

**Waquoit Bay (WQB) NERR Nutrient Metadata
(January 2010 to December 2010)
Latest Update 01/21/2015**

I. Data Set and Research Descriptors

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c) Other Contacts

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. Ideally, eventually all SWMP long-term water quality monitoring sites will have at least one years worth of diel nutrient sampling data.

3) 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. 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 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) to be filtered for nutrients and chlorophyll, and frozen (-20° C). The pre-baked (400 °C for four hours) glass filters that are used for filtering nutrients are also frozen for PC/PN analysis. In 2008 the frozen nutrient samples (including particulate filters) were delivered to the trace element laboratory at University of Massachusetts-Boston within one week for analysis.

b) Diel Sampling Program

Diel (24.75 hr or 2-full tidal cycles) grab 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. 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. 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. 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. Due to the use of ISCO auto samplers, ambient water rinses prior to sample collection are not possible. During the summer months ice is added inside the ISCO sampler in an effort to decrease sample alteration by providing cold storage conditions. All samples are filtered for nutrients and chlorophyll, the initial bottle and subsequent sample bottles (up to bottle #6) are collected and filtered after the ISCO begins the sampling cycle. The remaining samples are collected the next day when the ISCO sampler is finished. The frozen nutrient samples (-20° C) are delivered to the trace metal element lab at the University of Massachusetts-Boston for analysis within one week along with the grabs samples. At the time of sample collection for the first samples, water temperature, salinity, pH, specific conductivity, dissolved oxygen (mg/L and %), and depth are also measured with an YSI 650. Field parameters are not available for subsequent ISCO samples and, since the remaining samples are stored in the

refrigerator until processing, temperature and dissolved oxygen cannot be measured. However, after nutrients and chlorophyll samples and duplicates are filtered and stored, these samples are analyzed with a YSI 650 for salinity and pH.

4) Site location and character

a) 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 tikvahiae*, 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 northernmost 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 lies 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 Bay Watchers 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).

- b) The Metoxit Point station (MP) ($41^{\circ} 34.131' \text{ N } 070^{\circ} 31.294' \text{ W}$, 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.
- c) The Menauhant station (MH) ($41^{\circ} 33.156' \text{ N } 070^{\circ} 32.912' \text{ W}$, 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.
- d) The Child’s River station (CR) ($41^{\circ} 34.793' \text{ N } 070^{\circ} 31.854' \text{ W}$, 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.

- e) The Sage Lot station (SL) (41° 33.254' N 070° 30.612' W, 0.3 m deep MLW- MLW determined using two complete lunar cycles from July to September 2009) 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 muds. 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.

5) Code Variable Definitions

- wqbcnut – Waquoit Bay Child's River nutrients
- wqbmhnut – Waquoit Bay Menauhant nutrients
- wqbmpnut – Waquoit Bay Metoxit Point nutrients
- wqbslnut – Waquoit Bay Sage Lot nutrients
- 1 – grab sample (collected with van Dorn sampler)
- 2 – diel sample (collected with ISCO)

6) Data collection period

Diel Sampling:

Menauhant

Site	Start Date	Start Time	End Date	End Time
MH	01/05/2010	10:01	01/06/2010	10:46
MH	02/04/2010	07:35	02/05/2010	08:20
MH	03/08/2010	08:42	03/09/2010	09:27
MH	04/20/2010	08:00	04/21/2010	08:45
MH	05/18/2010	08:34	05/19/2010	09:19
MH	06/17/2010	06:32	06/18/2010	07:17
MH	07/14/2010	06:01	07/15/2010	06:46
MH	08/02/2010	16:09	08/03/2010	16:54
MH	09/13/2010	06:17	09/14/2010	07:02
MH	10/13/2010	07:31	10/14/2010	08:16
MH	11/16/2010	09:28	11/17/2010	10:13
MH	12/14/2010	10:12	12/15/2010	10:57

Grab Sampling:

Metoxit Point

Site	Start Date	Start Time	End Date	End Time
MP	04/20/2010	09:18	04/20/2010	09:23
MP	05/19/2010	08:10	05/19/2010	08:13
MP	06/17/2010	07:40	06/17/2010	07:44
MP	07/14/2010	07:27	07/14/2010	07:32
MP	08/02/2010	09:29	08/02/2010	09:33
MP	09/13/2010	07:32	09/13/2010	07:36
MP	10/13/2010	09:02	10/13/2010	09:05
MP	11/16/2010	11:07	11/16/2010	11:11
MP	12/15/2010	11:40	12/15/2010	11:43

Menauhant

Site	Start Date	Start Time	End Date	End Time
MH	01/06/2010	08:26	01/06/2010	08:28
MH	02/04/2010	07:32	02/04/2010	07:36
MH	03/08/2010	08:43	03/08/2010	08:50
MH	4/20/2010	7:55	04/20/2010	08:07
MH	05/19/2010	09:06	05/19/2010	09:11
MH	06/17/2010	06:25	06/17/2010	06:37
MH	07/14/2010	06:07	07/14/2010	06:10
MH	08/02/2010	07:28	08/02/2010	07:31
MH	09/13/2010	06:10	09/13/2010	06:15
MH	10/13/2010	07:30	10/13/2010	07:37
MH	11/16/2010	09:31	11/16/2010	09:35
MH	12/15/2010	09:22	12/15/2010	09:25

Childs River

Site	Start Date	Start Time	End Date	End Time
CR	01/06/2010	09:12	01/06/2010	09:16
CR	02/04/2010	08:05	02/04/2010	08:10
CR	03/08/2010	09:20	03/08/2010	09:25
CR	04/20/2010	08:25	04/20/2010	08:27
CR	05/19/2010	09:41	05/19/2010	09:44
CR	06/17/2010	06:57	06/17/2010	07:01
CR	07/14/2010	06:40	07/14/2010	06:43
CR	08/02/2010	08:03	08/02/2010	08:05
CR	09/13/2010	06:41	09/13/2010	06:45
CR	10/13/2010	07:57	10/13/2010	08:00
CR	11/16/2010	10:01	11/16/2010	10:04
CR	12/15/2010	09:47	12/15/2010	09:50

Sage Lot Pond

Site	Start Date	Start Time	End Date	End Time
SL	05/19/2010	12:10	05/19/2010	12:12
SL	06/17/2010	08:56	06/17/2010	08:58
SL	07/14/2010	08:49	07/14/2010	08:51
SL	08/02/2010	10:36	08/02/2010	10:38
SL	09/13/2010	09:05	09/13/2010	09:07
SL	10/13/2010	10:52	10/13/2010	10:54
SL	11/16/2010	12:21	11/16/2010	12:23

7) Associated researchers and projects

a) SWMP Water Quality Monitoring Data

In order to understand long-term changes in water quality, YSI 6600UPG 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 <http://cdmo.baruch.sc.edu/> if you are interested in the data.

b) BayWatchers

BayWatchers is a Citizen Water Quality Monitoring group based in Waquoit Bay since 1995. Volunteers measure for dissolved oxygen concentration, salinity, temperature (air and water), water clarity, chlorophyll-a and nutrients at 9 sites throughout the Reserve. Contact the reserve research coordinator to view the data.

c) SWMP Meteorological Data

Meteorological data are also collected at Waquoit Bay NERR and may be accessed at <http://cdmo.baruch.sc.edu/>.

d) Ocean Acidification-WHOI

Ocean acidification is due to the uptake of excess atmospheric carbon dioxide (CO₂) 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 (CaCO₃) shells. For more information visit <http://www.whoi.edu/sbl/liteSite.do?litesiteid=7193&articleId=17706>

8) Distribution

NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature, including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal Resource Management, National Ocean Service, National Oceanic and Atmospheric Administration. 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.

NERR water quality, nutrient and weather data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Section 1. 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 <http://cdmo.baruch.sc.edu/>. Data are available in text tab-delimited format, Microsoft Excel spreadsheet format and comma-delimited format.

II. Physical Structure Descriptors

9) Entry verification

At the University of Massachusetts-Boston laboratories, the nutrient data is imported directly from the instrument into an excel file. Therefore, it is not possible for human error to occur during data entry. The data is then QA/QC and checked over by Gordon Wallace at the UMass lab before being sent to WQB as an excel spreadsheet.. The Marine Chemistry Laboratory of the Environmental, Earth and Ocean Sciences at the University of Massachusetts Boston calculates and reports results in μM . For purposes of consistency in the NERR System, Waquoit Bay NERR calculates the concentrations as mg/L based on atomic weights of 14.01, 30.97, 28.09, and 12.01 for N, P, Si, and C respectively. Therefore, Waquoit Bay NERR staff multiplies the concentrations reported by the University of Massachusetts Marine Chemistry Lab by 0.01401, 0.03097, 0.02809, and 0.01201 to yield concentrations in mg/L as N, P, Si, and C respectively. Research technician Elizabeth Bonk also checked the chlorophyll and field parameters 100% against the field notebooks and data sheets.

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 automatically flags/codes values below 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; 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

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:	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	*Ammonium, Filtered	NH4F	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
	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 Parameters:			
	*Chlorophyll a	CHLA_N	µg/L
	Pheophytin a	PHEA	µg/L
	Silica, filtered	SiO4F	mg/L as Si
Field Parameters:			
	pH	PH_N	standard units
	Salinity	SALT_N	ppt

Notes:

1. Time is coded based on a 2400 hour clock and all times are changed to Eastern Standard Time (EST).
2. 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.

11) Measured and Calculated Laboratory Parameters –

a) Variables Measured Directly

Nitrogen species:	NO23F, NH4F, TDN, PON
Carbon species:	POC
Phosphorus species:	PO4F
Other:	CHLA, PHEA, SiO4F, SALT, PH

b) Computed Variables

DIN	NO23F+NH4F
DON	TDN-NH4F-NO23F

TN

TDN+PON

12) Limits of Detection

Table 1. **Method Detection Limits** (MDL) derived by the University of Massachusetts- Boston Laboratory (NO₂₃, NH₄, PO₄, SiO₄) and the Waquoit Bay NERR (CHLA and PHEA) for water quality parameters analyzed in 2009.

	NO ₂₃	NH ₄	PO ₄	SiO ₄	PON	POC	TDN	CHLA	PHEA
Month	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(µg/L)	(µg/L)
January	0.0006	0.0045	0.0009	0.0200	<i>0.0005</i>	<i>0.0005</i>	0.1292	0.5	0.5
February	0.0006	0.0045	0.0009	0.0200	<i>0.0005</i>	<i>0.0005</i>	0.1292	0.5	0.5
March	0.0008	0.0097	0.0013	0.1824	<i>0.0005</i>	<i>0.0005</i>	0.1292	0.5	0.5
April	0.0008	0.0097	0.0013	0.1824	<i>0.0005</i>	<i>0.0005</i>	0.1292	0.5	0.5
May	0.0004	0.0033	0.0012	0.0158	<i>0.0005</i>	<i>0.0005</i>	0.1292	0.5	0.5
June	0.0004	0.0033	0.0012	0.0158	<i>0.0005</i>	<i>0.0005</i>	0.0022	0.5	0.5
July	0.0026	0.0245	0.0004	0.0158	0.0001	0.0002	0.0188	0.5	0.5
August	0.0026	0.0245	0.0004	0.0158	0.0001	0.0002	0.0188	0.5	0.5
September	0.0026	0.0245	0.0004	0.0158	0.0001	0.0002	0.0188	0.5	0.5
October	0.0034	0.0067	0.0004	0.0029	0.0001	0.0002	0.1292	0.5	0.5
November	0.0034	0.0067	0.0004	0.0029	0.0005	0.0005	0.1292	0.5	0.5
December	0.0034	0.0067	0.0004	0.0029	0.0005	0.0005	0.1292	0.5	0.5

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 University of Massachusetts-Boston Laboratory. However, PON and POC MDLs are not available for January through June 2010. The MDLs applied between January and June 2010 for PON and POC measurements reflect a conservative estimate based on the maximum MDLs reported between July and December 2010 (shown in italics in Table 1).

13) Laboratory Methods

a) Laboratory Methods

The Nutrients values were analyzed by a Lachat QuikChem 8500 Flow Injection Nutrient at the Trace Element Analytical Facility (TEAF) at UMass-Boston. This method is consistent with and approved by the EPA. The laboratory benchmark for performance continues to be the available NIST or other reference standards. The SOP methods are similar between the two machines, except that the QuickChem 8500 utilizes slow injection. Lengthy descriptions of each nutrient analysis can be found on the Lachat website. It provides abbreviated method details. Go to the link: <http://www.lachatstruments.com/applications/AppsSearch.asp> or go to their website at <http://www.lachatstruments.com/index.asp> and go to the applications tab. Click on "Search our Methods Database" (at the bottom). The method number is a code (i.e. 31=brackish or seawater matrix).

Contact Waquoit Bay NERR Assistant Research Coordinator for a copy (electronic or hard) of the following SOP's (#i-vi). MaryKay.Fox@state.ma.us (508-457-0495 ext 109).

i) Parameter: NH₄F

UMass Boston Laboratory: Lachat method # 31-107-06-1-B, SOP: Appendix A

EPA Reference: 31-107-06-1-B

Method Reference: List of QuikChem® Methods considered Equivalent Methods for the National Pollutant Discharge Elimination System (NPDES) program of the US Environmental Agency (USEPA)

Method Descriptor: The determination of ammonia in estuarine and coastal waters using the TRAACS 800 (Bran+Luebbe brand) automated gas segmented continuous flow colorimeter. The term ammonia as used in this method denotes total concentration of ammonia, including both chemical forms, NH₃ and NH₄⁺. Ammonia in solution reacts with alkaline phenol and sodium hypochlorite at 37 °C to form indophenol blue in the presence of sodium nitroferricyanide as a catalyst. The absorbance of indophenol blue at 630 nm is linearly proportional to the concentration of ammonia in the sample.

Preservation Method: Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be stored at lower temperature.

ii) Parameter: NO₃F

UMass Boston Laboratory: Lachat method # 31-107-04-1-E, SOP: Appendix B

EPA Reference: 31-107-04-1-E

Method Reference: List of QuikChem® Methods considered Equivalent Methods for the National Pollutant Discharge Elimination System (NPDES) program of the US Environmental Agency (USEPA)

Method Descriptor: The determination of nitrite plus nitrate in estuarine and coastal Waters using the TRAACS 800 (Bran+Luebbe) automated gas segmented continuous Flow colorimeter. Samples are passed through a copper-coated cadmium reduction column. Nitrate in the sample is reduced to nitrite in an imidazole buffer solution (pH 7.5). The nitrite is then determined by diazotization, in acid conditions, with sulfanilamide (SAN) and coupling with N-1- naphthylethylenediamine dihydrochloride (NED) to form a color azo dye. The absorbance measured at 540 nm is linearly proportional to the concentration of nitrite + nitrate in the sample. When required, nitrite concentrations can be determined separately removing the cadmium reduction column from the above-described procedure. When required, nitrate concentrations can be calculated by subtracting nitrite values, from the nitrite + nitrate values.

Preservation Method: Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be stored at lower temperature.

iii) Parameter: PO₄F

UMass Boston Laboratory: Lachat method # 31-115-01-1-I (as in 'i'), SOP: Appendix C

EPA Reference: 31-115-01-1-I

Method Reference: List of QuikChem® Methods considered Equivalent Methods for the National Pollutant Discharge Elimination System (NPDES) program of the US Environmental Agency (USEPA)

Method Descriptor: The determination of orthophosphate in estuarine and coastal waters using the TRAACS 800 (Bran+Luebbe brand) automated gas segmented continuous flow Colorimeter. Ammonium molybdate and antimony potassium tartrate react in an acidic medium with dilute solutions of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The reduced blue phosphomolybdenum complex is read at 660 nm.

Preservation Method: Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be stored at lower temperature.

iv) Parameter: POC/PON

UMass Boston Laboratory: PerkinElmer 2400 Series II CHNS/O Elemental Analyzer UMB
SOP: Appendix D

EPA Reference: Pregl-Dumas methodology;

Method Reference: Method Descriptor: PerkinElmer CHN/OS EA2400 Elemental Analyzer

Method Descriptor: The PerkinElmer 2400 Series II CHNS/O Elemental Analyzer (2400 Series II) is a powerful instrument for the rapid determination of the carbon, hydrogen, nitrogen, sulfur or oxygen content in organic and other types of materials. The CHN mode is based on the classical Pregl-Dumas method where samples are combusted in a pure oxygen environment, with the resultant combustion gases measured in an automated fashion.

Preservation Method: Store filter in freezer until ready to analyze

v) Parameter: Silicate

UMass Boston Laboratory: Lachat method # 31-114-27-1-D, SOP: Appendix E

EPA Reference: 31-114-27-1-D; Standard Methods for the Examination of Water and Wastewater 19th Edition, #4500-Si D, pp4-118-120.

Method Reference: List of QuikChem® Methods considered Equivalent Methods for the National Pollutant Discharge Elimination System (NPDES) program of the US Environmental Agency (USEPA)

Method Descriptor: Ammonium molybdate at pH 1.2 reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acids. The intensity of the yellow color is proportional to the concentration of molybdate-reactive silica. The yellow molybdosilicic acid is reduced by means of aminonaphtholsulfonic acid to heteropoly blue. The blue color is more intense than the yellow and provides increased sensitivity.

Preservation Method: Filter the sample as soon as possible after collection through a 0.45 µm membrane filter using only plastic equipment. Store the sample in a 125 mL plastic bottle in the refrigerator until ready for analysis. Analyze the sample within 30 days of collection.

v) Parameter: TDN

UMass Boston Laboratory: Lachat method # 31-107-04-3-A, SOP: Appendix X

EPA Reference: # 31-107-04-3-A

Method Reference: "Determination of TN in Brackish Waters by Digestion Followed by Flow Injection Analysis." List of QuikChem® Methods considered Equivalent Methods for the National Pollutant Discharge Elimination System (NPDES) program of the US Environmental Agency (USEPA)

Method Descriptor: Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen-containing compounds to nitrate is achieved by heating at 100°C. The heating lowers the sample pH from 9.1 to about 3 as the persulfate decomposes. Additional energy is supplied by exposure to UV light. The digestion occurs prior to the injection valve. The resultant nitrate is then quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is then

coupled with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting pink dye absorbs light at 540 nm, and this absorbance is proportional to total nitrogen content.

Preservation Method: When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (maximum of 2 mL concentrated H₂SO₄ per liter) and refrigerated. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to ensure a representative sample, allow for replicate analysis (if required), and minimize waste disposal. Each injection requires 1.5 mL of sample. Samples may be determined without preservation or preserved with sulfuric acid as directed above. Both standards and samples should be carried through this procedure. If samples have been preserved with sulfuric acid, standards should be preserved in the same manner. Samples may be homogenized in a device designed for this purpose. However, turbid samples should be filtered since the digestion effectiveness on nitrogen containing particles is unknown.

vi) **Parameter: Chlorophyll *a* and Pheophytin *a***

Waquoit Bay NERR Laboratory

EPA Method Reference: USEPA Method 446.0

Method Reference: USEPA Method 446.0, "In Vitro Determination of Chlorophylls *a*, *b*, *c*1 + *c*2 and Pheopigments in Marine and Freshwater Algae by Visible Spectrophotometry."

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.

Preservation Method: Freeze filter at -20°C until ready to extract.

14) Field and Laboratory QA/QC Programs

a) **Precision –**

- i) **Field Variability** – WQBNERR collects two successive grab samples for the monthly grab sample program. We also store duplicate samples from the original analysis and keep these samples stored in -20 °C freezers in our lab for the possibility that UMass laboratories require reanalysis of our monthly samples due to questionable results or loss of samples in their laboratory
- ii) **Laboratory Variability** – The UMass laboratory analyzed replicates on 10% of our samples. In 2008 the replicates analyzed by the lab were always the second grab sample taken from Sage Lot Pond and the 9th diel sample collected by the ISCO.
- iii) **Inter-organizational splits** – none.

b) **Accuracy –**

- i) **Sample Spikes** – see lab protocols
- ii) **Standard Reference Material Analysis** – see lab protocols
- iii) **Cross Calibration Exercises** – Summer 2006-NERRs-wide inter-lab reference comparison.

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 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.

- 3 Data Rejected due to QAQC
- 2 Missing Data
- 1 Optional SWMP Supported Parameter (that was not collected)
- 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 QAQC checks

Sensor Errors

- SBL Value below minimum limit of method detection
- SCB Value calculated with a value that is below the MDL
- 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

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. MDL's for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section I, Part 12) of this document. Concentrations that are less than this limit are rejected. For example, if the measured concentrations of NO₃F 0.0005 mg/L as N (MDL=0.0008), the reported value would be rejected. In addition, if any of the components used to calculate a variable are below the MDL, or if a calculated value is negative, the calculated variable is rejected. If additional information on missing data or MDL's is needed, contact the Research Coordinator at the reserve submitting the data.

a) Suspect data (<1>):

All nutrient data, except CHLA and PHEA in March and August in 2010, surpassed specific holding times due to extenuating circumstances related to the sudden death of Gordon Wallace at the University of Massachusetts – Boston Laboratory. CHLA and PHEA exceeded specific holding times due to limitations at the Waquoit Bay NERR Laboratory.

b) CSM data notes:

June 18th diel sample taken at 7:17 - Filter sample lost/destroyed; POC and PON unavailable.

August 3rd diel sample taken at 16:54 – Filter sample lost/destroyed; POC and PON unavailable.

December Childs Rivers sample (Grab #1) – Filter sample lost/destroyed; POC and PON unavailable.

December Childs River sample (Grab #2) - Filter sample lost/destroyed; POC and PON unavailable.

POC and PON data: MDLs were not provided by the University of Massachusetts – Boston Laboratory for POC or PON between January and June in 2010. MDLs applied for those missing months reflect a conservative estimate based on the maximum MDLs reported between July and December in 2010 for these two parameters (see Table 1 in Section 12 of this document).