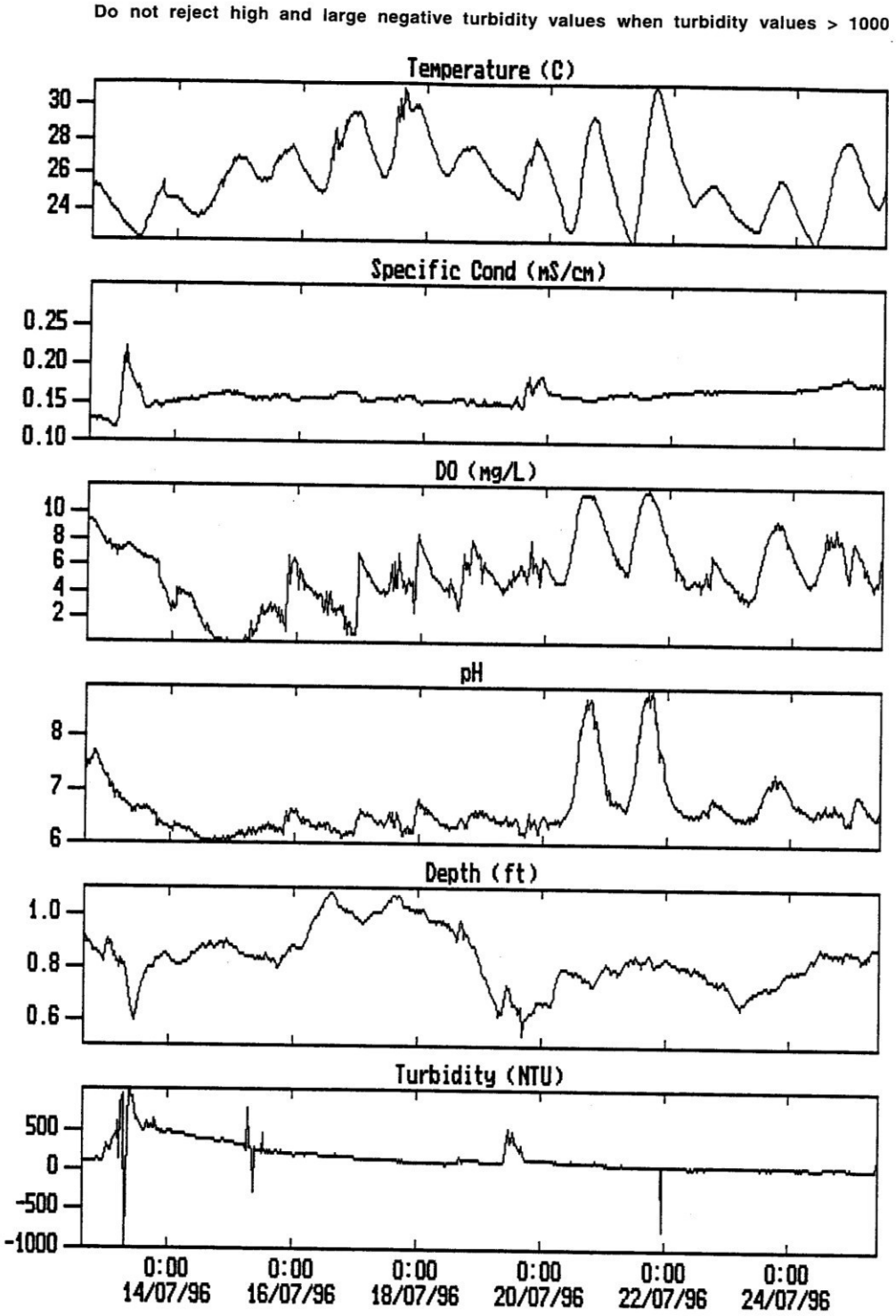


Figure 6-15. Turbidity & chlorophyll Spikes.

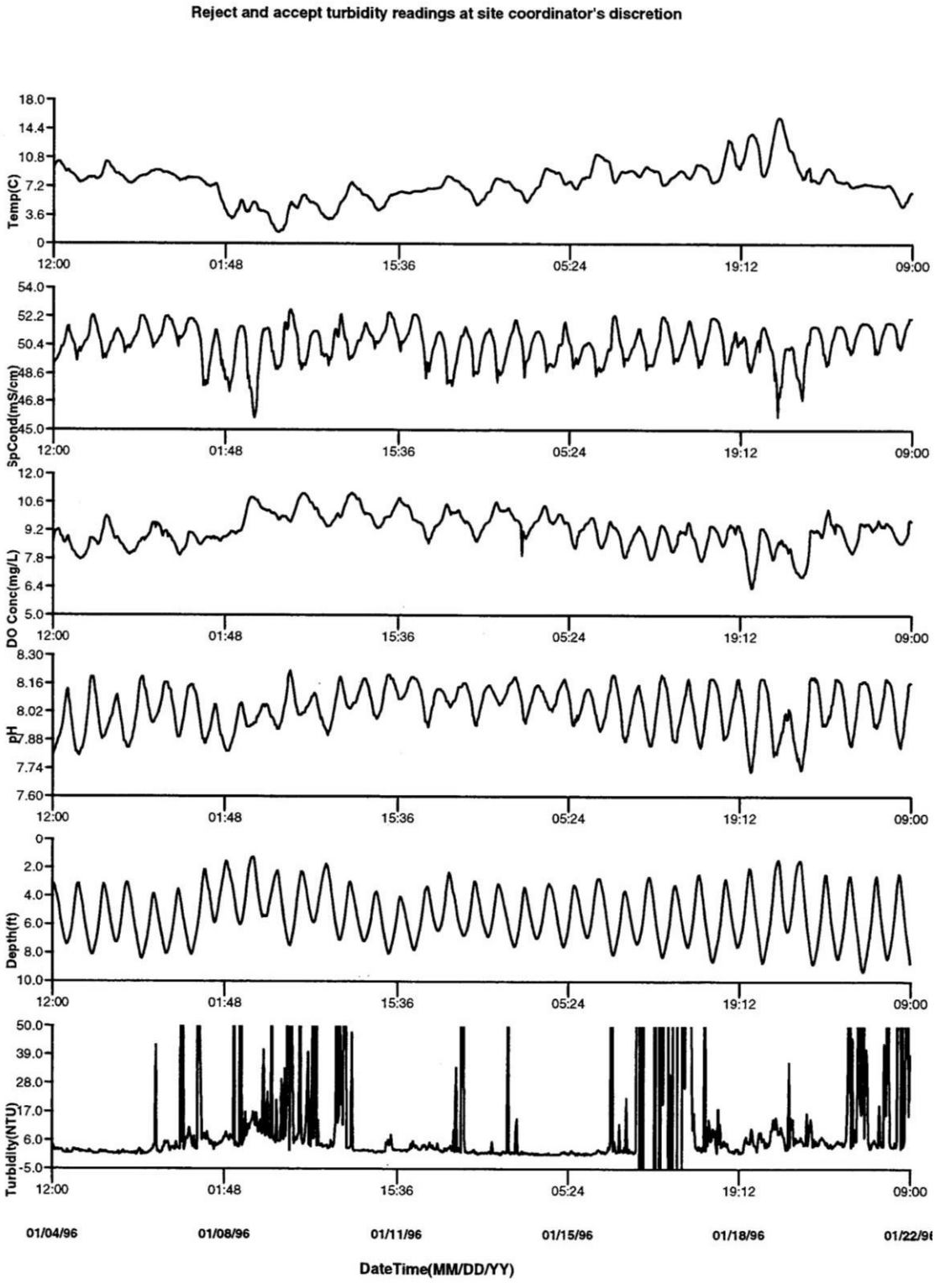


Figure 6-16. Highly Negative Turbidity Readings.

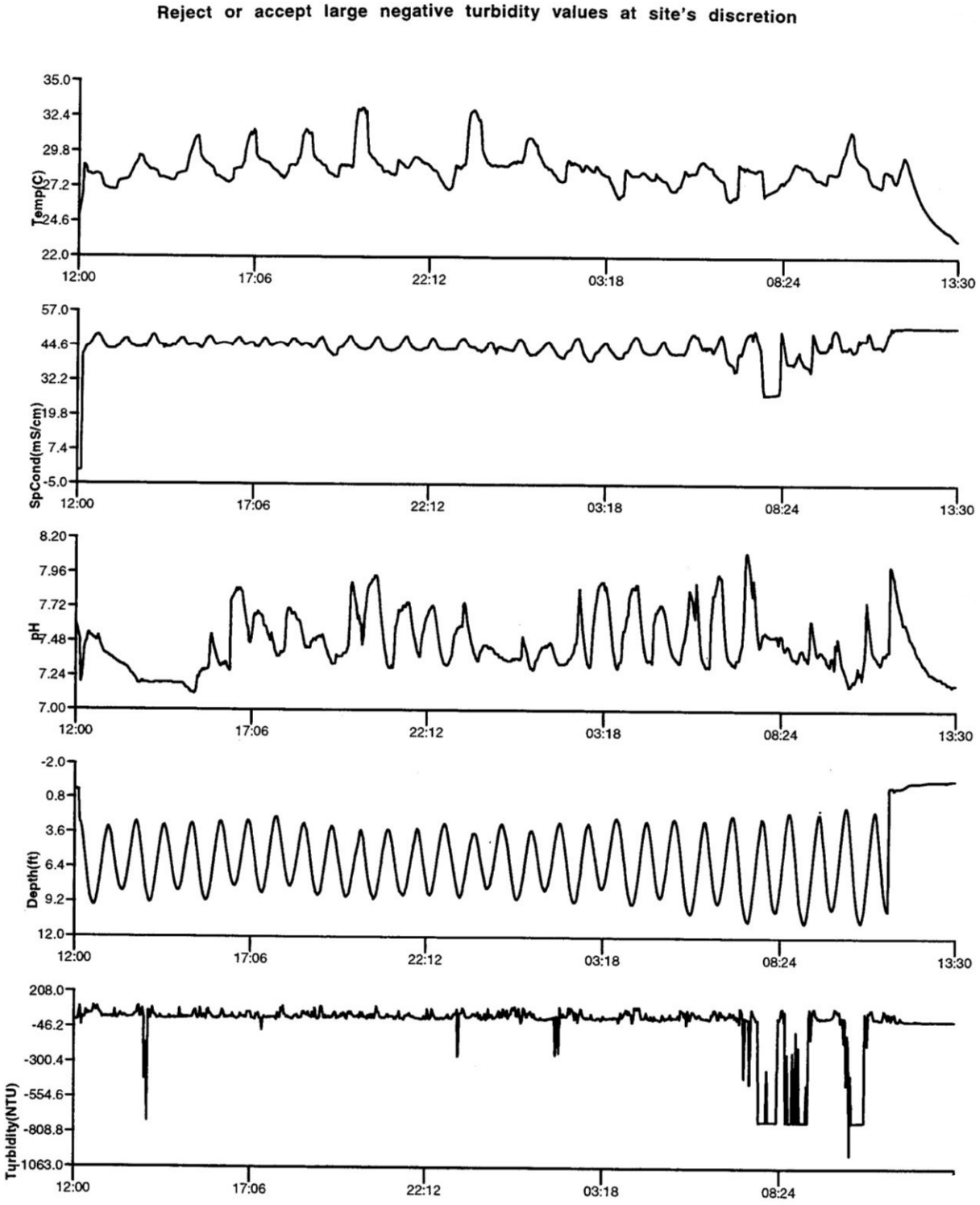


Figure 6-17. More Turbidity & Chlorophyll Spikes.

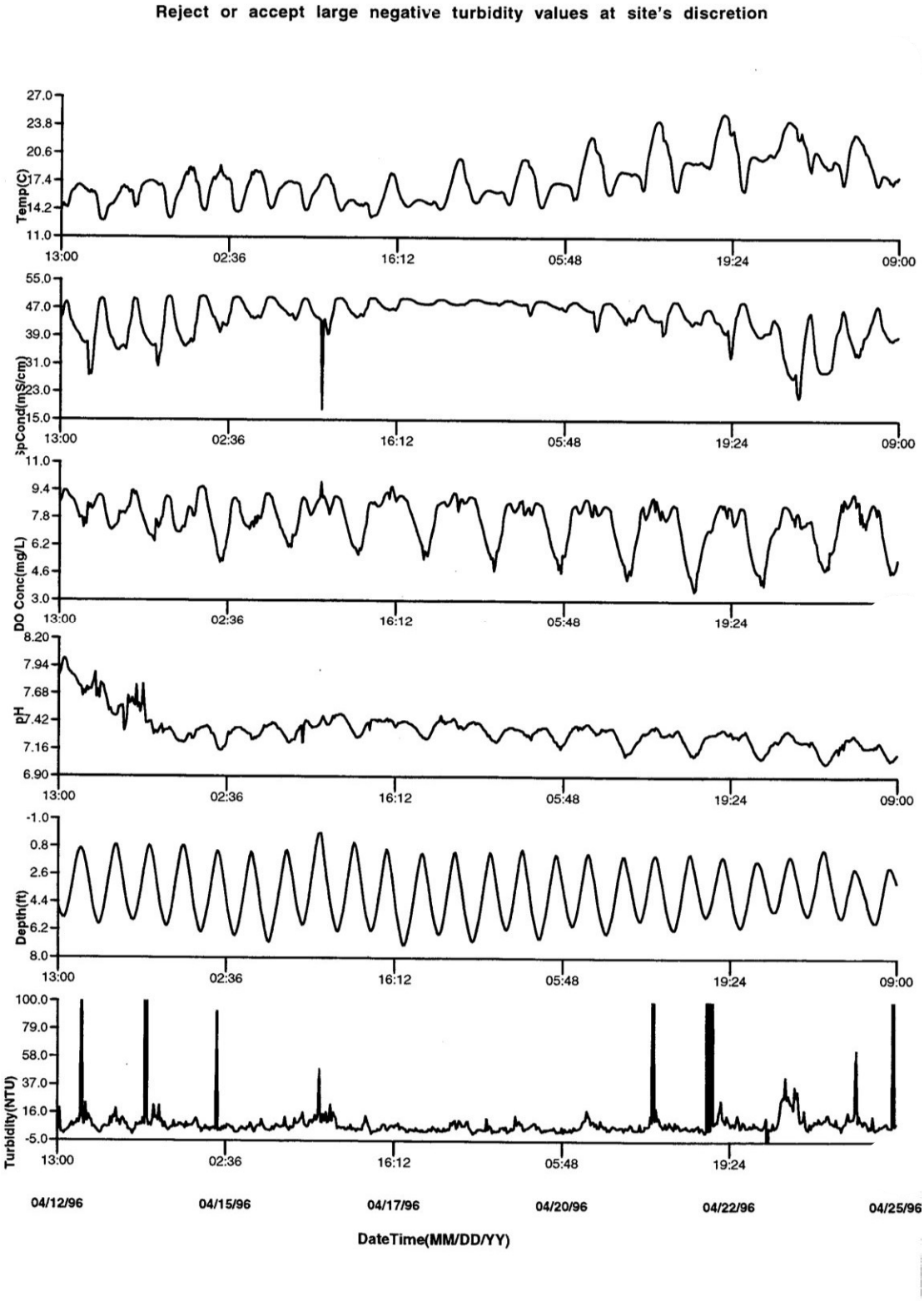
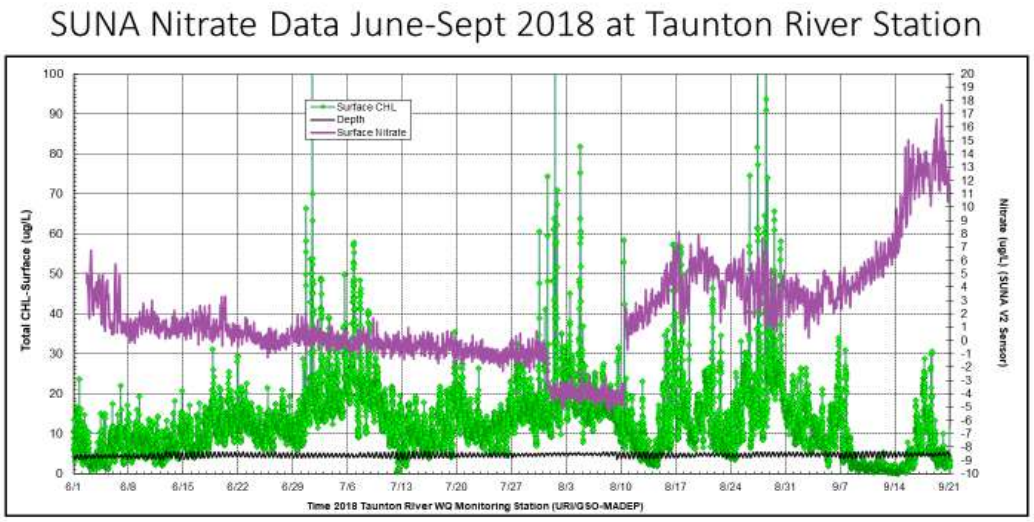


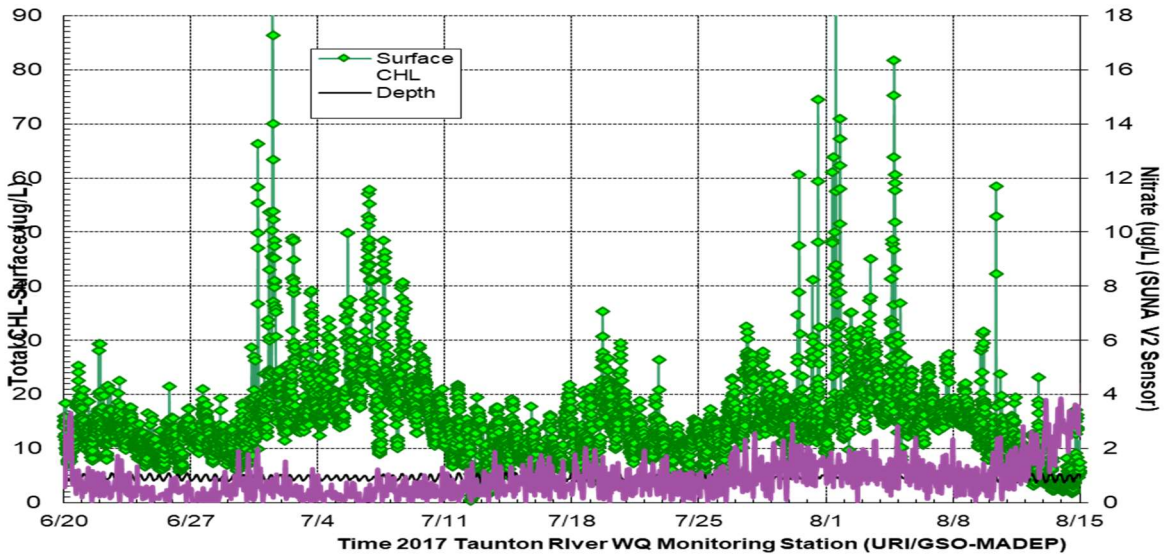
Figure 6-18 SUNA calibration offset, sensor drift, negative values



To start QA/QC data is plotted with lab results and other parameters for context. In this graph, there is a calibration offset from 7/31/2018 14:00 through 8/10/2018 8:00. The data is negative and erroneous. It is deleted in the edited file and a constant is added to apply a correction to the data.

Fouling can be somewhat subjective. Once an offset is documented, a graph of the data is used to determine where the primary offset began. Since it is a negative offset, the negative values that affect more than half the day consistently began on 7/6/18. From 7/6/2018 0:00 through 8/10/2018 8:00, the readings are deleted from the edited dataset. In the corrected dataset, a linear correction was applied to minimize the negative readings using the corrected offset as the end member for this correction.

Other random negative values are deleted and calculated using the mean values of adjacent times values. Below is the graph of the data with all corrections applied.



SOP-6
Buoy Preparation and Storage

Preparation for

Deployment End of the

Season Storage

It has been through experience that these monitoring buoy systems are not intended for year round use in the open bay conditions of Narragansett Bay. The mooring systems described in this section are not strong enough to hold the buoy in place through a bay-freezing event, a typical event during New England winters. The mooring lines and shackles should be replaced on a yearly basis to ensure maximum security. Therefore, it is recommended to retrieve the buoys on a seasonal basis.

The season maximum is recommended to be March through December. This will avoid the highest risk for potential damage to the buoy during the coldest months. It also allows for the time necessary to repair or replace damaged items of the buoy and the mooring system.

This section will discuss the preparation for deployment, the deployment, and the retrieval of the YSI EMM 770 water-quality monitoring module (the buoy). The preparation consists of inspecting for damage, buying replacement parts, cleaning and painting the buoy, setting up the mooring system, and preparing the DCP. Finally, this section will review the essential steps for storage at the end of the field- sampling season.

Preparation for Deployment:

The preparation for the next deployment begins when the buoy is retrieved at the end of the field season. All buoy parts have to be inspected for damage when retrieved to allow enough time for repairs before the next deployment. The replacement parts must be purchased in enough time to allow for the buoy set up. The setup of the buoy system must be complete and tested before deployment. The buoy preparation for deployment can be broken down into the following categories: damage inspection, purchasing replacement parts, buoy setup, and the final systems test.

Damage Inspection-

Once everything has been cleaned off after retrieval, an assessment for damage must be conducted. The evaluation consists of examining the electronics, the buoy structure, and mooring system.

The electronics assessment embodies the antenna tripod system, DCP, DCP batteries, sondes, and sonde cables. The antenna should be inspected for any water damage to antenna itself, the connectors, the light beacon, and the solar panels. The rubber fitting over the antenna should not show signs of age, such as, cracking in the rubber or bend easily. Water damage to the connectors can be as slight as green corrosion to pins being rusted away. Also check to make sure the connections make watertight seals and none of the connector pins are bent. Store all electronics in a cool dry place.

During the solar panel evaluation, the tripod structure can be checked for damage, as well. First examine the solar panels for cracks and any connection damage. Then check how well the solar panels are attached to the tripod. If extensive rust exists on the tripod or the welded joints have visible damage, the tripod will need to be sent in for repairs and possible replacement. If any of the described damage exists or any other uncertainties exist, contact YSI or your local YSI representative to assess and repair the damage.

The DCP evaluation includes a function test, examination of connectors, and fuses. Connect all electronic equipment (including sondes) to make sure it still functions properly after it has been retrieved and cleaned up from field use. During the connection process examine the connections for any damage. Always check the fuses before putting the DCP in the bucket. Make sure you have spares on hand. If everything is functioning properly, disconnect everything and put the cover over the connections until deployment.

The DCP batteries **must** be charged just before deployment. Check these batteries to make sure they are holding the charge when the buoy has been retrieved. Check the connections to the batteries and the connection from the batteries to the DCP. They should all be free of corrosion. These batteries should last about five years and therefore, replaced on a four to five-year schedule. However, any failures of these checks will warrant any early replacements.

The sondes should be evaluated on a minimum of a seasonal basis. Examining the sondes for damage is discussed in the calibration procedure section of this manual. Repairs must be made before the sondes are to be re-deployed.

The sonde cables are checked after they have been cleaned. Check the cables over for nick, cuts, and major kinks. The cable should wound in a circular fashion. The connections should be free of water damage. The pins should not be bent. The cable collar leading to the connectors should be stiff. They should not bend easily. Also, check the age of the cable connector ends by looking at the serial number. If no problems have been detected, the cables should be sent in to YSI for evaluation every four years.

The buoy structure entails the foam hull, stainless steel frame, the counterweight, and the DCP and battery housing bucket. The inspection of the foam hull and the stainless-steel frame can be performed simultaneously since they are permanently fixed to one another. The counterweight and DCP are detachable. They should both be removed for proper, cleaning, inspection, and storage.

Replacement Parts for Buoy Hardware-

The hardware for the buoy system should be replaced on a seasonal basis. The following list is an example of items that may need to be replaced. Using stainless steel is recommended for all hardware. The following list provides vendors and cost saving options. Remember that these items are designed for a site location in a semi-protected bay with a water depth of about 10 meters. Adjust line length, strength, and bottom paint based on the area the buoy is being deployed in.

Example of Supplies:

Marine Supplies for Buoy Hardware Estimate Prices 2010					
***Quantity based on what is needed to fully equip one monitoring buoy*					
Supply Companies:					
	BoatUS	(800) 937-2628			
	Bosun Supplies, Inc. (on-line) www.bosunsupplies.com	(201) 837-7007			
	NA Taylor (mooring floats)	(518) 773-9400			
	Samsons (rope)	(360) 384-4669			
	Trawlworks	(401) 789-3964			
	Wilcox Marine Supply of RI	(401) 789-1890			
	West Marine (Narragansett)	(401) 788-9977			
	Defender	(800)628-8225			
				Estimated	
Quantity	**Item**	**Size**	**Length**	**Price/ ea.**	Comments
2	mushroom anchor (mooring)	150 lbs/ea	---------	$250.00	
2	galvanized chain (from mooring to rope)	3/8-1/2"	60 ft.	$270.00	adjust to depth (40 ft may be fine)
4	double hard eye rope (for mooring/buoy and pick-up float)	1/2"	60 ft.	$150.00	
1	zinc couplings (for counterweight)	2"	---------	$60.00	comes with new buoy
2	shackles -stainless steel (*SS*) (anchor end)*	3/4"	---------	$60.00	
2	shackles -stainless steel (*SS*) (buoy end)*	5/8"	---------	$40.00	
8	shackles -(SS) *	1/2"	---------	$20.00	
	(anchor to chain, chain to rope, anchor to float rope, float rope to float)				
1	wire to secure shackles (SS)			$5.00	
1	wire to secure shackles (SS)			$5.00	
2	Mooring Float Balls(*Sur-Moor Hard-shell*)	15" dia	60lb	$90.00	can use old jugs for $0
2	Counterweight pins/bolts- (SS)	3/4"	1"	$1.00	should come with new buoy
1	Counterweight lag bolt w/ nuts and coddle pin (SS)	13/16"	3"	$3.00	should come with new buoy
2	Hose clamp - stainless steel (to secure counterweight)	no. 72	103mm	$5.00	
1 set	lettering (URI Oceanography)	2"	---------	$10.00	
1	*Rustoleum* Rust Metal Primer (#7769)	---------	---------	$6.00	don't need if buoy is new
1	*Krylon* Rust Tough Enamel Spray Paint (Cherry Red #RTA 9230)	---------	---------	$6.00	don't need if buoy is new
1	*SherwinWilliams* Acrylic Latex All Surface (SafetyYellow #6403-2965)	---------	---------	$20.00	don't need if buoy is new
1	Petit Bottom Paint Trinidad SR (black)			$200.00	don't need if buoy is new
	**** Galvanized can be substituted for stainless steel if buoys are deployed for 6months or less***				
2	***shackles -galvanized (anchor end)****	***3/4"***	---------	***$15.00***	
2	***shackles -SS 316 (buoy end)****	***5/8"***	---------	***$28.00***	
8	***shackles - (galvanized)****	***1/2"***	---------	***$6.00***	
	(anchor to chain, chain to rope, anchor to float rope, float rope to float)				

Buoy Setup-

Once all replacement parts have been received and a deployment date has been set, the buoy can be setup for deployment. The new mooring systems can be assembled at any time. The next step consists of cleaning and painting the buoy hull, counterweight, sonde support systems, and the sondes and sensors just prior to deployment. The electronics need to be setup for a system check. The system check should be done several times before deployment with a final system check the day before deployment. The final setup of securing the moorings to the buoy and securing the sondes to the buoy are completed during the actual deployment.

As soon as the replacement parts have been purchased, the mooring lines, chain, pick-up line, and mooring should be shackled together. The shackles should be ceased to prevent loosening during deployment. Do **NOT** shackle the mooring system to the buoy until the deployment. The mooring system needs to be separate from the buoy for transportation purposes. Examples of mooring systems are as follows:

Mooring Systems-

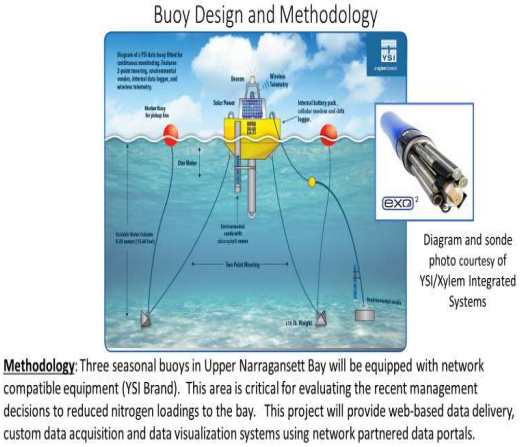


Figure 3-1. Two-Point Mooring System **Figure 3-2**. Counterweight and Mounting tube.

The second step in setting up a buoy for deployment requires cleaning and painting the buoy. A copper-based anti-fouling paint is recommended. YSI recommends *Pettit Trinidad SR p/n 1877* for the buoy and the sensors. The lettering and contact info should be put on after the buoy has been cleaned and painted. The following is a list of procedures for cleaning, prepping, and painting of all buoy equipment:

Cleaning and Painting-

1. Clean all surfaces at the end of the season and at the beginning of the next sampling season.
   Power washing is recommended. The end of season cleaning prevents damage from salt deposits. The beginning of season cleaning helps to prep surfaces for painting.
2. Prep surfaces for painting. Sanding or scrapping of old chipped paint may be necessary. Apply tape to guide painting process.
   Always, wear appropriate safety gear. Anti-fouling paint is harmful!
3. Apply one coat at a time. Let dry for 24 hours between coats. Thick coats may help deter growth. Paint in a cool, well ventilated, and dry place. Leave space for anodes on counterweight, etc.
   Anti-fouling paint should be applied just prior to deployment (1-2 weeks). The paint's effectiveness will deteriorate if painted too far in advance.
4. The sonde, sensors, and their buoy support structures should be treated with anti-fouling measures (pvc tape, copper tape, C-Spray). Refer to recommendations by YSI on anti-fouling process for YSI sondes and sensors.
5. The bucket that holds the electronics should be cleaned. The o-ring lip to the bucket must be smooth and free of any debris to be able to create an airtight seal. Once these steps have been completed the buoy is ready for the electronics.

The electronics consist of the DCP, two batteries, and the antenna tripod. The DCP and other equipment must be prepped before installing it in the bucket. The DCP stainless steel plate should be cleaned when retrieved from the field. It should be stored in a clean, dry place and covered to prevent dust from possibly damaging the electronics of the DCP. The following are the procedures for preparing the DCP for deployment:

DCP Installation-

1. Take out of storage and clean the bottom side of the DCP cover. This side of the DCP must be free of dirt to ensure and airtight seal.
2. Charge the DCP batteries. Sometimes requires 24 hours.
3. Connect the fully charged batteries to the DCP and listen for a long beep. The long beep indicates power is getting to the DCP.
4. Direct connect to the DCP to check proper function. Back–up configuration files. Then disconnect and prepare DCP and batteries to be installed in the buoy bucket.
5. Once charged, install the batteries and the protective bar across the top allowing the power cable to pass through.
6. Insert desiccant into the bucket. Several are better than just one.
7. Connect the power cable to the DCP. You should hear a beep as the DCP powers up.
8. Apply vacuum grease to the underside of the bucket and the O-ring for the bucket. Then place the DCP on top of the bucket. Make sure O-ring stays in the grove of the bucket. Be careful not to pinch or dent O-ring. Seal using Allen screws.
9. Once this is completed take the air vent off apply a vacuum seal to make sure the seal holds. Replace the valve.
10. Best to connect DCP and seal bucket and deploy either with buoy or after deployment.
11. Once in field, after the DCP has been properly attached, attach the solar panel. Use lock washers to secure it on the buoy frame. Connect the power and communication cables to the DCP ports and install sondes and cables to complete the DCP setup. The beacon should flash about every 4 seconds.

Be sure to use sondes and sensors that you plan on using at the buoy site. The buoy is now ready for its systems test, deployment, and use.

End of Field Season Storage:

Storage Options-

1. All items can be stored indoors once cleaned. This is the best option to avoid possible rusting of steel components. Make sure all electronics' power is disconnected for storage.
2. The buoy and mooring systems can be stored outdoors, if indoor facilities are not available. All items should be cleaned and covered with a tarp when possible.
3. For sonde storage refer to YSI manual, calibration section of this manual. For DCP storage see manufacturers manuals (Campbell Scientific, Nexsen, SUNA and/or YSI manual). ALL ELECTRONICS MUST BE STORED IN A TEMPERATURE CONTROLLED ENVIRONMENT!

SOP 8. Nutrient Sampling
MERL Methods QA/QC

Total Dissolved and Total Particulate Nitrogen and Phosphorus (Dissolved Inorganic Nutrients, TN/TP)
by Barbara L. Nowicki

1. **Background**

The method described here is an adaptation of the method published by Valderrama, 1981. The procedure is performed on a whole water sample to determine Total N + P, or on a filtered water sample to determine Total Dissolved N + P. Total particulate N + P can be determined by difference. The water sample is digested using a persulfate oxidation and then analyzed for nitrate and phosphate concentrations using a Technicon Autoanalyzer (Estoria Autoanalyzer as of 2009).

2. **Precision***

Nitrogen	± 0.1 μM at 10 μM level
	± 0.3 μM at 60 μM level
Phosphorus	± 0.04 μM at 1 μM level

*based on 6 replicate digestions of MERL seawater (TK8, 3/85)

3. **Range**

Limited to 0-50 μM NO_3 and 0-40 μM PO_4 by the Autoanalyzer technique currently in use. Standard additions of Urea and Glycine to MERL seawater were linear to 100 μM TN if diluted for auto analysis. Linearity is limited by the upper limit of linearity on the autoanalyzer, not the persulfate digestion, at least to 100μM TN.

4. **Average Blank**

Nitrogen	1-2 μM	depends heavily on the quality of the reagents in the Phosphorus
	0.3-0.5 μM	oxidation mixture and the deionized water available.

5. **Percent Recovery**

(as standard additions to MERL seawater)

Nitrogen	99-100%	Glycine
	99%	Urea
	98%	Caffeine
Phosphorus	99%	Fructose 1,6-Diphosphate

6. **Procedure**

For Total Dissolved N and P, replicate 20 mL unfiltered (total) and filtered (total Dissolved) aliquots are poured into digestion tubes to an etched 20 mL mark. Digestion tubes are 50 mL glass screw-cap tubes (Nalgene caps) that are "pre-digested" with oxidizing reagent, rinsed with deionized water, and oven dried (200°C) immediately prior to use. (Don't oven dry the caps!) 2.5 mL of persulfate oxidizing reagent is added to each 20 mL sample immediately, and the digestion tubes are tightly capped.

Persulfate Oxidizing Reagent:

50 g Potassium persulfate Low N (<0.0003%)
30 g Boric Acid (Baker 0084)
350 mL 1 M NaOH (40 g/L)

Dilute above reagents to 1 1 final volume with low N, low P deionized water and store in an amber 5 mL repipet.

A glycine standard curve in artificial seawater is used for Total N and a fructose 1,6 diphosphate standard curve is used for Total P. An artificial seawater blank should be made up with 20 mL of artificial seawater plus 20 mL of deionized water added after the digestion step should also be done.

All samples and standards are digested by cooking, tightly capped, in a boiling water bath for 15 min. (Although no tube explosions have ever occurred, it is best to do this step in a pot with a heavy lid and to use extreme caution in handling the tubes when they are hot). It is important that during this step the tubes be placed in a room-temperature water bath and gradually brought to a boil. After digestion, the tubes are cooled to room temperature, 20 mL of deionized water is added to each of the reagent blank tubes, and all tubes are then analyzed for $NO_2 + NO_3$ and PO_4 by routine Technicon Auto analysis (Lambert & Oviatt, 1983). Total N and total P are determined by regressing glycine or fructose diphosphate standards versus peak height on the autoanalyzer. Percent recovery of the organic standards is checked against recovery of inorganic nitrate and phosphate standards. In all calculations don't forget to correct for any NO_3 or PO_4 originally present in the artificial seawater used for standards.

7. Sample Storage

Samples for total or dissolved N and P should not be stored, the persulfate digestion mixture should be added to them as soon as possible after the samples are taken.

How Soon After Digestion Must AA Analysis be Done??

Samples run on the AA one week after digestion were not significantly different than those run immediately.

Can the Oxidizing Reagent be Used to Preserve Samples - How Soon After Adding the OR Must the Samples Be Digested?

Filtered MERL Seawater samples kept for 0, 2, 5, and 7 days after adding the oxidizer but before digestion were without significant change.

Recovery of N on day 0 = 97%
Recovery of N on day 7 = 93%
Recovery of P on day 0 = 100%
Recovery of P on day 7 = 90%

Variability between replicates did not increase over the 7-day period. Precision

was ± 0.15 μM at the 1 μM level for TP over the 7-day period.

These results do suggest, however, that it would be better to store samples in digested form if possible.

8. **Sample Dilution**

Samples that are likely to contain more than about 50 μM N are diluted before digestion with artificial seawater. Care must be taken to correct the results for N and P present in the artificial seawater.

9. **Summary**

Summary of the results forms various methods (March 1985). Concentrations are in μML^{-1} and represent a mean of 6 replicates ± 1 s.d.

Portion of Sample	Method	Results	
		Total N	Total P
Unfiltered Sample	Persulfate Digestion	60.3 ± 0.3	2.0 ± 0.08
Filtered Sample	Persulfate Digestion	31.7 ± 0.3	1.16 ± 0.04
Particulates	By difference above	28.6	0.83
Particulates	Persulfate Digestion on filters	30.8 ± 1.5	1.2 ± 0.04
Particulates	CHN Analysis of filters	33 ± 6	----
Particulates	HCL digestion of filters	----	2.4 ± 0.05

9. **Data Reporting**

Data files are kept on MERL computer for long-term storage in an excel spreadsheet. Data is distributed to users based on request. MASSDEP has requested TR and CR station data to be distributed to them annually, in an excel spreadsheet. GB data will be distributed to NERACOOS annually with SUNA data.

Data Files will consist of site name, date collected, date processed, PO4, SiO2, NH3, NO2, NO3, TN technicon raw, TN Ast./Tech fixed, TP, and NOTES. The data is only distributed with the SUNA data for TR, CR, GB, and GD.

11. **References**

Koroleff, F., 1976
Total and organic nitrogen. In: K. Grasshoff (ed.), Methods of Seawater Analysis. Verlag Chemie, Weinheim, pp. 167-175.

Lambert, C.E., and C.A. Oviatt. 1983.
Manual of Biological and Geochemical Techniques in Coastal Areas. MERL Series 1 Marine Technical Report No. 85., 281 pp.

Solorzano, L. 1969.
Determination of ammonia in natural waters by the phenol hypochlorite method. Limnol. Oceanogr. 14: 799-801.

Solorzano, L., and J. Sharp, 1980.
Determination of total dissolved phosphorus and particulate phosphorus in natural Waters. Limnol. Oceanogr. 25(4): 754-758.

Strickland, J.D.H. and T.R. Parsons. 1968.
A Practical Handbook of Seawater Analysis. Fisheries Res. Bd. Can. Bull, 167.

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

Wood, E.D., F.A.J. Armstrong, F.A. Richards. 1967.
Determination of nitrate in seawater by cadmium-copper reduction to nitrite. J.
[1] Mar. Biol. Assoc. U.K. 47: 23.

[1] Lambert, C.E. and C.A. Oviatt. 1986. Manual of biological and geochemical techniques in coastal areas. MERL Series, Report No. 1, second edition, The University of Rhode Island, Kingston, RI.

Dissolved Inorganic Nutrients

Oviatt and Hindle (1994) described the analysis of dissolved inorganic nutrients. Dissolved inorganic nutrient concentrations are determined for samples that have been passed through a Poretics or Nuclepore (0.4 □m pore size, 47-mm diameter) membrane filter. The concentrations of ammonium, nitrate, nitrite, silicate, and phosphate are measured colorimetrically on a Technicon II Autoanalyzer. This instrument automates standard manual techniques for the analysis of nutrients. The analysis of ammonium will be based on the technique of Solorzano (1969) whereby absorbance of an indophenol blue complex is measured at 630 nm. Nitrite is measured by the method of Bendschneider and Robinson (1952). The total of nitrate and nitrite is determined by reducing all nitrate in the sample to nitrite and analyzing for nitrite as above. The concentration of nitrate is obtained by difference. The reduction is accomplished using a cadmium column (Morris and Riley, 1963). The analysis of phosphate is based on the molybdate blue procedure of Murphy and Riley (1962). The colormetric analysis of silicate is based on that of Brewer and Riley (1966).

A 60-mL syringe will be used to inject sample water from a transfer jar, through an in-line filter (Nuclepore 47–mm–diameter, 0.4-µm-membrane-fiber filter) and into a 60-mL white polyethylene bottle. After rinsing the bottle three times, 40 mL of the remaining sample will be filtered into the bottle for analysis. The sample bottle will be labeled, and the sample will be frozen. The samples will remain frozen until analyzed.

Water Column Sample Analyses

Parameter	Lab	Units	Instrument	Reference
Dissolved ammonium	URI	µM	Technicon Autoanalyzer II	Lambert and Oviatt (1986); Solorzano (1969)
Dissolved inorganic nitrate and inorganic nitrite	URI	µM	Technicon Autoanalyzer II	Bendschneider and Robinson (1952), and Morris and Riley (1963)
Dissolved inorganic phosphorus	URI	µM	Technicon Autoanalyzer II	Murphy and Riley (1962)
Dissolved inorganic silicate	URI	µM	Technicon Autoanalyzer II	Brewer and Riley (1966); Lambert and Oviatt (1986)

Sample Volumes, Containers, and Processing for Field Samples

Parameter	Station Types	Sample Volume (Target) (mL)[a]	Sample Containers[c]	Shipboard Processing/ Preservation[c]	Maximum Holding Time to Analysis
Dissolved inorganic nutrients	All but Z	40	60-mL polyethylene bottle	Pass through a Nuclepore membrane filter. Freeze until analysis.	28 days

Calibration Procedures for Laboratory Instruments

Parameter	Instrument Type	Initial Calibration			Continuing Calibration		Corrective Ation
		No. Stds	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	
Dissolved inorganic nutrients	Technicon II Autoanalyzer	4-5	r ≥.999	Prior to analytical run	PD from initial #15%;	Every 20 samples	Investigate, recalibrate

Data Quality Objectives

		Frequency	Data Quality Indicator	Corrective Action
Procedural Blanks				
	Dissolved nutrients	1 per batch of 20	≤5 times MDL	
Filter Blanks				
	Particulate nutrients	1 per batch of 20	≤5 times MDL	
	Biogenic silica	1 per batch of 20	≤5 times MDL	
	Chlorophyll *a*/phaeophytin	Once daily	≤5 times MDL (0.02 ug/L MDL)	
	Total suspended solids	1 per batch of 20	≤5 times MDL	
Prepared Standards and SRM				
	Dissolved nutrients	Twice per year	85% - 115% recovery	
	Chlorophyll *a*/phaeophytin (Turner standard: 20 and 200 mg/L) [1]	2 levels immediately after initial calibration	≤5% RPD	
Laboratory Duplicates				
	Particulate nutrients	10% of samples	≤15% RPD	
	Chlorophyll *a*/phaeophytin	1 per batch of 20	≤15% RPD	
	TOTAL SUSPENDED SOLIDS	Every sample	≤10% RPD	
Laboratory Triplicates				
	Dissolved nutrients	All samples	≤2% RPD	
Field Duplicates				
Particulate carbon Particulate nitrogen Particulate phosphorus Biogenic silica Chlorophyll a/phaeophytin		Each mid-depth	<50% RPD	

The MDL values for Dissolved inorganic nutrients:
NO3+NO2 = 0.10 µMole
PO4 = 0.05 µMole
SiO2 = 0.07 µMole
NH3= 0.05 µMole
NO2 = 0.02 µMole

An experiment designed to test the holding time for dissolved inorganic nutrients was conducted in 2002. Water samples were collected from Narragansett Bay on 03/06/2002 and filtered. Ten samples were immediately analyzed, and the remaining samples were kept frozen until the analysis date. Based on the results presented below, it has been determined that samples can be held frozen for up to 60 days prior to analysis with no significant change in results and possibly as long as 80 days, although variability increases somewhat.

DISSOLVED INORGANIC NUTRIENT HOLDING TIME EXPERIMENT

DATE COLLECTED	DATE ANALYZED	NO_3+NO_2	PO_4	SIO_2	NH_3	NO_2
03/06/02	03/06/02	0.52	0.62	1.91	1.39	0.05
03/06/02	03/06/02	0.49	0.63	1.88	1.35	0.05
03/06/02	03/06/02	0.47	0.62	1.82	1.33	0.05
03/06/02	03/06/02	0.48	0.62	1.82	1.33	0.05
03/06/02	03/06/02	0.49	0.62	1.82	1.39	0.05
03/06/02	03/06/02	0.49	0.61	1.81	1.39	0.06
03/06/02	03/06/02	0.50	0.62	2.05	1.36	0.06
03/06/02	03/06/02	0.51	0.60	1.82	1.39	0.06
03/06/02	03/06/02	0.51	0.61	1.84	1.36	0.06
03/06/02	03/06/02	0.50	0.59	1.79	1.38	0.08
USED ALL POINTS	**AVG**	**0.50**	**0.61**	**1.86**	**1.37**	**0.06**
	STD DEV	**0.02**	**0.01**	**0.08**	**0.03**	**0.01**
	C.V.	**3.0%**	**1.9%**	**4.1%**	**1.8%**	**16.6%**
DROPPED HIGHEST AND LOWEST POINTS	**AVG**	**0.50**	**0.62**	**1.84**	**1.37**	**0.06**
	STD DEV	**0.01**	**0.01**	**0.04**	**0.02**	**0.01**
	C.V.	**2.1%**	**1.2%**	**2.1%**	**1.6%**	**9.7%**

DATE COLLECTED	DATE ANALYZED	NO_3+NO_2	PO_4	SIO_2	NH_3	NO_2
03/06/02	3/25/2002	0.59	0.53	2.16	1.27	0.08
19 Days	**% RECOVERED**	**118.0%**	**86.9%**	**116.1%**	**92.7%**	**140.4%**
03/06/02	4/1/2002	0.42	0.61	1.95	1.23	0.02
26 Days	**% RECOVERED**	**84.0%**	**100.0%**	**104.8%**	**89.8%**	**35.1%**
03/06/02	4/8/2002	0.61	0.65	2.01	1.61	0.05
33 Days	**% RECOVERED**	**122.0%**	**106.6%**	**108.1%**	**117.5%**	**87.7%**
03/06/02	4/24/2002	0.47	0.66	1.83	1.17	0.05
49 Days	**% RECOVERED**	**94.0%**	**108.2%**	**98.4%**	**85.4%**	**87.7%**
03/06/02	5/3/2002	0.44	0.58	1.86	1.20	0.04
03/06/02	5/3/2002	0.51	0.65	1.95	1.26	0.04
03/06/02	5/3/2002	0.50	0.64	1.82	1.26	0.04
03/06/02	5/3/2002	0.49	0.61	1.82	1.26	0.03
03/06/02	5/3/2002	0.51	0.65	1.81	1.20	0.05
03/06/02	5/3/2002	0.47	0.60	1.82	1.29	0.04
	AVG	**0.50**	**0.63**	**1.84**	**1.25**	**0.04**
	STD DEV	**0.03**	**0.03**	**0.05**	**0.04**	**0.01**
	C.V.	**5.6%**	**4.7%**	**2.9%**	**3.0%**	**15.8%**
59 Days	**% RECOVERED***	**99.2%**	**103.3%**	**99.1%**	**91.5%**	**70.2%**
03/06/02	5/22/2002	0.44	0.59	2.11	1.46	0.07
03/06/02	5/22/2002	0.42	0.62	2.05	1.32	0.06
03/06/02	5/22/2002	0.46	0.60	2.03	1.37	0.06
03/06/02	5/22/2002	0.42	0.62	2.08	1.34	0.06
03/06/02	5/22/2002	0.45	0.62	1.98	1.33	0.07
	AVG	**0.44**	**0.61**	**2.05**	**1.36**	**0.06**
	STD DEV	**0.27**	**0.29**	**0.80**	**0.51**	**0.24**
	C.V.	**3.9%**	**2.4%**	**3.1%**	**5.1%**	**3.2%**
78 Days	**% RECOVERED***	**87.6%**	**100.0%**	**110.2%**	**99.6%**	**112.3%**

% RECOVERED* is based on the average value for the day.

References:

Bendschneider, K. and R. J. Robinson, 1952. A new spectrophotometric determination of nitrite in seawater. *J. Mar. Res.* 11:87-96.

Brewer, P. G. and J. P. Riley, 1966. The automatic determination of silicate-silicon in natural waters with special reference to seawater. *Anal. Chim. Acta* 35:514-519.

Cohen K., 1995. A comparison of three chlorophyll *a* extraction methods. University of Rhode Island. Unpublished manuscript.

Lorenzen, C. J., 1966. A method of the continuous measurement of *in vivo* Chlorophyll concentration. *Deep Sea Res.* 13, 223-227.

Model 700 TOC Total Organic Carbon Analyzer User's Manual, OI Analytical.

Murphy, J. and J. P. Riley, 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta*, 27:31-36.

Oviatt, C. A. and K. M. Hindle, 1994. Manual of biological and geochemical techniques in coastal areas. MERL Series, Report No. 1. Third Edition. The University of Rhode Island, Kingston, Rhode Island.

Platt, T., C. L. Gallegos, and W. G. Harrison, 1980. Photoinhibition of photosynthesis and light for natural assemblages of coastal marine phytoplankton. *J. Mar. Res.* 28:687-701.

SAS. 1988. *SAS Procedures Guide, release 6.03 ed.* SAS Institute, Inc., Cary, NC.

Solorzano, L., 1969. Determination of ammonia in natural waters by phenolhypochlorite method. *Limnol. Oceanogr.* 14:799-801.

Solorzano, L., and J. Sharp, 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. *Limnol. Oceanogr.* 25(4):754-758.

Strickland, J. D. H. and T. R. Parson, 1968. A Practical Handbook of Seawater Analysis. *Fisheries Res. Bd. Can. Bull*, 167.

Webb, W.L., M. Newton, and D. Starr. 1974. Carbon dioxide exchange of *Alnus rubra*: a mathematical model. *Oecologia* 17: 281-291.

Yentsch, C. S. and D. W. Menzel, 1963. A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. *Deep Sea Res.* 10, 221-231.