# Waquoit Bay (WQB) NERR Nutrient Metadata January 2015 to December 2015 Latest Update 07/11/2017

## I. Data Set and Research Descriptors

## 1) Principal investigator(s) and contact persons –

#### a) Reserve Contacts

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## b) Laboratory Contacts

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## 2) Research objectives

The main purpose of the SWMP program is to aid Waquoit Bay NERR in one of its priority missions: to perform as a living laboratory and platform for coastal and estuarine research. The long term, continuous detailed monitoring of the estuary's basic hydro-physical, meteorological and chemical parameters are an essential tool and context for any research activities located here.

Besides this overarching mission, there are also several specific research interests. One primary issue for the Waquoit Bay ecosystem is the influence of anthropogenic induced alterations by nitrogen enrichment. Waquoit Bay receives nitrogen from several sources, such as septic systems (their leachate percolates into groundwater which then enters the bay), run off from roads, run off containing domestic and agricultural fertilizer and animal waste, and atmospheric sources. This elevated nitrogen loading to the bay has resulted in enhanced eutrophication that has contributed to the alteration of the bay's habitats. For example, thick mats of seaweeds (macroalgae) now cover the bottom where eelgrass meadows thrived in the 1970's. Unfortunately, there are few definitive records of the bay's water quality conditions during that period, which makes it difficult to evaluate the rates of change. To facilitate future evaluation, long-

term records from SWMP can be used to track water column conditions. Of obvious interest are measurements of dissolved nutrients in the bay's water column, as well as measurements of dissolved oxygen (DO), turbidity, and chlorophyll concentration. Such records will facilitate evaluation of changes which may come about from a continuation of watershed alteration that result from current development patterns (i.e., non-sewered residential areas served by private septic systems typically consisting of septic tanks and leach fields) as well as non-industrial commercial development, such as golf courses, cranberry bogs, and retail shopping outlets. The records will be useful for evaluating the efficacy of remediation efforts intended to reduce the nitrogen loading from these sources to Waquoit Bay.

Another focus of long-term research interest is the detection of climate change and the determination of its effects on the estuarine environment. Characterizing the variability of the various water column parameters, such as their scale, magnitude and frequency, is likely to be an important aspect of the estuarine ecosystem that may be sensitive to climate change. Related to this focus is an interest in the impact of storms (hurricanes and northeasters) and other extreme meteorological events on the estuary. For example, what temperature and wind field thresholds exist that might bring about or trigger certain conditions within the bay? The observations recorded by the SWMP will allow for these types of studies.

## a) Monthly Grab

Monthly grab samples are collected to quantify the horizontal spatial and seasonal variability of important nutrients in the water column at the four long-term water quality monitoring sites located throughout the Waquoit Bay system representative of the local salinity and habitat gradients as well as differences in upland and marine influence.

## b) Diel Sampling Program

Once per month, samples are collected every 135 minutes (2.25 hrs) through a lunar day tidal cycle (24.75 hrs) at the Menauhant SWMP long-term water quality monitoring site to quantify the temporal variability of important nutrients in the water column as a function of tidal and daily cycle dynamics. The sampling site was moved in 2007 from the Child's River (2002 to 2006), where it has been in the past, in order to characterize other SWMP sites.

#### 2) Research methods

## a) Monthly Grab Sampling Program

Monthly grab samples are taken at the four principal long term SWMP stations in the Waquoit Bay watershed (Metoxit Point, Child's River, Menauhant and Sage Lot Pond). Grab samples are taken on the same day, collected between +3 hours before slack low-water and slack low-water. No distinction is made between neap and spring tide conditions. Efforts are made to collect samples at approximately monthly (30 day) intervals.

Grab samples are reflective of the water mass sampled by the water quality data sonde (YSI 6600), at depths approximately 0.5 m above the bottom. Samples were taken following SWMP protocol, with two sequential grab samples (in immediate sequence – 1-3 minute interval between samples) obtained from each site for a total of eight grab samples from 4 sites. At the time of sample collection, water temperature, salinity, pH, specific conductivity, dissolved oxygen (mg/L and %saturation), and depth are also measured with an YSI 650. Depth data are not reported in this dataset, but are available by contacting the Reserve directly (see contact information for Jordan Mora on page 1).

All samples are collected in amber, wide-mouth, Nalgene 1000mL sample bottles that are acid-washed with 10% HCL and rinsed 3 times with distilled water. Samples are collected using a custom-designed 1L Van Dorn sampler, with the sample bottle rinsed 3 times with ambient water prior to collection of the sample. Samples are immediately returned to the lab (within one hour) and stored at 4°C until filtered for nutrients and chlorophyll (within 24 - 48hours). Once filtered/processed, samples are transported to the SMAST lab where they are held at -30°C if they are unable to be processed immediately.

## b) Diel Sampling Program

Diel (24.75 hr or 2-full tidal cycles) samples were taken monthly at the Menauhant long-term SWMP water quality station, and diel sampling is scheduled to overlap with the monthly grab sampling. Diel sampling generally begins in the morning and is scheduled without regard for tide state as it captures 2 full tidal cycles in any case (also no distinction is made between neap and spring tide conditions). Overall, twelve samples are collected over a lunar day (24hr and 45min) time period at 2.25 hour intervals using an ISCO auto-sampler. All samples are filtered for nutrients and chlorophyll. The samples are collected the next day when the ISCO sampler is finished.

Sampling depth of the ISCO ranges between 0.5 to 1.2 meters depending on the tidal stage, but the sampling height above the bottom is fixed at 0.4 meters, where the adjacent YSI data sonde sensors are located. Due to the use of ISCO auto samplers, ambient water rinses prior to sample collection are not possible.

For each 2.25 hour sampling interval, two 1 L bottles are filled simultaneously to assure that enough water is collected for nutrients and chlorophyll analysis and duplicate samples kept for re-sampling if needed. Samples are collected in 1000mL clear polypropylene bottles (kept dark inside the ISCO until returning to the lab) that are pre-cleaned with 10% HCl and rinsed 3 times with distilled water. During the summer months ice is added inside the ISCO sampler in an effort to decrease sample alteration by providing cold storage conditions. Samples are immediately returned to the lab and stored at 4°C until filtered for nutrients and chlorophyll (within 24 - 48hours). Once filtered/processed, samples are transported to the SMAST lab where they are held at -30°C if they are unable to be processed immediately. Field parameters are not available for ISCO samples.

#### 3) Site location and character

General description of Waquoit Bay estuarine system:

The Waquoit Bay National Estuarine Research Reserve (WBNERR) is located in the northeastern United States on the southern coast of Cape Cod, Massachusetts. About 8,000 people maintain permanent residency in Waquoit Bay's drainage area, which covers parts of the towns of Falmouth, Mashpee, and Sandwich. During summer months, the population swells 2-3 times with the greatest housing concentrations immediate to the coastline (water views and frontage). In addition, the upper portions of the watershed include a military base, Otis Air Force Base and the Massachusetts Military Reservation, portions of which have been designated by the EPA as Superfund sites due to past practices of dumping jet fuel and other volatile groundwater contaminants.

WBNERR's estuaries are representative of shallow tidal lagoons that occur from Cape Cod to Sandy Hook, New Jersey. WBNERR is within the northern edge of the Virginian biogeographic province, on the transitional border (Cape Cod) with the Acadian biogeographic province to the north and east. Like many

embayments located on glacial outwash plains, Waquoit Bay is shallow (< 5 m), fronted by prominent barrier beaches (i.e., those of South Cape Beach State Park and Washburn Island), and is backed by salt marshes and upland coastal forests of scrub pine and oak. Two narrow, navigable inlets, one reinforced with granite jetties, pass through two barrier beaches to connect Waquoit Bay with Vineyard Sound to the south.

Bottom sediments in the bay are organic rich (Corg conc. ~ 3-4%) silts and medium sands. Sediment cores taken in summer of 2002 indicate that the depth of these estuarine sediments is up to 9 m thick in places. Dating work on these sediment cores suggests that the Waquoit Bay basin has been inundated by the sea for about 5000 years, and sedimentation rates over the past 500 years are estimated to be range from 1.6 to 4.9 mm/yr. Thick (up to 0.3 m) macroalgae (seaweed) mats overlie much of the bottom of the bay, and largely consist of species *Cladophora vagabunda*, *Gracilaria tikvahiayae*, and *Enteromorpha*. The dominant marsh vegetation in Waquoit Bay is *Spartina alterniflora* and *Spartina patens*. Dominant upland vegetation includes mixed forests of red oak, white oak, and pitch pine, and other shrubs and plants common to coastal New England. Land-use in the bay's watershed is about 60% natural vegetation, but the remaining land is largely residential housing, with some commercial (retail malls), and minor amounts of agriculture (~3%) (Cranberry bogs).

Dense housing developments cover the two peninsulas that form the western shore of the Waquoit Bay estuarine system. Although the developments themselves are outside of the Reserve boundaries, dissolved nitrogen in discharges from their septic systems (via groundwater) and in fertilizer run-off from their lawns has significant effects on the functioning of the Waquoit Bay ecosystem. These impacts have been a primary subject of study at the Reserve since its designation (1988). One outcome of this research has been the delineation of sub-watersheds within the overall drainage area for Waquoit Bay, of which WBNERR is a small part. This knowledge allows for the design of experiments based on the spatial variation of nutrient loading and other land-use related impacts.

At the northern end of the bay, an area comprising a separate sub-watershed, coastal bluffs of glacial till rise 30 feet above sea level. The northern basin of the bay, just below these bluffs, is its deepest area (approximately 3 m MLW), while much of the remainder of the bay is about 1.5 m. Bourne, Bog, and Caleb Ponds are freshwater kettle hole ponds on the northern-most shore of the bay. As components of the same sub-watershed, they have a common albeit minor freshwater outflow into the bay's northern basin via a narrow channel through a brackish marsh. To the east and south, other sub-watersheds surround several tidal and freshwater ponds, including Hamblin and Jehu Ponds, brackish salt ponds that are connected to the main bay by the tidal waters of Little and Great Rivers, respectively. The shorelines of the ponds are developed with residences that are occupied both seasonally and year round. Hamblin Pond and Little River are components of one sub-watershed, and Jehu Pond and Great River are elements of a separate sub-watershed. Further south lays Sage Lot Pond. It is in the least developed sub-watershed and also contains a barrier beach and salt marsh ecosystem of the reserve's South Cape Beach State Park. To the east of Sage Lot Pond and within the same sub-watershed, lies the highly brackish Flat Pond. It receives minimal tidal flows of salt water from Sage Lot Pond through a narrow, excavated and culverted channel. The preponderance of the input to Flat Pond is groundwater and run off, both of which are likely affected (e.g., nutrients, pesticides, bacteria) by an adjacent golf course and near-by upper-scale residential development.

The largest source of surface freshwater to Waquoit Bay is the Quashnet / Moonakis River. Although named "river", this and Child's River are more appropriately described as "streams" because of their small channels and discharge ~1.0 CFS. A component of yet another sub-watershed, it originates in John's Pond situated north of the bay and traverses forests, cranberry bogs, residential areas, and the Quashnet Valley Golf Course before entering the bay near the southern "boundary" of the northern basin. ("Quashnet" applies to that portion of the river within the town of Mashpee, and "Moonakis" refers to the

brackish estuary at the river's mouth, lying in the town of Falmouth. Quashnet will be used hereafter to refer to the entire river.) The Quashnet River's tidal portion has sufficient numbers of coliform bacteria to cause it to be closed to shell fishing most of the time. The source(s) of these bacteria (human or avian) is unknown at this time.

The Child's River is the second largest input of surface freshwater to the bay. A component of another sub-watershed, it runs through densely developed residential areas. The Child's River sub-watershed receives the highest nitrogen loading and is the largest nitrogen contributor to the Waquoit Bay system of all the sub-watersheds. In the upper tidal portions of the river we have consistently recorded the highest nutrient and chlorophyll levels and the lowest dissolved oxygen readings of any region in the bay and so this location represents an end-member for looking at anthropogenic inputs and impacts on the system. Another, albeit smaller, source of freshwater is the discharge of Red Brook through brackish marshlands into Hamblin Pond. Additional freshwater enters the bay elsewhere through groundwater seepage (perhaps up to 50% of all freshwater input into the bay), precipitation and the flows of smaller brooks. There is relatively little surface water runoff entering directly into the bay due to the high percolation rates of Cape Cod's coarse, sandy soils.

Knowledge of the homo/heterogeneity of the water masses in Waquoit Bay was originally derived from measurements made by reserve staff and from data obtained by the reserve's volunteer water quality monitoring group, the Waquoit BayWatchers who have collected depth profiles of Waquoit Bay water quality since 1993. Subsequent research by reserve staff (including some numerical modeling by T. Isaji) has revealed that lateral mixing has considerable influence because tidal currents follow a general course through the bay. This results in an overall structure to horizontal patterns of water quality characteristics. The pattern it produces is a gyre in the central portion of the main bay whereby currents follow a generally counter-clockwise flow around a central area that exhibits reduced exchange with the remainder of the bay. The flushing rate within the gyre is diminished when compared with other more peripheral areas of the bay. The location of the gyre meanders slightly, apparently under the influence of tides and wind). Because of the shallow conditions, restricted tidal inlets, and low amplitude tidal forcing of Vineyard Sound here (tides are semi-diurnal with a range about 0.5 m) water levels in the bay are also strongly influenced by wind forcing. Southerly winds increase tidal heights and advance the phase of the flood and retard the phase of ebb (Northerly winds have the opposite effect).

System-Wide Monitoring Water Quality Stations:

## a) Metoxit Point (MP)

The Metoxit Point station (41° 34' 8.04" N 70° 31' 17.76" W; 1.0 m deep MLW- MLW determined two complete lunar cycles from July to September 2009) is located in the main basin of Waquoit Bay and was selected to be within or near the outer regions of the gyre (described above) and more or less represents "typical" water mass conditions and residence times for the bay. The location is at least a half mile from shore, well flushed by tides, and is in an area that is minimally disturbed by routine activities on the bay (e.g. boat traffic, shell fishing, etc.). Bottom sediments at the site are organic rich muds overlain by thick algal mats. Because of this site's fairly open exposure to south (greatest fetch over the bay), we have observed that when sustained southerly winds are greater than about 20 kts, the Metoxit Point site experiences increased turbidity (sediment suspension event). A mean tidal range of 0.46m (SD = 0.17) is calculated (based on one month of data from May 2003), with a minimum of 0.13 m and a maximum of 0.91 m. Mean monthly salinity range (calculated for 2002) was 4.2 ppt from a mean monthly minimum of 27.8 ppt to 32.0 ppt.

## b) Menauhant Station (MH)

The Menauhant station (41° 33' 9.36" N 70° 32' 54.60": W; 0.4 m deep MLW- MLW determined using two complete lunar cycles from July to September 2009) is located within the Eel Pond Inlet at the Menauhant Yacht Club dock. Eel Pond Inlet is the westernmost of the two main tidal inlets into the Waquoit Bay system. The site was chosen because it occupies one of the strategic locations for gauging the system's water mass characteristics. Entering waters represent the marine end-member while outflows represent the final product of estuarine water mass modification and export to shelf waters. The site also has easy walk-in access to a secure private pier that extends into the throat of the inlet. Also, because of the turbulent tidal flow within the inlet, conditions are vertically well mixed, and the site can be maintained year round even through ice-over conditions in the rest of the bay. Bottom sediments at this site are clean sands and gravels with almost no attached bottom vegetation. Since inception, we have noted that strong south to southeast (onshore) winds tend to produce turbidity events at this site from the wave induced suspension of fine sediments and organic material in the upstream near-shore zone. While we have found that these types of turbidity events are localized to windward near-shore areas in the bay, the transport of these sediments at inlet mouths during such times is perhaps a dominant sedimentation process within the estuarine system. In other words, while the choice of our location may be producing a localized signal in one of our measured parameters that signal may reflect key processes in the system at large. A mean tidal range of 0.48m (SD = 0.19) is calculated based on one month of data (May 2003), with a minimum of 0.11 m and a maximum of 0.99 m. Mean monthly salinity range (calculated for 2002) was 3.9 ppt from a mean monthly minimum of 28.5 ppt to 32.4 ppt.

## c) Childs River (CR)

The Child's River station (41° 34' 47.28" N 70° 31' 51.24" W; 0.6 m deep MLW- MLW determined using two complete lunar cycles from July to September 2009) is located on a dock piling at Edwards Boat Yard, a commercial marina near the upper tidal reaches of Child's River— the second largest input of surface freshwater to the bay. It runs through densely developed residential areas. The Child's River sub-watershed receives the highest nitrogen loading and is the largest nitrogen contributor to the Waquoit Bay system of all the sub-watersheds. In the upper tidal portions of the river we have consistently recorded the highest chlorophyll levels and the lowest dissolved oxygen readings of any region in the bay and so this location represents an end-member for looking at anthropogenic inputs and impacts on the system. This location is very strongly stratified, characterized by a salt wedge with fresher river water overlying saline ocean water. Vertical salinity ranges can run from 0-10 ppt at the surface to more than 30 ppt just 1 m below. The sonde sensors are usually well within the salt wedge portion of the water column, nonetheless this location is also our freshest SWMP site, and is at the opposite end of Child's River from the seaward Menauhant station. Bottom sediments are fine organic rich muds. This location represents the most terrigenously and anthropogenically-impacted SWMP site. Monthly water quality, collected near this location for the past decade, shows very high chlorophyll concentrations during the warmer months and more recent dissolved nutrient records show very high nutrient-loads. Boat traffic at the marina likely leads to increased turbidity during the boating season as well. As this site is dockside at a private marina, general security is high along with easy access. The station is also serviceable year-round and usually not subject to seasonal shutdown due to ice over. A mean tidal range of 0.46 m (SD = 0.17) is calculated based on one month of data (May 2003), with a minimum of 0.11 m and a maximum of 0.95 m. Mean monthly salinity range (calculated for 2002) was 14.7 ppt from a mean monthly minimum of 15.8 ppt to 30.5 ppt.

## d) Sage Lot (SL)

The Sage Lot station (41° 33' 15.12" N 70° 30' 30.20" W; 0.3 m deep) is located in deeper portion of Sage Lot Pond – a small sub-estuary of Waquoit Bay (20 ha) surrounded by salt marsh and barrier beach. Its small watershed is the least developed of all of Waquoit Bay's sub-watersheds and Sage Lot Pond is considered to be its least impacted and most pristine sub-estuary. Bottom sediments are organic rich mud. Sage Lot Pond possesses one of the few remaining eelgrass beds in the Waquoit Bay system. Indeed the Child's River and Sage Lot Pond sites are considered to represent opposite end-members of nutrient-loading and human-induced influence. Researchers often locate their experiments in these two locations to take advantage of this difference. However, Sage Lot Pond is hydrologically connected to an upstream brackish source -- Flat Pond – via a series of tidal creeks, drainage ditches and culverts. Flat Pond borders a country club and golf course and some concern exists for its impact on the water quality of Sage Lot Pond. A mean tidal range of 0.40m (SD = 0.14) is calculated based on one month of data (May 2003), with a minimum of 0.11 m and a maximum of 0.67 m. Mean monthly salinity range (calculated for 2002) was 4.9 ppt from a mean monthly minimum of 27.2 ppt to 32.1 ppt.

## 4) Code Variable Definitions

```
    wqbcrnut – Waquoit Bay Child's River nutrients
    wqbmhnut – Waquoit Bay Menauhant nutrients
    wqbmpnut – Waquoit Bay Metoxit Point nutrients
    wqbslnut – Waquoit Bay Sage Lot nutrients
```

## Monitoring program:

monthly grab sample program = 1 (collected with custom-designed van Dorn sampler) diel grab sample program = 2 (collected with ISCO)

# 5) Data collection period (all times listed in EST)

# **Diel Sampling:**

# Menauhant

Month	Start Date	Start Time	End Date	End Time
Jan	NS	NS	NS	NS
Feb	02/25/2015	10:06	02/26/2015	10:51
Mar	03/10/2015	6:47	03/11/2015	7:32
Apr	04/13/2015	9:14	04/14/2015	9:59
May	05/26/2015	9:07	05/27/2015	9:52
June	06/09/2015	9:41	06/10/2015	10:26
July	07/07/2015	8:41	07/08/2015	9:26
Aug	08/04/2015	7:27	08/05/2015	8:12
Sept	09/22/2015	10:16	09/23/2015	11:01
Oct	10/20/2015	9:22	10/21/2015	10:07
Nov	11/03/2015	10:28	11/04/2015	11:13
Dec	12/01/2015	9:05	12/02/2015	9:50

# **Grab Sampling:**

# Menauhant (MH)

Month	Sample 1 Date	Sample 1 Time	Sample 2 Date	Sample 2 Time
Jan	NS	NS	NS	NS
Feb	02/25/2015	10:17	02/25/2015	10:23
Mar	03/11/2015	8:27	03/11/2015	8:32
Apr	04/13/2015	9:24	04/13/2015	9:33
May	05/27/2015	10:47	05/27/2015	10:52
June	06/10/2015	9:40	06/10/2015	9:43
July	07/08/2015	9:53	07/08/2015	9:59
Aug	08/05/2015	8:53	08/05/2015	8:57
Sept	09/22/2015	10:28	09/22/2015	10:32
Oct	10/21/2015	10:23	10/21/2015	10:28
Nov	11/04/2015	11:09	11/04/2015	11:17
Dec	12/01/2015	9:21	12/01/2015	9:26

# Metoxit Point (MP)

Month	Sample 1 Date	Sample 1 Time	Sample 2 Date	Sample 2 Time	
Jan	NS	NS	NS	NS	
Feb	NS	NS	NS	NS	
Mar	NS	NS	NS	NS	
Apr	NS	NS	NS	NS	
May	05/27/2015	9:19	05/27/2015	9:25	
June	06/10/2015	10:35	06/10/2015	10:40	
July	07/08/2015	8:24	07/08/2015	8:28	
Aug	08/05/2015	7:18	07/08/2015	7:24	
Sept	09/22/2015	9:25	09/22/2015	9:30	
Oct	10/21/2015	8:54	10/21/2015	9:00	
Nov	11/04/2015	9:42	11/04/2015	9:46	
Dec	12/01/2015	8:14	12/01/2015	8:17	

Sage Lot Pond

Month	Sample 1 Date	Sample 1 Time	Sample 2 Date	Sample 2 Time
Jan	NS	NS	NS	NS
Feb	NS	NS	NS	NS
Mar	NS	NS	NS	NS
Apr	NS	NS	NS	NS
May	05/27/2015	12:20	05/27/2015	12:23
June	06/10/2015	12:04	06/10/2015	12:07
July	07/08/2015	11:10	07/08/2015	11:13
Aug	08/05/2015	10:08	08/05/2015	10:11
Sept	09/22/2015	11:58	09/22/2015	12:01
Oct	10/21/2015	11:57	10/21/2015	12:03
Nov	11/04/2015	12:43	11/04/2015	12:48
Dec	12/01/2015	10:53	12/01/2015	10:56

# Child's River

Month	Sample 1 Date	Sample 1 Time	Sample 2 Date	Sample 2 Time
Jan	NS	NS	NS	NS
Feb	02/25/2015	10:49	02/25/2015	10:55
Mar	03/11/2015	7:55	03/11/2015	8:01
Apr	04/13/2015	9:53	04/13/2015	9:58
May	05/27/2015	11:12	05/27/2015	11:17
June	06/10/2015	9:10	06/10/2015	9:14
July	07/08/2015	9:21	07/08/2015	9:26
Aug	08/05/2015	8:20	08/05/2015	8:24
Sept	09/22/2015	10:51	09/22/2015	10:56
Oct	10/21/2015	9:54	10/21/2015	9:58
Nov	11/04/2015	10:45	11/04/2015	10:50
Dec	12/01/2015	9:47	12/01/2015	9:51

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### 6) Associated researchers and projects

## a) SWMP Water Quality Monitoring Data

In order to understand long-term changes in water quality, YSI 6600-series data loggers are deployed. For all sites, measurements of dissolved oxygen, salinity, temperature, pH, depth and turbidity are taken at each of the 4 sites at 15 minute intervals, continuously. At the Menauhant site, a satellite system was installed in July 2006. The data collected provides background data for other research about the ecology of these habitats. Visit <a href="www.nerrsdata.org">www.nerrsdata.org</a> if you are interested in the data.

### b) BayWatchers

BayWatchers is a citizen science group based in Waquoit Bay since 1993. Volunteers measure for dissolved oxygen concentration, salinity, temperature (air and water), water clarity, chlorophyll-*a* and nutrients at 9 sites throughout the Waquoit Bay watershed. Contact Jordan Mora, Research Associate, to view the data.

#### c) SWMP Meteorological Data

Meteorological data are also collected at Waquoit Bay NERR and may be accessed at www.nerrsdata.org.

#### d) Ocean Acidification-WHOI

Ocean acidification is due to the uptake of excess atmospheric carbon dioxide (CO<sub>2</sub>) by the ocean. Dr. Daniel McCorkle's lab at the Woods Hole Oceanographic Institute (WHOI) is collecting water samples in concurrence with monthly nutrient sampling in order to better understand the seasonal rhythm and natural variation of dissolved carbon dioxide in the estuary ecosystem, specifically focusing on the effect of ocean acidification on marine organisms with calcium carbonate (CaCO<sub>3</sub>) shells. For more information visit:

http://www.whoi.edu/sbl/liteSite.do?litesiteid=7193&articleId=17706

#### 8) Distribution

NOAA retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The NERRS retains the right to be fully credited for having collected and process the data. Following academic courtesy standards, the NERR site where the data were collected should be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

#### Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2012.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page <a href="https://www.nerrsdata.org">www.nerrsdata.org</a>. Data are available in comma separated version format.

#### **II. Physical Structure Descriptors**

## 9) Entry verification

Data is received from the University of Massachusetts-Dartmouth School of Marine Science and Technology (SMAST) on a quarterly basis (including EPA-regulation QA data and any necessary rerun samples). SMAST provides the data in mg/L so no conversion is necessary once the data is received. Chlorophyll-a and pheophytin analysis is completed at the Waquoit Bay NERR laboratory using the spectrophotometer method until August 2015 and the fluorometer method starting September 2015. All calculations for chlorophyll-a and pheophytin concentration are determined using Excel. Please request SOPs from Jordan Mora, Research Associate (see contact information on page 1) to view calculation formulas.

Nutrient data are entered into a Microsoft Excel worksheet and processed using the NutrientQAQC Excel macro. The NutrientQAQC macro sets up the data worksheet, metadata worksheets, and MDL worksheet; adds chosen parameters and facilitates data entry; allows the user to set the number of significant figures to be reported for each parameter and rounds using banker's rounding rules; allows the user to input MDL values and then automatically flags/codes measured values below MDL and inserts the MDL; calculates parameters chosen by the user and automatically flags/codes for component values below MDL, negative calculated values, and missing data; allows the user to apply QAQC flags and codes to the data; produces summary statistics; graphs selected parameters for review; and exports the resulting data file to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database

Jordan Mora, Research Associate, is responsible for these tasks and data QAQC.

## 10) Parameter Titles and Variable Names by Data Category

Required NOAA/NERRS System-wide Monitoring Program water quality parameters are denoted by an asterisks "\*".

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus:	*Orthophosphate	PO4F	mg/L as P
•	•		-
Nitrogen:	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	*Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Total Dissolved Nitrogen	TDN	mg/L as N
	Dissolved Organic Nitrogen	DON	mg/L as N
	Total Organic Nitrogen	TON	mg/L as N
	Particulate Organic Nitrogen	PON	mg/L as N
	Total Nitrogen	TN	mg/L as N
Carbon:	Particulate Organic Carbon	POC	mg/L as C
	-		
Other Lab Parame	eters:		
	*Chlorophyll a	CHLA_N	μg/L
	Pheophytin a	PHEA	μg/L
	Silicate, filtered	SiO4F	mg/L as Si
	,		C
Field Paramete	ers:		
	Water temperature	WTEMP N	°C
	рН	PH N	standard units
	Salinity	SALT N	ppt
	Dissolved oxygen, saturation	DO S N	% %
	Dissolved oxygen, concentration	DO N	mg/L
	, , , , , , , , , , , , , , , , , , , ,	_	<i>-</i>

#### **Notes:**

- 1) Time is coded based on a 2400 hour clock and all times are changed to Eastern Standard Time (EST).
- 2) Reserves have the option of measuring either NO2 and NO3 or they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3. Waquoit Bay Reserve measured NO2 until July 2003 after one year of monthly measurements, when it was determined that NO2 was not usually a significant component of NO23 and so NO23 is considered to be overwhelmingly NO3. Since July 2003, NO23 and NH4 were the only measured DIN species.
- 3) PON/POC began to be measured in April 2003, allowing calculation of TN.
- 4) Diel salinity measurements are taken in the lab at SMAST from leftover sample using a refractometer. No other field measurements are available for diel samples.

### 11) Measured and Calculated Laboratory Parameters

a) Variables Measured Directly

Nitrogen species: NO23F, NH4F, TDN, PON

Carbon species: POC
Phosphorus species: PO4F

Other: CHLA\_N, PHEA, SiO4F

### b) Computed Variables

 DIN
 NO23F+NH4F

 TON
 TN-NH4F-NO23F

 DON
 TDN-NH4F-NO23F

TN TDN+PON

## 12) Limits of Detection

Table 1. **Method Detection Limits** (MDL) for measured water quality parameters for each sample month's nutrient analysis

month 5 nati	Terre arrary	710							
	NO23	NH4	PO4	SiO4	POC	PON	TDN	CHLA	PHEA
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(µg/L)	(µg/L)
January	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
February	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
March	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
April	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
May	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
June	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
July	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
August	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
September	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
October	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
November	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5
December	0.001	0.001	0.003	0.01	0.01	0.01	0.001	0.5	0.5

<sup>\*</sup>NS = No sample due to staff limitations and ice cover.

Monthly MDL's for CHLA and PHEA were a priori set at 0.5 ug/L. MDL's for NO23F, NH4F, PO4F, PON/POC and TDN are determined by the School for Marine Science and Technology.

### 13) Laboratory Methods

Contact Waquoit Bay NERR Research Associate for a copy (electronic or hard) of the following SOP's (a-g). <u>jordan.mora@state.ma.us</u> (508-457-0495 ext 128).

## a) Parameter: NH4F

<u>SMAST Laboratory Method</u>: Indophenol/hypochlorite method, Spectrophotometer <u>EPA Reference Method</u>: 350.1

Method References:

1) Scheiner, D. 1976. Determination of ammonia and kjeldahl nitrogen by indophenols method. Water Research, 10:31-36.

2) Standard Methods for the Examination of Water and Wastewater. 19<sup>th</sup> edition. Method 4500-NH4-F.

<u>EPA Method Descriptor:</u> Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside and measured colorimetrically.

<u>Preservation Method:</u> Samples are filtered (cellulose acetate geofilters, 0.20μm, 47mm) as soon as possible following collection, and are stored in the dark at 4°C for 12-24 hours or at -30°C for no more than 28 days before analysis.

## b) Parameter: NO23F

<u>SMAST Laboratory Method</u>: Lachat analysis using copperized cadmium reduction and colorimetric assay.

EPA Reference Method: 353.2

#### Method References:

- 1) Standard Methods for the Examination of Water and Wastewater, 19<sup>th</sup> edition. Method 4500-NO3-F.
- 2) Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. Journal of Marine Biology Ass. U.K. 47: 23-31.
- 3) Bendschneider, K. R. Robinson. 1952. A new spectrophotometer method for the determination of nitrite in seawater. Journal of Marine Research. 11: 87-96.

<u>EPA Method Descriptor:</u> A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

Preservation Method: Samples are filtered (cellulose acetate geofilters, 0.20μm, 47mm) as soon as possible following collection, and are stored in the dark at 4°C for 48 hours or at -30°C for no more than 28 days before analysis.

#### c) Parameter: PO4F

SMAST Laboratory Method: Molybdate/ascorbic acid method

EPA Reference Method: 365.3

## Method References:

- 1) Standard Methods for the Examination of Water and Wastewater, 19<sup>th</sup> edition. Method 4500-P-E.
- 2) Murphy, J. and J.P. Riley. 1962. A modified single solution method for determination of phosphate in natural waters. Analytica Chimica Acta, 27: 31-36.

<u>EPA Method Descriptor</u>: Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

<u>Preservation Method:</u> Samples are filtered (cellulose acetate geofilters, 0.20μm, 47mm) as soon as possible following collection, and are stored in the dark at 4°C for 12-24 hours or at -30°C for no more than 28 days before analysis.

## d) Parameter: POC/PON

SMAST Laboratory Method: Micro-Dumas combustion technique

EPA Reference Method: 440.0

Method References:

- 1) Kirsten, W. 1983. Organic Elemental Analysis: Ultramicro, Micro, and Trace Methods. Academic Press/Harcourt Brace Jovanovich, NY.
- 2) Perkin-Elmer Model 2400 CHN Analyzer Technical Manual.

<u>EPA Method Descriptor:</u> An accurately measured amount of particulate matter from an estuarine water sample or an accurately weighed dried sediment sample is combusted at 975°C using an elemental analyzer. The mixture is released to a series of thermal conductivity detectors/traps, measuring in turn by difference, hydrogen (as water vapor), C (as carbon dioxide) and N (as N<sub>2</sub>). <u>Preservation Method:</u> Sample filtration (combusted 25mm GF/F) within 24 hours of collection, dried, and stored in dessicator for no more than 28 days before analysis.

## e) Parameter: Silicate

SMAST Laboratory Method: Molybdate/silicomolybdate complex method

EPA Reference Method: 370.1

Method References:

- 1) Mullin and Riley. 1955. Analytica Chimica Acta, 12: 162.Standard Methods for the Examination of Water and Wastewater. 17<sup>th</sup> edition, 1989, p.4-181.
- 2) Strickland, J.D.H. and T.R. Parsons. 1965. A Manual of Seawater Analysis. Fisheries Research Board of Canada.

EPA Method Descriptor: A well-mixed sample is filtered through a 0.45 μm membrane filter. The filtrate, upon the addition of molybdate ion in acidic solution, forms a greenish-yellow color complex proportional to the dissolved silica in the sample.

Preservation Method: Samples are filtered (cellulose acetate geofilters, 0.20μm, 47mm) as soon as possible following collection, and are stored in the dark at 4°C for 12-24 hours or at -30°C for no more than 28 days before analysis.

### f) Parameter: TDN

SMAST Laboratory Method: Lachat method, Persulfate digestion

Reference Method: 31-107-04-4-C

Method References:

- 1) Standard Methods for the Examination of water and Wastewater. 19<sup>th</sup> edition. Method 4500-Norg.
- 2) D'Elia, C.F., P.A. Stuedler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnology and Oceanography, 22: 760-764.

<u>Lachat Method Descriptor:</u> A well-mixed sample is filtered through a  $0.45~\mu m$  membrane filter. Filtered and unfiltered samples can be oxidized to nitrate and then analyzed using the persulfate digestion method.

<u>Preservation Method:</u> Samples are filtered (cellulose acetate geofilters, 0.20μm, 47mm) as soon as possible following collection, and are stored in the dark at 4°C for 12-24 hours or at -30°C for no more than 28 days before analysis.

# g) Parameter: Chlorophyll a and Pheophytin a

January – July 2015

Waquoit Bay NERR Laboratory

EPA Method Reference: USEPA Method 446.0

Method Reference:

- 1) USEPA Method 446.0, "In Vitro Determination of Chlorophylls a, b, c1 +c2 and Pheopigments in Marine and Freshwater Algae by Visible Spectrophotometry."
- 2) Eaton, A.D., L.S. Clesceri, and A.E. Greenberg (1995) Spectrophotometric determination of chlorophyll in Standard Methods for the Examination of Water and Wastewater 10-18.

Method Description: Water samples are filtered through Glass Fiber Filters (25mm) using a vacuum pump until flow through slows substantially (filtered volume normally between 250ml and 600ml). Three drops of magnesium carbonate solution are added to the filters with a final DI rinse (< 3mL). Filters are immediately added to centrifuge tubes with ~12mL of 90% acetone, shaken vigorously, and frozen at -20°C for at least 24 hours before analysis on the spectrophotometer (samples are processed within one week of initial freezing). Upon removal from the freezer, the vials are shaken vigorously for roughly 10 seconds and after settling at room temperature for 30 minutes to 1 hour, centrifuged for 15 minutes before analysis. (Note: This method started with October 2013 samples, the Waquoit Bay laboratory no longer grinds filters before adding acetone extraction solution.)

<u>Preservation Method:</u> Filters are frozen (GF/F, 25mm) in 90% acetone at -20°C for at least 24 hours but analysis is conducted within one week of extraction.

August - December 2015

Waquoit Bay NERR Laboratory

EPA Method Reference: EPA Method 445.0.

Method Reference:

1) EPA Method 445.0. In Vitro Determination of Chlorophyll-a and Pheophytin-a in Marine and Freshwater Algae by Fluorescence.

Method Description: Water samples are filtered through Glass Fiber Filters (25mm) using a vacuum pump until flow through slows substantially (filtered volume normally between 250ml and 600ml). Three drops of magnesium carbonate solution are added to the filters with a final DI rinse (< 3mL). Filters are immediately added to centrifuge tubes with ~12mL of 90% acetone, shaken vigorously, and frozen at -20°C for at least 24 hours before analysis on fluorometer (samples are processed within one week of initial freezing). Upon removal from the freezer, the vials are shaken vigorously for roughly 10 seconds and after settling at room temperature for 30 minutes to 1 hour, centrifuged for 15 minutes before analysis.

<u>Preservation Method:</u> Filters are frozen (GF/F, 25mm) in 90% acetone at -20°C for at least 24 hours, but no more than one week, before analysis.

## 14) Field and Laboratory QA/QC Programs

#### a) Precision -

- i. **Field Variability** WQBNERR collects two successive grab samples for the monthly grab sample program. Additionally, at Waquoit Bay NERR, one field duplicate is collected at one site per sampling event (the site chosen for the duplicate rotates among the four sites). Field duplicates must be within  $\pm 10\%$  for NO3, NH4, PO4, and within 20% for TDN, PON, POC, and SiO4 to be deemed acceptable.
- ii. **Laboratory Variability** Laboratory duplicates are assayed in duplicate for at least 15% of the samples with a 5% tolerance between duplicates required for acceptances.
- iii. **Inter-organizational splits** none.

#### b) Accuracy -

- i. **Sample Spikes** see annual SMAST QAQC results (available upon request from SMAST, CDMO, or Waquoit Bay NERR)
- ii. Standard Reference Material Analysis –The UMASS Dartmouth-SMAST has been successfully tested by the MassDEP on a series of blind certification standards. In addition, they regularly analyze a series of AccuStandard © test samples for accuracy and precision. SMAST has also been approved for nutrient and biogeochemical assays by USGS, EPA, and the States of Florida and Connecticut under specific for specific projects related to surface water, groundwater and marine waters.
- iii. Cross Calibration Exercises In summer 2010, the Waquoit Bay passed a NERRs-wide inter-lab reference comparison. In fall 2015, the Waquoit Bay fluorometer was taken to neighboring Reserve labs at Great Bay in New Hampshire and Wells in Maine for cross-comparison of replicate chlorophyll-a samples. The results showed comparable values across all three instruments. These data are available upon request.

### 15) QAQC flag definitions

QAQC flags provide documentation of the data and are applied to individual data points by insertion into the parameter's associated flag column (header preceded by an F\_). QAQC flags are applied to the nutrient data during secondary QAQC to indicate data that are out of sensor range low (-4), rejected due to QAQC checks (-3), missing (-2), optional and were not collected (-1), suspect (1), and that have been corrected (5). All remaining data are flagged as having passed initial QAQC checks (0) when the data are uploaded and assimilated into the CDMO ODIS as provisional plus data. The historical data flag (4) is used to indicate data that were submitted to the CDMO prior to the initiation of secondary QAQC flags and codes (and the use of the automated primary QAQC system for WQ and MET data). This flag is only present in historical data that are exported from the CDMO ODIS.

- -4 Outside Low Sensor Range
- -3 Data Rejected due to QAQC
- -2 Missing Data
- -1 Optional SWMP Supported Parameter
- 0 Data Passed Initial QAQC Checks
- 1 Suspect Data
- 4 Historical Data: Pre-Auto QAQC
- 5 Corrected Data

### 16) QAQC code definitions

QAQC codes are used in conjunction with QAQC flags to provide further documentation of the data and are also applied by insertion into the associated flag column. There are three (3) different code categories, general, sensor, and comment. General errors document general problems with the sample or sample collection, sensor errors document common sensor or parameter specific problems, and comment codes are used to further document conditions or a problem with the data. Only one general or sensor error and one comment code can be

applied to a particular data point. However, a record flag column (F\_Record) in the nutrient data allows multiple comment codes to be applied to the entire data record.

### General errors

GCM Calculated value could not be determined due to missing data
GCR Calculated value could not be determined due to rejected data
GDM Data missing or sample never collected
GQD Data rejected due to QA/QC checks
GQS Data suspect due to QA/QC checks
GSM See metadata

### Sensor errors

SBL	Value below minimum limit of method detection
SCB	Calculated value could not be determined due to a below MDL
	component
SCC	Calculation with this component resulted in a negative value
SNV	Calculated value is negative
SRD	Replicate values differ substantially
SUL	Value above upper limit of method detection

### **Parameter Comments**

CAB	Algal bloom
CDR	Sample diluted and rerun
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample

## Record comments

CAB	Algal bloom
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample
Cloud cover	r
CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)

CFY foggy

CHY hazy

CCC cloud (no percentage)

## Precipitation

PNP none

PDR drizzle

PLR light rain

PHR heavy rain

PSQ squally

PFQ frozen precipitation (sleet/snow/freezing rain)

PSR mixed rain and snow

# Tide stage

TSE ebb tide

TSF flood tide

TSH high tide

TSL low tide

## Wave height

WH0 0 to <0.1 meters

WH1 0.1 to 0.3 meters

WH2 0.3 to 0.6 meters

WH3 0.6 to > 1.0 meters

WH4 1.0 to 1.3 meters

WH5 1.3 or greater meters

#### Wind direction

N from the north

NNE from the north northeast

NE from the northeast

ENE from the east northeast

E from the east

ESE from the east southeast

SE from the southeast

SSE from the south southeast

S from the south

SSW from the south southwest

SW from the southwest

WSW from the west southwest

W from the west

WNW from the west northwest

NW from the northwest

NNW from the north northwest

## Wind speed

WS0 0 to 1 knot

WS1 > 1 to 10 knots

WS2 > 10 to 20 knots

WS3 > 20 to 30 knots

WS4 > 30 to 40 knots WS5 > 40 knots

## 17) Other Remarks/Notes

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of NO23F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the Reserve submitting the data.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2007-2010 were also flagged/coded, but either reported as the measured value or a blank cell. Any 2007-2011 nutrient/pigment data downloaded from the CDMO prior to November of 2011 will reflect this difference.

#### **GSM/CSM Notes:**

Menauhant (MH)

- ➤ 04/13/2015 20:29, <1>(CSM) Chlorophyll-a and pheophytin values are elevated due to macroalgae fragments on the filter.
- ➤ 04/14/2015 7:44, <1>(CSM) Chlorophyll-a and pheophytin values are elevated due to macroalgae fragments on the filter.

Sage Lot (SL)

➤ 09/22/2015, <1> (CSM) – Chlorophyll-a, pheophytin, PON, TN, POC, and SiO4 are flagged as suspect because they were all abnormally high during this sampling event.

Childs River (CR)

➤ 05/27/2015, <1> (GSM) – NO23, TDN, DIN, and TN are above average for this sampling event so they are marked as suspect.

Metoxit Point (MP)

 $\triangleright$  09/22/2015, <1> (CSM) – Salinity levels are suspiciously low.

#### **CHB Notes:**

## Chlorophyll-a and Pheophytin-a (August – December 2015)

Due to the loss of the laboratory spectrophotometer which started showing signs of unstable readings in July 2015, the chlorophyll-a and pheophytin readings were delayed until a new instrument could be assembled for the analysis. At this delay interval, we shifted from the spectrophotometer method to the fluorometer method. The fluorometer needed new filters and lamps. Additionally, we conducted a comparative experiment with the Great Bay and Wells NERRs, which also use fluorometers for these analyses, to confirm the data quality of the new instrument. Those results are available upon request – contact Jordan Mora, Research Associate.

All other CHB (past holding time) flagging indicates that an analysis occurred more than 28 days after the sample was collected and delivered to the UMASS-Dartmouth School for Marine Science and Technology (SMAST). All samples that are processed later than 24-48hours after collection are stored at -30°C at SMAST until analyzed. See Table 2 (page 21) for processing dates.

Table 2. Dates that nutrient analyses were performed for the 2015 samples. Dates in red indicate analysis occurred after the CDMO recommended holding times (>28days at -20°C). (Note: CDMO does not provide recommended holding times for POC, PON, or SiO4 because they are not required parameters.) Chlorophyll (CHL) and pheophytin (PHEA) are processed at the Waquoit Bay Reserve Laboratory. Phosphate (PO4), ammonium (NH4), nitrate/nitrite (NO23), total dissolved nitrogen (TDN), particulate organic carbon (POC), particulate organic nitrogen (PON), and silicate (SiO4) are processed at the UMASS-Dartmouth School for Marine Science and Technology.

SAMPLE	CHL &							
DATE	PHEA	PO4	NH4	NO23	TDN	POC	PON	SiO4

2/24/2015 —	2/2/2015	2/27/2015	2/27/2015	4/2/2015	4/0/2015	2/10/2015	2/10/2015	4/22/2015
2/25/2015	3/2/2015	2/27/2015	2/27/2015	4/2/2015	4/8/2015	3/19/2015	3/19/2015	4/22/2015
3/10/2015- 3/11/2015	3/13/2015	3/12/2015	3/12/2015	4/2/2015	4/8/2015	3/19/2015	3/19/2015	4/22/2015
4/13/2015- 4/14/2015	4/20/2015	4/16/2015	4/16/2015	7/2/2015	7/2/2015	6/24/2015	6/24/2015	6/18/2015
5/26/2015- 5/27/2015	6/1/2015	5/28/2015	5/28/2015	7/2/2015	7/2/2015	6/24/2015	6/24/2015	6/18/2015
6/9/2015- 6/10/2015	6/15/2015	6/11/2015	6/11/2015	7/2/2015	7/2/2015	6/24/2015	6/24/2015	6/18/2015
7/7/2015- 7/8/2015	7/13/2015	7/10/2015	7/10/2015	11/19/2015	11/27/2015	10/27/2015	10/27/2015	1/7/2015
8/4/2015- 8/5/2015	1/20/2016	8/4/2015	8/4/2015	11/19/2015	11/27/2015	10/27/2015	10/27/2015	1/7/2015
9/22/2015- 9/23/2015	1/20/2016	9/26/2015	9/26/2015	11/19/2015	11/27/2015	10/27/2015	10/27/2015	1/7/2015
10/20/2015- 10/21/2015	1/20/2016	11/12/2015	11/12/2015	11/19/2015	11/27/2016	10/27/2015	10/27/2015	1/7/2016
11/3/2015- 11/4/2015	1/11/2016	11/5/2015	11/5/2015	1/6/2016	1/20/2016	12/14/2015	12/14/2015	1/7/2016
12/1/2015- 12/2/2015	1/11/2016	12/10/2015	12/10/2015	1/6/2016	1/20/2016	12/14/2015	12/14/2015	1/7/2016