Waquoit Bay (WQB) NERR Nutrient Metadata

January – December 2023 Latest Update: 06/12/2024

Note: This is a provisional metadata document; it has not been authenticated as of its download date. Contents of this document are subject to change throughout the QAQC process and it should not be considered a final record of data documentation until that process is complete. Contact the CDMO (cdmosupport@baruch.sc.edu) or reserve with any additional questions.

### I. Data Set and Research Descriptors

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

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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. Climate change is already affecting the magnitudes, extreme event frequencies, or seasonal timings of various water quality and nutrient parameters. 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, are there temperature and wind field thresholds that might trigger certain conditions within the bay? The observations recorded by SWMP will allow for these types of studies.

# a) Monthly Grab Sampling Program

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.

#### 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 three 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 reflect the same water mass sampled by the water quality data sonde (EXO2), at depths approximately 0.5 m above the bottom (0.5 - 1.0m below water surface at Childs River, 1.0m at Metoxit Point, and 1.0m at Menauhant; 0.25m below water surface at Sage Lot Pond). Samples were taken following SWMP protocol, with two sequential grab samples (in immediate sequence – 3-5 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 percent saturation), and depth are also measured with an YSI EXO1.

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 and 48 hours, respectively).

### b) Diel Sampling Program

Diel (24.75 hr or 2-full tidal cycles) grab samples are 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 0.5 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. Ice is added inside the ISCO sampler in an effort to decrease sample alteration by providing cold storage conditions. Field parameters are not available for ISCO samples but salinity of each sample is measured at the analytical lab.

#### 4) 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 (organic Carbon concentration ~ 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. In the spring of 2008 two (2) channel culverts were replaced, one with a bridge and the second with a wider, less restrictive culvert to aid in tidal flushing of the pond. 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 nearby 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 subwatershed, 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 (Valiela et al. 2004) 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 (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 and enhance drainage of the bay.

Site name	Childs River
Latitude and longitude	41° 34' 48.47" N, 70° 31' 49.87" W
Tidal range (meters)	1.30
Salinity range (psu)	0-10 ppt at the surface to >30 ppt about 1 m below. A salt wedge exists at this station.
Type and amount of freshwater input	Riverine system also affected by runoff and groundwater
Water depth (meters, MLW)	~0.83
Sonde distance from bottom (meters)	~0.5 m
Bottom habitat or type	Soft mud and cladophora mats
Pollutants in area	Highest nitrogen loading site. Site is at a commercial marina – affected by boat traffic.
Description of watershed	The Child's River station 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.  This station has undergone a few moves. On October 4, 2021, WBNERR staff had to remove the station to allow for a massive renovation and construction project at the marina as it re-designed its whole pier structure and layout. Construction finished in the spring of 2022, and after months of attempts to coordinate and communicate with marina

management, the Childs River station was placed back in the water successfully on 1/25/2023. A sonde was then deployed on 1/30/2023.

The station's new location is now 41° 34' 48.47" N, 70° 31' 49.87" W and 0.5m above sediment. It was initially thought to be as close as possible to the previous location around 41° 34' 48.60" N, 70° 31' 49.84" W. However, the CDMO website and all previous metadata logged the previous location at a different point, in the SW part of the marina at 41° 34' 47.28" N 70° 31' 51.24" W. We now know that these coordinates provided in the metadata and on the CDMO website were not correct. As far back as we can tell, the Childs River sonde station was in reality located at 41° 34' 48.60" N, 70° 31' 49.84" W, making this current move a slight one, shifting only ~4.1m south.

Site name	Menauhant Yacht Club
Latitude and longitude	41° 33' 9.36" N, 70° 32' 54.60" W
Tidal range (meters)	1.55 (based on 2014 – 2016 data)
Salinity range (psu)	31.3 – 32.1 (based on 2014 data)
Type and amount of freshwater input	Freshwater input from the Eel River and Childs River to the north. However, much more strongly influenced by waters of Nantucket Sound.
Water depth (meters, MLW)	~0.71
Sonde distance from bottom (meters)	~0.30
Bottom habitat or type	Sands and gravels
Pollutants in area	
Description of watershed	The Menauhant station (41° 33'9.36" N 70° 32'54.60" W) 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.

Site name	Metoxit Point
Latitude and longitude	41° 34' 8.04" N, 70° 31'17.76" W
Tidal range (meters)	0.90 (based on 2014 – 2016 data)
Salinity range (psu)	13.7 – 32.1 (based on 2014 data)
Type and amount of freshwater input	The Quashnet River feeds into the main body of Waquoit Bay.
Water depth (meters, MLW)	~1.23 (based on data through 2016)
Sonde distance from bottom (meters)	~0.50
Bottom habitat or type	Algal mats (cladophora) and fine black mud
Pollutants in area	
Description of watershed	The Metoxit Point station 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).

Site name	Sage Lot Pond
Latitude and longitude	(41° 33'15.12" N, 70° 30'30.20" W)
Tidal range (meters)	0.99 (based on 2014 – 2016 data)
Salinity range (psu)	24.2 – 32.3
Type and amount of freshwater input	Potentially some groundwater influence.
Water depth (meters, MLW)	0.60 (based on 2014 – 2016 data)
Sonde distance from bottom (meters)	0.25
Bottom habitat or type	Organic rich muds

Pollutants in area	
Description of watershed	The Sage Lot station 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 possessed one of the few remaining eelgrass beds in the Waquoit Bay system, but no eelgrass has been seen since 2022. 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.

All Waquoit Bay NERR historical nutrient/pigment monitoring stations:

Station	SWMP	Station	Location	Active	Reason	Notes
Code	Status	Name		Dates	Decommissioned	
wqbcrnut	P	Childs	41° 34′ 48.47" N,	07/01/2002	NA	NA
		River	70° 31' 49.87" W	- current		
wqbmhnut	P	Menauhant	41° 33′ 9.36" N,	07/01/2002	NA	NA
			70° 32′ 54.60" W	- current		
wqbmpnut	P	Metoxit	41° 34′ 8.04″ N,	07/01/2002	NA	NA
		Point	70° 31' 17.76" W	current		
wqbslnut	P	Sage Lot	41° 33′ 15.12" N,	07/01/2002	NA	NA
			70° 30' 30.20" W	- current		

# 5) Coded 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

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

## 6) Data collection period -

Nutrient sampling began in July of 2002 at all four sites. The 24-hour diel samples were collected at Childs River until December 2006. Starting in January 2007, the 24-hour diel samples were collected at Menauhant.

# Diel Sampling at Menauhant (MH):

Month	Start Date	Start Time	End Date	End Time
Jan	01/17/2023	09:30	01/18/2023	10:15
Feb	02/13/2023	08:57	02/14/2023	09:42
Mar	03/21/2023	09:06	03/22/2023	09:51
Apr	04/10/2023	08:07	04/11/2023	08:52
May	05/09/2023	08:17	05/10/2023	09:02
June	06/05/2023	09:24	06/06/2023	10:09
July	07/05/2023	09:14	07/06/2023	09:59
Aug	08/08/2023	07:54	08/09/2023	08:39
Sept	09/05/2023	09:40	09/06/2023	10:25
Oct	10/02/2023	08:56	10/03/2023	09:41
Nov	11/06/2023	09:47	11/07/2023	10:32
Dec	12/11/2023	09:46	12/12/2023	10:31

# Grab Sampling:

# Menauhant (MH)

Month	Sample 1 Date	Sample 1 Time	Sample 2 Date	Sample 2 Time
Jan	01/18/2023	12:31	01/18/2023	12:37
Feb	02/14/2023	10:40	02/14/2023	10:45
Mar	03/22/2023	09:20	03/22/2023	09:25
Apr	04/11/2023	09:58	04/11/2023	10:14
May	05/10/2023	11:28	05/10/2023	11:32
June	06/06/2023	10:42	06/06/2023	10:44
July	08/09/2023	10:00	08/09/2023	10:04
Aug	08/16/2022	10:42	08/16/2022	10:45
Sept	09/06/2023	11:18	09/06/2023	11:21
Oct	10/03/2023	12:45	10/03/2023	12:48
Nov	11/07/2023	12:12	11/07/2023	12:15
Dec	12/12/2023	11:45	12/12/2023	11:49

# 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	04/11/2023	-	04/11/2023	-
May	05/10/2023	10:35	05/10/2023	10:39
June	06/06/2023	07:55	06/06/2023	07:57
July	07/06/2023	09:27	07/06/2023	09:33
Aug	08/09/2023	09:03	08/09/2023	09:07
Sept	09/06/2023	10:18	09/06/2023	10:23
Oct	10/03/2023	11:55	10/03/2023	11:59
Nov	11/07/2023	10:59	11/07/2023	11:03
Dec	12/12/2023	10:40	12/12/2023	10:44

<sup>\*</sup>NS = no sample due to ice/winter conditions.
- = Time of sample was not recorded

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	04/11/2023	13:52	04/11/2023	13:55
May	05/10/2023	09:28	05/10/2023	09:34
June	06/06/2023	09:14	06/06/2023	09:16
July	07/06/2023	08:00	07/06/2023	08:04
Aug	08/09/2023	08:55	08/09/2023	08:59
Sept	09/06/2023	09:05	09/06/2023	09:09
Oct	10/03/2023	14:02	10/03/2023	14:07
Nov	11/07/2023	09:45	11/07/2023	09:49
Dec	12/12/2023	09:43	12/12/2023	09:47

<sup>\*</sup>NS = no sample due to ice/winter conditions.

#### Child's River

Month	Sample 1 Date	Sample 1 Time	Sample 2 Date	Sample 2 Time
Jan	01/18/2023	13:13	01/18/2023	13:17
Feb	02/14/2023	09:57	02/14/2023	10:02
Mar	03/22/2023	08:55	03/22/2023	08:59
Apr	04/11/2023	09:42	04/11/2023	09:45
May	05/10/2023	08:18	05/10/2023	08:23
June	06/06/2023	10:24	06/06/2023	10:26
July	07/06/2023	10:30	07/06/2023	10:33
Aug	08/09/2023	09:41	08/09/2023	09:44
Sept	09/06/2023	10:55	09/06/2023	10:58
Oct	10/03/2023	09:49	10/03/2023	09:54
Nov	11/07/2023	12:29	11/07/2023	12:33
Dec	12/12/2023	11:23	12/12/2023	11:30

<sup>\*</sup>NS = no sample due to construction at marina where sample site is located

#### 7) Associated researchers and projects-

#### a) SWMP Water Quality Monitoring Data

In order to understand long-term changes in water quality, automatic data loggers are deployed at each of the four stations where nutrients are also sampled. The data collected provides background data for other research about the ecology of these habitats. For all sites, measurements of dissolved oxygen, salinity, temperature, pH, depth, turbidity, and chlorophyll fluorescence at 15 minute intervals. At the Menauhant site, a telemetry system was installed in July 2006. Visit the <a href="CDMO website">CDMO website</a> if you are interested in the data.

#### b) Waquoit 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 collect samples which are analyzed for a suite of nutrients (ammonium, nitrate/nitrite, phosphate, and silicate). The program consists of nine sites which are located throughout the Waquoit Bay watershed. Contact Theo Collins, Research Associate, for the data.

#### c) SWMP Meteorological Data

As part of the SWMP long-term monitoring program, WQB NERR also monitors 15-minute meteorological and water quality data which may be correlated with this nutrient/pigment dataset. These data are available at <a href="https://www.nerrsdata.org">www.nerrsdata.org</a>.

# 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 processed 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 2022.

Also include the following excerpt in the metadata to address how and where the data can be obtained.

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="www.nerrsdata.org">www.nerrsdata.org</a>. Data are available in comma separated version format.

#### II. Physical Structure Descriptors

#### 9) Entry verification –

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.

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 was completed at the Waquoit Bay NERR laboratory using the spectrophotometer method until August 2015 and then using the fluorometer method starting September

2015. WBNERR's fluorometers broke in June 2022, and a new one was not able to be purchased until June 2023. Between June 2022 and December 2023 Chlorophyll-a and pheophytin analysis was performed by SMAST.

#### 10) Parameter titles and variable names by category -

Required NOAA NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisk "\*".

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and	l Nitrogen:		
1	*Orthophosphate	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Dissolved Organic Nitrogen	DON	mg/L as N
	Total Dissolved Nitrogen	TDN	mg/L as N
	Particulate Organic Nitrogen	PON	mg/L as N
	Total Nitrogen	TN	mg/L as N
Plant Pigments:			
O	*Chlorophyll a	CHLA_	_N μg/L
	Phaeophytin	PHEA	μg/L
Carbon:	• •		. 0
	Particulate Organic Carbon	POC	mg/L as C
Other Lab Paras	meters:		
	Silicate, Filtered	SiO4F	mg/L as Si
Microbial:			
Field Parameter	s:		
	Water Temperature	WTEM_	_N °C

#### Notes:

- 1. Time is coded based on a 2400 clock and is referenced to Standard Time.
- 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.

#### 11) Measured or calculated laboratory parameters –

#### a) Parameters measured directly

Nitrogen species: NH4F, NO2F, NO23F, TDN, PON

Phosphorus species: PO4F

Other: CHLA\_N, PHEA, SiO4F, POC

## b) Calculated parameters

DIN = NO23F+NH4FDON = TDN - DINTON = PON + DONTN = TDN + PON

### 12) Limits of detection -

MDL's for NO23F, NH4F, PO4F, PON/POC, TDN, CHLA, and PHEA are determined by the School for Marine Science and Technology (SMAST). At SMAST, the MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. These values are reviewed annually. The spike and blank values from at least seven of the Quality Assurance (QA) analyses run during the year are used to calculate the MDL (see Tables 4-9 for QA results). The table below lists the MDLs for data collected in 2022 as well as the dates of the analyses which contributed to the MDL calculation.

Parameter	Start Date	End Date	MDL
NH4F	01/01/2023	12/31/2023	0.001
NO23F	01/01/2023	12/31/2023	0.001
TDN	01/01/2023	12/31/2023	0.001
PO4F	01/01/2023	12/31/2023	0.003
POC	01/01/2023	12/31/2023	0.001
PON	01/01/2023	12/31/2023	0.001
SiO4F	01/01/2023	12/31/2023	0.001
CHLA	01/01/2023	12/31/2023	
PHEA	01/01/2023	12/31/2023	

## 13) Laboratory methods –

Contact Waquoit Bay NERR Research Associate for a copy (electronic or hard) of the following SOP's (a-g) at theophilos.j.collins@mass.gov or (508-457-0495; Direct Line: 774-255-4272).

#### a) Parameter: NH4F

SMAST Laboratory Method: Indophenol/hypochlorite method, Spectrophotometer

EPA Reference Method: 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. 19th 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: NO2F

SMAST Laboratory Method: Lachat analysis using copperized cadmium reduction and colorimetric assay. EPA Reference Method: 353.2

#### Method References:

- Standard Methods for the Examination of Water and Wastewater, 19th 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.

EPA Method Descriptor: A filtered sample is passed through a column containing granulated coppercadmium 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. <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 48 hours or at -30°C for no more than 28 days before analysis.

#### a) 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, 19th 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.

#### b) 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.

EPA Method Descriptor: 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.

#### c) 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. 17th 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.

#### a) 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. 19th 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 μm 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.

#### b) Parameter: Chlorophyll a and Pheophytin a

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, 0.7  $\mu$ m) 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 10 minutes before analysis. When samples cannot be processed within one week of filtration, the filters are placed in aluminum foil and frozen at -20°C until extraction.

<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. When samples cannot be processed within one week of filtration, the filters are placed in aluminum foil and frozen at -20°C until extraction.

\*\* Note that in June of 2022, WBNERR's fluorometer broke, requiring samples to be sent to the SMAST lab for analysis. They use the same procedure detailed above.

### 14) Field and Laboratory QAQC programs -

#### a) Precision

- i) Field variability Waquoit Bay NERR 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 ±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 Quality Control Tables in the final section of this document for % recovery of spike tests. Thresholds used by SMAST for acceptable recoveries are available in the caption headings for the tables.

- ii) Standard reference material analysis The UMASS Dartmouth-SMAST has been successfully tested by the Massachusetts Department of Environmental Protection 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. In spring of 2018, another NERRS-wide inter-lab comparison was conducted including nitrite/nitrate, nitrite, and phosphate analyses for freshwater and saltwater samples. The results indicated that the SMAST provides results with acceptable accuracy. The results from this comparison 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 -

[Instructions/Remove: This section details the secondary QAQC Code definitions used in combination with the flags above and requires no additional information. <u>Include the following excerpt.</u>]

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 Co	omments
CAB	Algal bloom
CDR	Sample diluted and rerun
СНВ	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
365	The unity of From dispreserved sample
Record comm	nents
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 Tide stars	mixed rain and snow
Tide stage	abb side
TSE	ebb tide
TSF	flood tide
TSH TSL	high tide low tide
Wave height	10w tide
w ave neigni	

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 metersWH4 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 Е 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 NWfrom the northwest **NNW** from the north northwest Wind speed WS0 0 to 1 knot WS1 > 1 to 10 knots WS2 > 10 to 20 knots > 20 to 30 knots WS3 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 NERR 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.

Sample hold times for 2023: Samples are held at -20°C. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30) at -20°C, plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect <1>and coded (CHB). If measured values were below MDL, this resulted in <-4> [SBL] flagging/coding.

Sample hold times for 2023: NERRS SOP allows nutrient samples to be held for up to 24 hours if held at 4°C with no preservation, for NH4F and NO23F up to 28 days if acidified and held at 4°C, and up to 28 days (CHLA for 30 days) if held at -20°C. Tier II parameters, with a few exceptions, are subject to the same sample hold times. In all cases, up to an additional 5 days is allowed for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect and coded CHB in the data set.

SAMPLE DATE	Salinity & Conductivity	NH4 & PO4	NOx	TDN	POC & PON	Si	Chla
1/17/2023	1/20/2023	1/20/2023	1/31/2023	2/1/2023	1/18/2023	3/24/2023	5/8/2023
2/13/2023	2/22/2023	2/15/2023	2/16/2023	2/17/2023	2/14/2023	3/24/2023	5/8/2023
3/21/2023	3/27/2023	3/24/2023	3/23/2023	3/27/2023	3/22/2023	3/24/2023	5/8/2023
4/10/2023	4/13/2023	4/17/2023	4/19/2023	4/20/2023	4/11/2023	7/31/2024	5/8/2023
5/9/2023	5/15/2023	5/12/2023	5/18/2023	5/19/2023	5/10/2023	7/31/2024	06/29/23
6/6/2023	6/9/2023	6/7/2023	6/22/2023	6/23/2023	6/6/2023	7/31/2024	09/28/23
7/5/2023	7/11/2023	7/7/2023	7/21/2023	7/25/2023	7/6/2023	7/31/2024	09/28/23
8/9/2023	8/11/2023	8/14/2023	8/15/2023	8/21/2023	8/9/2023	10/4/2024	09/28/23
9/5/2023	9/11/2023	9/8/2023	9/15/2023	9/18/2023	9/6/2023	10/4/2024	09/28/23
10/4/2023	10/10/2023	10/17/2023	10/4/2023	10/10/2023	10/3/2023	10/4/2024	10/31/23
11/7/2023	11/10/2023	11/8/2023	11/8/2023	11/9/2023	11/7/2023	1/5/2024	01/05/24
12/11/2023	12/13/2023	12/22/2023	12/21/2023	12/22/2023	12/12/2023	1/5/2024	01/05/24

<sup>\*</sup>Highlighted cells are samples which were held beyond specified holding time, and will be flagged as suspect.

#### NOTE

Sage Lot and Metoxit Point are only accessible by boat, and conditions through winter and into spring often prevent access. No samples were taken January through March.

#### <-2>[GDM]/[GCM]

Menauhant (wqbmhnut) diel sampling schedule, samples at 09/05/2023 18:40 and 09/06/2023 10:25. The ISCO pump and distributor malfunctioned. Sample bottles were only filled partially, with other sample water ending up in the bottle basin. Not enough sample was collected to perform the PON, POC, or TDN analysis. This also affected the TN and TON calculated variables for those samples, which carry the [GCM] flag code

### <-2>[GSM]/[GCM]

Menauhant (wqbmhnut) sample on 02/14/2023 at 10:45 for PON, POC, and TDN, with the [GCM] code affecting TN and TON. A machine error occurred at this sample, and PON, POC, and TDN were not able to be collected. Thus, the calculated variables TN and TON were not able to be calculated either and hence they carry the [GCM] flag code.

#### <-4>[SBL]

- All Childs River (wqbcrnut) samples on 02/14/2023 for PO<sub>4</sub>. This is an example of the measured orthophosphate concentration being below the MDL. Other examples of measured PO<sub>4</sub> concentrations below the MDL include:
  - o Sage Lot (wqbslnut) samples on 03/22/2023.

- O All grab samples on 4/11/2023 and several diel samples collected between 4/10/2023 4/11/2023.
- o Sage Lot (wqbslnut) grab samples on 5/10/2023
- o Childs River (wqbcrnut) and Sage Lot (wqbslnut) grab samples on 6/6/2023
- O Sage Lot (wqbslnut) grab samples on 7/6/2023
- Sage Lot (wqbslnut) grab samples on 12/12/2023
- Menauhant (wqbmhnut) grab sample taken on 9/6/2023 at 11:18 shows a NH<sub>4</sub> concentration below the MDL. The Metoxit Point (wqbmpnut) grab sample taken on the same day at 10:18 and two of the Sage Lot (wqbslnut) samples taken at 09:06 and 09:09 all showed similar results. Other examples of NH<sub>4</sub> concentrations being below the MDL include:
  - o Menauhant (wgbmhnut) samples taken at 7/6/2023 at 10:46 and 10:52
  - o Menauhant (wqbmhnut) diel samples taken on 7/5/2023 at 09:14, 15:59, and 18:14.
  - o Menauhant (wqbmhnut) grab sample taken on 5/10/2023 at 11:28
  - o Menauhant (wqbmhnut) diel samples taken at 5/9/2023 21:47 and 5/10/2023 00:02

### <-4>[SCB]

- Menauhant (wqbmhnut) 05/10/2023 11:28 sample. This is an example of calculated parameters (like DIN and DON) not able to be determined because one of the measured components making up the calculation was below the MDL. In these cases, the measured component below the MDL was NH<sub>4</sub>. Other examples of NH<sub>4</sub> concentrations being below the MDL and affecting other calculated parameters include:
  - o Menauhant (wqbmhnut) samples taken at 7/6/2023 at 10:46 and 10:52
  - o Menauhant (wqbmhnut) diel samples taken on 7/5/2023 at 10:14, 16:59, and 19:14.
  - o Menauhant (wqbmhnut) grab sample taken on 5/10/2023 at 11:28
  - o Menauhant (wqbmhnut) diel samples taken at 5/9/2023 21:47 and 5/10/2023 00:02

## <1>[GQS]

- ➤ Childs River (wqbcrnut) on 07/06/2023 at 10:30 for Chl-a. This was identified by the SMAST lab as a possible outlier datum.
- Menauhant (wqbmhnut) on 07/06/2023 at 10:49 for NH<sub>4</sub>. This was identified by the SMAST lab as a possible outlier datum.
- Menauhant (wqbmhnut) diel sample on 07/06/2023 at 06:29 for NH<sub>4</sub>. This was identified by the SMAST lab as a possible outlier datum.

#### <1>[GQS](CSM)

- February, March, May NH<sub>4</sub>: Lab duplicates during the analysis of these samples had more than 5% variance. See section 14.a.ii on Laboratory Duplicate threshold tolerances. Refer to the SMAST Quality Control Tables below for the lab duplicate variance numbers.
- February, July, and August PO<sub>4</sub>: Lab duplicates during the analysis of these samples had more than 5% variance. See section 14.a.ii on Laboratory Duplicate threshold tolerances. Refer to the SMAST Quality Control Tables below for the lab duplicate variance numbers.
- April, May, July, November, December NO<sub>2</sub>/NO<sub>3</sub>: Lab duplicates during the analysis of these samples had more than 5% variance. See section 14.a.ii on Laboratory Duplicate threshold tolerances. Refer to the SMAST Quality Control Tables below for the lab duplicate variance numbers.
- April December SiO2: Lab duplicates during the analysis of these samples had more than 5% variance. See section 14.a.ii on Laboratory Duplicate threshold tolerances. Refer to the SMAST Quality Control Tables below for the lab duplicate variance numbers.

#### <1>[GSM]

Menauhant (wqbmhnut) diel sampling schedule, samples from 09/05/2023 18:40 – 09/06/2023 10:25. The ISCO pump and distributor malfunctioned. Sample bottles were only filled partially, with other sample water ending up in the bottle basin. All the samples and all the data in this time period are considered suspect because it is possible that spraying water ended up in an adjacent bottle and a possible source of cross-contamination.

## <1>[GSM](CHB)

- > This label was applied to data from samples that were held at the SMAST lab beyond SWMP-recommended holding times. These include:
  - o Chl-a: January March 2023
  - o Chl-a: May August 2023
  - o Chl-a: November December 2023
  - o SiO<sub>2</sub>: April December 2023
- ➤ Menauhant (wqbmhnut) Diel sample on 5/10/2023 at 06:47 Potential outlier datum, but unknown reason.

# <1>[SRD]

- ➤ This label was applied to data whose replicates' measurements were either >10% different for PO<sub>4</sub>, NO<sub>2</sub>/NO<sub>3</sub>, or NH<sub>4</sub>, OR >20% different for TN, TDN, PON, POC, or SiO<sub>2</sub>. Examples include (but are not limited to):
  - o POC, PON, SiO<sub>2</sub>, TN in January 2023
  - o TN, TDN, SiO<sub>2</sub> in March 2023

## <1>[CSM]

This flag code was applied to the same TN values which had one of its measured-parameter components (NH<sub>4</sub>, NO<sub>2,3</sub>, or PON) flagged as <1>[SRD] (see immediately above). Those replicate values showing wide enough variance to be considered suspect in one of these components would also potentially be suspect when added towards TN.

# **SMAST Quality Control Tables**

#### NH<sub>4</sub> Assay

NH4 Blanks							
Analysis Date	Mean(uM)	CV	STD	MIN	MAX	Range	n
1/20/2023	0.00						1
2/15/2023	0.22						1
3/24/2023	0.29	0.30	0.09	0.27	0.30	0.03	5
4/17/2023	0.29						1
5/12/2023	0.00	0.00	0.00	0.00	0.00	0.00	6
6/7/2023	0.00						1
7/7/2023	0.20	1.18	0.23	0.00	0.00	0.00	7
8/14/2023	0.19	1.12	0.21	0.57	0.17	-0.40	8
9/8/2023	0.31	1.17	0.37	0.57	0.10	-0.47	4
10/17/2023	0.63	0.00	0.73	0.00	0.11	0.00	5
11/8/2023	0.00	0.00	0.00	0.00	0.00	0.00	2
12/22/2023	0.00	0.00	0.00	0.00	0.00	0.00	2

10 uM NH4 STANDARDS							
Analysis Date	Mean (uM)	CV	STD	MIN	MAX	Range	n

1/20/2023	11.82						1
2/15/2023	10.79						1
3/24/2023	11.48	0.05	0.60	11.90	11.06	0.85	2
4/17/2023	10.53						1
5/12/2023	10.53	0.00	0.00	10.53	10.53	0.00	2
6/7/2023	10.19						1
7/7/2023	10.14	0.02	0.19	10.03	10.12	0.09	6
8/14/2023	10.77	0.05	0.58	9.73	11.19	1.47	7
9/8/2023	11.03	0.04	0.47	11.75	10.80	0.95	4
10/17/2023	11.02	0.05	0.55	10.22	11.33	1.11	4
11/8/2023	0.00						1
12/22/2023	0.00						1

NH4 LAB DUPS								
Analysis Date	Avg % dif.	n						
1/20/2023	4.79%	1						
2/15/2023	5.48%	1						
3/24/2023	19.35%	2						
4/17/2023	0.00%	1						
5/12/2023	17.25%	2						
6/7/2023	3.74%	4						
7/7/2023	0.00%	2						
8/14/2023	0.00%	3						
9/8/2023	3.74%	3						
10/17/2023	0.00%	3						
11/8/2023	0.00%	1						
12/22/2023	0.00%	3						

NH4 Standard	Additions	(5uM
Spike)		
Analysis Date	Avg %	n
	rec	
1/20/2023	82.16%	1
2/15/2023	83.70%	3
3/24/2023	116.63%	1
4/17/2023	82.16%	1
5/12/2023	82.16%	3
6/7/2023	81.93%	1
7/7/2023	116.63%	2
8/14/2023	81.93%	1
9/8/2023	84.34%	3
10/17/2023	89.00%	1
11/8/2023	80.19%	1
12/22/2023	89.00%	1

# PO<sub>4</sub> Assay

PO4 BLANI	PO4 BLANKS								
Analysis	Mean(uM)	CV	STD	MIN	MAX	Range	n		
Date									
1/20/2023	0.04	1.41	0.05	0.00	0.07	0.07	2		
2/15/2023	0.00						1		
3/24/2023	0.00		0.00	0.00	0.00	0.00	7		
4/17/2023	0.00		0.00	0.00	0.00	0.00	5		
5/12/2023	0.08						1		
6/7/2023	0.00						1		
7/7/2023	0.03	1.03	0.03	0.00	0.06	0.06	2		
8/14/2023	0.03	2.65	0.08	0.10	0.10	0.00	5		
9/8/2023	0.00	1.41	0.00	0.00	0.00	0.00	2		
10/17/2023	0.03	0.56	0.02	0.00	0.00	0.00	5		
11/8/2023	0.05						1		
12/22/2023	0.00						1		

PO4 5 uM STANDARDS							
Analysis Date	Mean	CV	STD	MIN	MAX	Range	n
1/20/2023	4.89	0.04	0.19	4.76	5.02	0.26	2
2/15/2023	5.02						1
3/24/2023	4.79						1
4/17/2023	5.02						1
5/12/2023	4.89						1
6/7/2023	5.32						1
7/7/2023	5.3	0.01	0.03	5.32	5.37	0.05	6
8/14/2023	5.29	0.03	0.14	4.84	5.04	0.20	5
9/8/2023	5.37	0.04	0.21	5.30	5.70	0.40	6
10/17/2023	4.99	0.00	0.00	4.99	4.99	0.00	2
11/8/2023	5.02						1
12/22/2023	5.07	0.06	0.31	4.78	5.50	0.72	3

PO4 LAB DUPS							
Analysis	Avg % dif.	n					
Date							
1/20/2023	36.36%	1	*values				
			very low				
2/15/2023	7.05%	1					
3/24/2023	0.00%	3					
4/17/2023	0.00%	1					

5/12/2023	0.00%	2	
6/7/2023	0.00%	2	
7/7/2023	8.11%	1	
8/14/2023	16.22%	3	
9/8/2023	0.00%	3	
10/17/2023	0.00%	2	
11/8/2023	0.00%	1	
12/22/2023	0.00%	2	

PO4 Standard Addit	PO4 Standard Additions (5uM Spike)						
Analysis	Avg %	n					
Date	dif.						
1/20/2023	84.82%	2					
2/15/2023	80.54%	2					
3/24/2023	83.84%	1					
4/17/2023	83.84%	1					
5/12/2023	80.65%	1					
6/7/2023	88.00%	1					
7/7/2023	105.89%	1					
8/14/2023	79.76%	3					
9/8/2023	107.27%	3					
10/17/2023	112.24%	1					
11/8/2023	103.68%	2					
12/22/2023	105.31%	2					

# NO<sub>3</sub> Assay

NO2/NO3 BLANKS							
Analysis	Mean(uM)	CV	STD	MIN	MAX	Range	n
Date							
1/31/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
2/16/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
3/23/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
4/19/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
5/18/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
6/22/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
7/21/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
8/15/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
9/15/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
10/4/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
11/8/2023	0.00	0.00	0.00	0.00	0.00	0.00	1

12/21/2023	0.00	0.00	0.00	0.00	0.00	0.00	1
12/21/2023	0.00	0.00	0.00	0.00	0.00	0.00	1

NO2/NO3 5 uM STANDARDS							
Analysis	Mean	CV	STD	MIN	MAX	Range	n
Date							
1/31/2023	4.65						1
2/16/2023	5.71	0.10	0.56	6.10	6.10	0.00	2
3/23/2023	4.64	0.04	0.16	5.10	5.15	0.05	2
4/19/2023	4.15	0.00	0.02	4.90	5.02	0.12	2
5/18/2023	5.03	0.00	0.02	5.01	5.04	0.03	2
6/22/2023	5.06	0.00	0.02	5.05	5.08	0.03	2
7/21/2023	5.07	0.01	0.03	5.05	5.10	0.05	2
8/15/2023	5.05						1
9/15/2023	4.92	0.11	0.54	4.70	5.05	0.36	17
10/4/2023	5.02	0.03	0.15	4.98	5.28	0.30	8
11/8/2023	5.00	0.02	0.09	4.89	5.12	0.23	5
12/21/2023	4.87	0.03	0.15	4.76	4.97	0.21	2

NO2/NO3 Lachat r	NO2/NO3 Lachat reps						
Analysis	Avg %	n					
Date	dif.						
1/31/2023	4.54%	11					
2/16/2023	1.79%	8					
3/23/2023	0.42%	12					
4/19/2023	19.67%	10					
5/18/2023	7.16%	3					
6/22/2023	0.81%	4					
7/21/2023	9.55%	15					
8/15/2023	1.80%	1					
9/15/2023	0.63%	12					
10/4/2023	0.00%	8					
11/8/2023	12.92%	6					
12/21/2023	20.19%	6					

NO2/NO3	Standard	additions	(5	uM
Spike)				
Analysis	A	.vg %		n
Date	re	ec		
1/31/2023	1	05.43%		9
2/16/2023	1	09.66%		7
3/23/2023	9	3.96%		16
4/19/2023	1	03.02%		7

5/18/2023	121.15%	7
6/22/2023	100.69%	5
7/21/2023	114.50%	12
8/15/2023	98.23%	7
9/15/2023	118%	9
10/4/2023	81.72%	10
11/8/2023	104.76%	3
12/21/2023	105.81%	8

# TDN Assay

F		
TDN Lab dups		
Analysis	Avg %	n
Date	dif.	
2/1/2023	0.00%	15
2/17/2023	0.00%	7
3/27/2023	0.00%	6
4/20/2023	0.00%	10
5/19/2023	0.00%	18
6/23/2023	0.00%	7
7/25/2023	0.00%	8
8/21/2023	0.00%	9
9/18/2023	0.00%	5
10/10/2023	0.00%	8
11/9/2023	4.75%	1
12/22/2023	0.28%	6
TDN STD ADDS		
Analysis	A 0/	
1111a1y818	Avg %	n
Date	dif.	n
3		n 8
Date	dif.	
Date 2/1/2023	dif. 107.4%	8
Date 2/1/2023 2/17/2023	dif. 107.4% 111.3%	8 8
Date 2/1/2023 2/17/2023 3/27/2023	dif. 107.4% 111.3% 105.1%	8 8 2
Date 2/1/2023 2/17/2023 3/27/2023 4/20/2023	dif. 107.4% 111.3% 105.1% 103.2%	8 8 2 6
Date 2/1/2023 2/17/2023 3/27/2023 4/20/2023 5/19/2023	dif. 107.4% 111.3% 105.1% 103.2% 113.7%	8 8 2 6 2
Date 2/1/2023 2/17/2023 3/27/2023 4/20/2023 5/19/2023 6/23/2023	dif. 107.4% 111.3% 105.1% 103.2% 113.7% 123.6%	8 8 2 6 2 5 2 8
Date 2/1/2023 2/17/2023 3/27/2023 4/20/2023 5/19/2023 6/23/2023 7/25/2023	dif. 107.4% 111.3% 105.1% 103.2% 113.7% 123.6% 97.9%	8 8 2 6 2 5 2
Date 2/1/2023 2/17/2023 3/27/2023 4/20/2023 5/19/2023 6/23/2023 7/25/2023 8/21/2023	dif. 107.4% 111.3% 105.1% 103.2% 113.7% 123.6% 97.9% 117.7%	8 8 2 6 2 5 2 8
Date 2/1/2023 2/17/2023 3/27/2023 4/20/2023 5/19/2023 6/23/2023 7/25/2023 8/21/2023 9/18/2023	dif. 107.4% 111.3% 105.1% 103.2% 113.7% 123.6% 97.9% 117.7% 125.4%	8 8 2 6 2 5 2 8 5

# PON Assay

PON BLAN	PON BLANKS								
Analysis	Mean(uM)	CV	STD	MIN	MAX	Range	n		
Date									
1/18/2023	0.00	1.83	0.00	0.00	0.00	0.00	9		
2/14/2023	0.76	2.26	1.72	0.00	0.02	0.02	7		
3/22/2023	0.00	2.98	0.01	0.00	0.03	0.03	7		
4/11/2023	0.11	2.41	0.25	0.00	0.01	0.01	7		
5/10/2023	0.00	87.11	0.25	0.00	0.00	0.00	7		
6/6/2023	0.11	0.11	0.01	0.00	0.00	0.00	7		
7/6/2023	0.01	1.83	0.01	0.00	0.04	0.04	7		
8/9/2023	0.03	7.51	0.25	0.00	0.04	0.04	7		
9/6/2023	0.11	0.87	0.09	0.00	0.01	0.01	7		
10/3/2023	0.11	2.40	0.25	0.01	0.02	0.01	7		
11/7/2023	0.00	1.51	0.01	0.00	0.06	0.06	7		
12/12/2023	0.00	1.51	0.01	0.00	0.06	0.06	7		

PON K FAC	TORS (10.38	3)					
Analysis	Mean(uM)	CV	STD	MIN	MAX	Range	n
Date							
1/18/2023	10.40	0.01	0.08	10.26	10.34	0.09	11
2/14/2023	10.37	0.01	0.07	10.28	10.43	0.15	8
3/22/2023	10.37	0.00	0.04	10.38	10.38	0.00	8
4/11/2023	10.35	0.01	0.06	10.35	10.37	0.03	8
5/10/2023	10.36	0.00	0.05	10.32	10.39	0.07	8
6/6/2023	10.38	0.01	0.06	10.36	10.38	0.02	8
7/6/2023	10.38	0.02	0.20	10.39	10.40	0.01	8
8/9/2023	11.19	0.12	1.30	10.41	10.42	0.01	8
9/6/2023	11.06	0.17	1.85	10.15	10.15	0.00	12
10/3/2023	10.36	0.02	0.19	10.35	10.42	0.07	8
11/7/2023	10.37	0.00	0.03	10.35	10.37	0.02	8
12/12/2023	10.37	0.00	0.02	10.35	10.37	0.02	8

# Si Assay

Si BLANKS								
	Mean (uM)	CV	STD	MIN	MAX	Range	n	
3/24/2023	0.00						1	

7/31/2024	0.00	 	 	 1
10/4/2024	0.00	 	 	 1
1/5/2024	0.00	 	 	 1

Si 10 uM STANDARDS							
	Mean (uM)	CV	STD	MIN	MAX	Range	n
3/24/2023	10.08						1
7/31/2024	10.08						1
10/4/2024	10.65						1
1/5/2024	11.39						1

Si LAB DUPS		
Analysis	Avg %	n
Date	dif.	
3/24/2023	0.00%	3
7/31/2024	7.07%	2
10/4/2024	12.06%	2
1/5/2024	6.63%	2
Si Standard Additio	ns (5uM Spike)	•
Analysis	Avg %	n
Date	rec	
3/24/2023	81%	3
7/31/2024	83%	2
10/4/2024	88%	1
1/5/2024	86%	1

# Salinity Assay

32.7 Salinity STANDARDS							
Analysis Date	Mean	CV	STD	MIN	MAX	Range	n

1/20/2023	33.00	0.00	0.00	32.70	33	0.30	2
2/22/2023	32.75	0.00	0.07	32.70	32.70	0.00	2
3/27/2023	32.77	0.00	0.12	32.8	32.9	0.10	5
4/13/2023	33.00	0.01	0.31	32.9	33.4	0.50	2
5/15/2023	32.90	0.00	0.14	33	33,4	0.40	3
6/9/2023	32.90	0.00	0.14	32.8	33	0.20	3
7/11/2023	n/a	n/a	n/a	n/a	n/a	n/a	1
8/11/2023	n/a	n/a	n/a	n/a	n/a	n/a	1
9/11/2023	n/a	n/a	n/a	n/a	n/a	n/a	1
10/10/2023	32.80	0.00	0.00	32.9	33	0.10	2
11/10/2023	32.90	0.00	0.06	32.7	32.8	0.10	2
12/13/2023	33.35	0.02	0.78	32.7	32.8	0.10	2

50mS Conduc	ctivity STAN1	DARDS					
Analysis	Mean	CV	STD	MIN	MAX	Range	n
Date							
1/20/2023	50.90	0.00	0.00	50.4	50.9	0.5	2
2/22/2023	50.45	0.00	0.07	50.7	50.7	0	2
3/27/2023	32.73	0.01	0.17	50.5	50.7	0.2	5
4/13/2023	51.03	0.00	0.14	51.1	51.1	0	2
5/15/2023	50.60	0.00	0.00	50.3	50.4	0.1	3
6/9/2023	50.50	0.00	0.14	50.2	50.6	0.4	3
7/11/2023	n/a	n/a	n/a	n/a	n/a	n/a	1
8/11/2023	n/a	n/a	n/a	n/a	n/a	n/a	1
9/11/2023	n/a	n/a	n/a	n/a	n/a	n/a	1
10/10/2023	50.40	0.00	0.14	50.3	50.8	0.5	2
11/10/2023	50.60	0.00	0.10	50.3	51	0.7	2
12/13/2023	51.35	0.02	1.20	50.3	50.4	0.1	2

# Chlorophyll Assay

CHLA ASSAY					
	ug/L	n			
05/08/23	0.0	1			
06/29/23	0.0	1			
09/28/23	0.0	1			
10/31/23	0.0	1			
01/05/24	0.0	1			