## Great Bay Estuary (GRB) NERR Nutrient Metadata January 2024 through December 2024

Latest Update: June 13, 2025

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@belle.baruch.sc.edu) or Reserve with any additional questions.

#### I. Data Set and Research Descriptors

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## a) Principal Investigators and Reserve Contacts

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#### 2) Research Objectives

Nutrient monitoring in GBNERR has been conducted since the late 1980s with the basic goal of developing and maintaining temporally intensive long-term datasets of physicochemical parameters of water quality at locations that are representative of the Great Bay estuarine system. The Great Bay site is relatively unimpacted, while the three tidal river sites (Lamprey, Oyster and Squamscott) have large drainage basins and are impacted by both point (wastewater treatment plants) and nonpoint sources of pollution. In addition to establishing a baseline of water quality and understanding the spatial and temporal variability of

important indicators of estuarine water quality, the data are used by researchers in the analysis of physical and biological processes and by decision makers in the management of the estuary and watershed.

#### a) Monthly Grab Sampling Program

Monthly grab samples are collected to quantify the horizontal spatial variability of important nutrients in the water column at sites located in the upper and lower estuary representative of the local salinity and habitat gradients.

## b) Diel Sampling Program

Once per month, samples are collected over a complete lunar day to quantify the temporal variability of important nutrients in the water column as a function of tidal dynamics.

## 3) Research Methods

## a) Monthly Grab Sampling Program

Monthly grab samples are collected at the Great Bay (GB), Squamscott River (SQ), Oyster River (OR), and Lamprey River (LR) locations. These sites are where the EXO2 water quality dataloggers are located. All grab samples from these stations are collected on the same day, within the same tidal cycle. They are collected during ebbing tides, within 3 hours before low tide. Under normal conditions, the Great Bay and Squamscott River samples are collected from a motorboat. Oyster River and Lamprey River are usually sampled from a floating dock close to the location of the water quality datalogger or staff kayak out to the sonde pipe. Historically, two replicate samples were collected at each station at a depth of approximately 0.5 meters from the surface. Beginning June 2009, a single sample was collected at three of the four stations and a triplicate sample performed at the fourth station every month. The triplicate site is chosen randomly. No distinction is made between spring and neap tides.

Each bottle is opened individually, rinsed three times with estuarine water, then filled facing into the current. For replicates, subsequent samples are collected immediately following the first. All samples are collected in one liter amber HDPE bottles that were previously acid washed (10% HCl), rinsed three times with deionized water and then dried. Filled bottles are capped and stored in a dark cooler with ice for the remainder of the sampling cruise. Upon arrival at the laboratory, dissolved nutrients, chlorophyll, and particulate samples are filtered and preserved immediately. Water used for dissolved nutrients is filtered through MilliporeSigma Durapore 0.45 μm membrane filters and then aliquoted into smaller bottles for analysis. Dissolved nutrients are frozen at -20°C and then transferred to the analytical laboratory on the UNH main campus. Chlorophyll filters are wrapped in aluminum foil and preserved in liquid nitrogen. They are processed within a month of collection. Particulate samples are oven-dried for 24 hours at 60°C, then stored in a desiccator until they are transferred to the analytical laboratory at UNH main campus.

Field parameter data including salinity, temperature, dissolved oxygen, and dissolved oxygen percent saturation are collected using a YSI ProSolo Digital Water Quality instrument. The meter is operated and calibrated according to manufacturer instructions. Measurements are made at grab sample depth (0.5 m) immediately following grab sample collection.

Light attenuation readings in the water column are taken using a LI-COR LI-193 spherical underwater quantum sensor and incident solar irradiance is measured with a LI-COR LI-190 quantum sensor. Data from both sensors are logged with a LI-COR LI-1500 data logger. Care is taken to conduct individual casts during times of consistent solar irradiance and in an area that is not shaded. Measurements are made at 0.1 meter,

and then every 0.25 meters, to a depth of two meters. Where possible, eight or more readings are taken per cast. Triplicate light casts are done if triplicate grab samples are being collected.

The light attenuation coefficient for PAR (Kd) is obtained by computing the linear regression of sample depth vs. ln (PAR) and then by taking the absolute value of the inverse of the slope of the regression. Values for Kd are considered robust if the R<sup>2</sup> of the regression is >0.95. Values that fail this test are not included in the dataset. At Oyster River, it is not possible to do light attenuation measurements due to shallow water depth. It should be noted that according to the manufacturer, K0 is a more appropriate designation for the data measured with this spherical sensor. The Kd designation is used for the purposes of this data set.

Cloud cover, precipitation, tidal stage, wave height, wind direction, and wind speed observations are also reported for grab samples. Wave height, wind speed, and direction are estimated. A compass is used to verify direction.

## b) Diel Sampling Program

Once per month an autosampler is deployed from a fixed wharf near the sonde location on the Lamprey River. A Teledyne Isco 6712 autosampler was used for the entire 2024 field season. Before 2020, a Hach Sigma 900 Max autosampler was used.

Historically, this device was programmed to collect two 850 ml water samples one minute apart every 2 hours and 30 minutes for 22.5 hours such that ten time points were sampled, each with a replicate. Beginning in May 2009, the sampling scheme was changed to ensure that sampling incorporated a full lunar day while improving temporal resolution. Samples are now collected at 2 hour and 4-minute intervals over the lunar day. The first three samples of the deployment are a triplicate set taken within 2 minutes of each other. A total of fifteen time points is sampled. The autosampler is always programmed so that a sample is taken at true low tide. During warm months, the autosampler is filled with ice to prevent sample degradation.

All samples are pumped into polyethylene sample bottles that were previously acid washed (10% HCL), rinsed four times with deionized water, and then dried. At the end of the sampling period, the samples are kept in the dark and returned to the laboratory for immediate processing as outlined above.

#### 4) Site Location and Character

The Great Bay is a macro-tidal drowned river valley estuary located in northern New England. Seven major tributaries contribute runoff to Great Bay draining a total area of roughly 2,400 km<sup>2</sup>. Strong tidal and wind-driven currents drive circulation patterns, vertical mixing, and resuspension of sediments, which in turn affect primary productivity. The estuary contains five major habitat types in the form of mud flat, eelgrass meadows, salt marsh, channel bottom, and rocky shore. Four permanent stations are monitored as a part of the water quality and nutrient long-term monitoring programs. They are located in the middle of Great Bay proper, and in the Lamprey, Oyster and Squamscott Rivers.

#### Site #1 Great Bay

Site name	Great Bay (GB)
Latitude and longitude	43° 04' 20" N, 70° 52' 10" W
Tidal range	2.7 meters
Salinity range	5-32 psu (seasonally); 0-5 psu from high to low tide

Type and amount of freshwater input	Squamscott, Lamprey, and Winnicut Rivers plus smaller streams. High tide influence from Little Bay and associated rivers
Water depth	6.5 meters at MLW (estimated)
Sonde distance from bottom	Sonde is ~0.5 meters off the bottom although it is attached to a mushroom anchor that is not at a fixed location. (See Section 15 for more details.)
Bottom habitat or type	Mud, shell, and rock channel bottom
Pollutants in area	Unimpacted reference site
Description of watershed	Central area of Great Bay proper

# Site #2 Squamscott River

Site name	Squamscott River (SQ)
Latitude and longitude	43° 03' 11" N, 70° 54' 45" W
Tidal range	2.7 meters
Salinity range	0-32 psu (seasonally); 5-20 psu from high to low tide
Type and amount of freshwater input	Exeter River, adjacent marshes
Water depth	3.5 meters at MLW (estimated)
Sonde distance from bottom	Sonde is 0.5 meters off the bottom
Bottom habitat or type	Mud/oyster shell channel bottom
Pollutants in area	Urban stormwater, agriculture, two municipal wastewater treatment plants, residential septic systems
Description of watershed	Mid-channel of the Squamscott River - Boston and Maine Railroad Bridge, Stratham, NH

# Site #3 Lamprey River

Site name	Lamprey River (LR)
Latitude and longitude	43° 04' 48" N, 70° 56' 04" W
Tidal range	2.7 meters
Salinity range	0-30 psu (seasonally); difference of ≤15 psu between high and low tides
Type and amount of freshwater input	Lamprey River
Water depth	3.5 meters at MLW (estimated)

Sonde distance from bottom	Sonde is 0.5 meters off the bottom
Bottom habitat or type	Mud/rock
Pollutants in area	Urban stormwater, adjacent marina, upstream and downstream wastewater treatment plants, upstream agriculture
Description of watershed	West bank of the tidal portion of the Lamprey River, approximately 300 m downstream of the dam at Route 108 in Newmarket, NH

# Site #4 Oyster River (OR)

Site name	Oyster River (OR)
Latitude and longitude	43° 08' 04" N, 70° 54' 35" W
Tidal range	2.7 meters (maximum)
Salinity range	0-32 psu (seasonally); difference of ≤15 psu between high and low tides
Type and amount of freshwater input	Oyster River
Water depth	0.3 meters at MLW, 3 meters at maximum high tide (estimated)
Sonde distance from bottom	Sonde is ≤0.5 meters off the bottom although it is attached to a mushroom anchor that is not at a fixed location. (See Section 15 for more details.)
Bottom habitat or type	Mud
Pollutants in area	Urban stormwater, mooring field and crew dock, downstream wastewater treatment plant, upstream agriculture, residential on-site sewage disposal
Description of watershed	In the center channel of the tidal portion of the Oyster River, approximately 300 m downstream of the head of tide dam adjacent to Jackson's Landing in Durham, NH

# GRB NERR nutrient/pigment monitoring stations

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
GB	P	Great Bay	43° 04' 20" N, 70° 52' 10" W	07/1995 – present	NA	NA
LR	P	Lamprey River	43° 04' 48" N, 70° 56' 04" W	05/1998 – present	NA	NA
OR	P	Oyster River	43° 08' 04" N, 70° 54' 35" W	06/2000 – present	NA	NA

SQ	P	Squamscott River	43° 03' 11" N, 70° 54' 45" W	07/1997 – present	NA	NA
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#### 5) Coded Variable Definitions

GRB = Great Bay NERR Nut = nutrients

grbgbnut = Great Bay nutrients grbsqnut = Squamscott River nutrients grblrnut = Lamprey River nutrients grbornut = Oyster River nutrients

NUT = Nutrient Sampling Program

1 = Monthly Grab Sample Program

2 = Diel Grab Sample Program

For example, a sample code of 'GRBLRNUT' indicates that the sample was collected at the Great Bay NERR Lamprey River site and is being reported as part of the Nutrient Sampling Program Data Report. A Monitoring Program Code of '2' indicates that the sample was collected as part of the Diel Grab Sample Program.

## 6) Data Collection Period

Sampling in the Great Bay Estuary is typically completed only April through December because parts of the bay freeze during the winter months. This year diel and grab samples were collected from April through December at all sites. Grab samples were collected at Station "grbgbnut" January – March also.

#### **Grab Sampling**

Station grbgbnut Sample Date and	Station grblrnut Sample Date and	Station grbornut Sample Date and	Station grbsqnut Sample Date and
Time	Time	Time	Time
01/19/2024 13:53			
02/27/2024 08:45			
03/27/2024 08:30			
04/15/2024 12:25	04/15/2024 12:51	04/15/2024 11:50	04/15/2024 12:50
04/15/2024 12:26	05/13/2024 11:30	05/13/2024 10:15	05/13/2024 11:00
04/15/2024 12:27	05/13/2024 11:31	06/10/2024 09:15	06/10/2024 09:45
05/13/2024 11:20	05/13/2024 11:32	07/09/2024 08:45	06/10/2024 09:46
06/10/2024 10:10	06/10/2024 11:15	07/09/2024 08:46	06/10/2024 09:47
07/09/2024 09:35	07/09/2024 09:45	07/09/2024 08:47	07/09/2024 09:20
08/05/2024 07:04	08/05/2024 08:15	08/05/2024 07:15	08/05/2024 07:29
08/05/2024 07:05	09/09/2024 10:45	09/09/2024 09:45	09/09/2024 10:40
08/05/2024 07:06	09/09/2024 10:46	10/21/2024 08:52	10/21/2024 09:33
09/09/2024 10:55	09/09/2024 10:47	10/21/2024 08:53	11/05/2024 09:10
10/21/2024 09:45	10/21/2024 10:00	10/21/2024 08:54	11/05/2024 09:11
11/05/2024 09:25	11/05/2024 09:00	11/05/2024 07:55	11/05/2024 09:12
12/09/2024 12:35	12/09/2024 13:30	12/09/2024 12:27	12/09/2024 13:15
12/09/2024 12:36			

## Diel Sampling Station grblrnut

Station Si Silinat	
<b>Start Date and Time</b>	<b>End Date and Time</b>
04/29/2024 09:22	04/30/2024 10:06
05/29/2024 08:01	05/30/2024 08:45
06/25/2024 08:02	06/26/2024 08:46
07/25/2024 10:29	07/26/2024 11:13
08/29/2024 07:53	08/30/2024 08:37
09/25/2024 07:24	09/26/2024 08:08
10/29/2024 07:43	10/30/2024 08:27
11/25/2024 09:39	11/26/2024 10:23
12/17/2024 08:40	12/18/2024 07:20

## 7) Associated Researchers and Projects

As part of the SWMP long-term monitoring program, GRBNERR 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>.

The SWMP nutrient data set is one of several water quality monitoring programs in the Great Bay Estuary that include both physical and chemical properties. More information including over ten years of additional nutrient data can be found at <a href="http://www.ciceet.unh.edu/">http://www.ciceet.unh.edu/</a>. A spatially explicit non-exhaustive list and description of additional programs can be found at <a href="http://www.gulfofmaine.org/esip/map/">http://www.gulfofmaine.org/esip/map/</a>.

Submerged Aquatic Vegetation (SAV) research - Dr. David Burdick; Dr. Gregg Moore; Dr. Fred Short - Jackson Estuarine Laboratory. Supported by Piscataqua Region Estuaries Partnership and NH Department of Environmental Services.

EPA National Coastal Assessment Program - Dr. Stephen H. Jones, Jackson Estuarine Laboratory. Funded by the US-EPA.

Oyster reef mapping and restoration – Dr. Ray Grizzle, Jackson Estuarine Laboratory. Supported by NH Fish and Game, the NOAA-UNH Joint Hydrographic Center and the Center for Coastal and Ocean Mapping.

#### 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 2024.

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

All field and lab data were collected following protocols described in the SWMP standard operating procedures and methods detailed in this report. Data for dissolved nutrients, particulate carbon, and particulate nitrogen are emailed from the analytical lab on campus to Lara Martin (NERR Research Technician) in the form of an Excel spreadsheet. The data are then transferred to a process workbook that also contains TSS, Kd, chl-a, and environmental conditions data. The analytical lab reports some nutrient concentrations in ug/L. These values are converted to mg/L. Tom Gregory and Lara Martin are responsible for data conversions.

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.

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

The following is a list of water-quality and environmental parameters included in the GRB SWMP Nutrient Database. Required NOAA/NERRS System-wide Monitoring Program water quality parameters are denoted by an asterisk "\*".

Data Category	Parameter	Variable Name	<b>Units of Measure</b>
Phosphorus:	*Orthophosphate, Filtered	PO4F	mg/L as P
Nitrogen:	*Nitrite + Nitrate, Filtered *Ammonium, Filtered Dissolved Inorganic Nitrogen Dissolved Organic Nitrogen Total Dissolved Nitrogen Particulate Organic Nitrogen	NO23F NH4F DIN DON TDN PON	mg/L as N mg/L as N mg/L as N mg/L as N mg/L as N mg/L as N

#### **Plant Pigments:**

	*Chlorophyll-a	CHLA_N	μg/L
Other Lab Paramet	ters:		
	Dissolved Organic Carbon	DOC	mg/L as C
	Particulate Organic Carbon	POC	mg/L as C
	Total Suspended Solids	TSS	mg/L
Microbial (Lampre	y River site only):		
	Escherichia coli	ECOLI_CFU	CFU
	Enterococci	ENTERO_CFU	CFU
	Total Fecal Coliforms	FECCOL_CFU	CFU
Field Parameters:			
	Water Temperature	WTEM_N	°C
	Salinity	$SALT_N$	pps
	Dissolved Oxygen	DO N	mg/L
	Dissolved Oxygen Saturation	DO S N	%
	Light Extinction Coefficient	Kd_N	m <sup>-1</sup>

#### Notes:

- 1. Time is coded based on a 24:00 clock and is converted to Eastern Standard Time.
- 2. Reserves have the option of measuring NO2 and NO3, or they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3. NO2 has been shown to be a minor component relative to NO3 in Great Bay and so, beginning in 2009, Great Bay NERR ceased to report NO2 and NO3 separately.

#### 11) Measured and Calculated Laboratory Parameters

The following parameters are reported in the 2024 nutrient dataset for GRB

#### a) Variables Measured Directly

Nitrogen species: NH4F, NO23F, TDN

Phosphorus species: PO4F

Other: TSS, CHLA\_N, DOC, POC, PON

FECCOL, ECOLI, ENTERO

#### b) Computed Variables

DIN: NO23F + NH4FTN: TDN + PON

DON: TDN - NH4F - N023F

#### 12) Limits of Detection

The following Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established for the UNH laboratory that performed analyses in 2024. (See Table 1) Concentrations below the MDL are changed to the parameter's respective MDL and are flagged <-4> [SBL]. Samples that fall above the maximum range of the chemistry are diluted so that the analysis output falls within the analytical range of the chemistry and these values are multiplied by the

dilution factor (e.g., 10 for a 1:10 dilution) and reported in the database. MDL values are reviewed and revised periodically.

The Method Detection Limit for CHLA N was determined by GRB Reserve staff in 2023.

Table 1. University of New Hampshire Water Quality Analysis Laboratory Method Detection Limits (MDL) for measured water quality parameters.

Parameter	Start Date	<b>End Date</b>	MDL
DOC	01/01/2024	12/31/2024	$0.20~\mathrm{mg/L}$
NH4F	01/01/2024	12/31/2024	0.008  mg/L
NO23F	01/01/2024	12/31/2024	0.014  mg/L
PO4F	01/01/2024	12/31/2024	0.003  mg/L
POC	01/01/2024	12/31/2024	0.004  mg/L
PON	01/01/2024	12/31/2024	0.002  mg/L
TDN	01/01/2024	12/31/2024	0.05  mg/L
TSS	01/01/2024	12/31/2024	1.0  mg/L
CHLA-N	01/01/2024	12/31/2024	$0.18 \mu g/L$

Total Fecal Coliform, *Escherichia coli*, and Enterococcus values less than 4 #/100ml may be below the detection limit.

#### 13) Laboratory Methods

The University of New Hampshire Water Quality Analysis Laboratory (Jody Potter) was responsible for the processing of GRB nutrient data. Methods for each parameter are presented below.

#### a) Parameter: NH4F

i) <u>Method Reference</u>: Westco Scientific Instruments, SmartChem Discrete Analyzer. SmartChem Method #210-200B. Method is based on USEPA 350.1.

Spectrophotometric and Kinetics Investigation of the Bertholt Reaction for the Determination of Ammonia, Analytical Chemistry, 1977, Vol. 49, #3, P.464-469.

- ii) Method Description: This method is based on the Berthholt reaction. Ammonia reacts in alkaline solution with hypochlorite to form monochloramine which, in the presence of phenol, catalytic amounts of nitroprusside (nitroferricyanide) and excess hypochlorite, gives indophenol blue. The formation of monochloramine requires a pH between 8 and 11.5. At higher pH, ammonia may begin to oxidize to nitrate. At pH greater than 9.6, some precipitation of calcium and magnesium as hydroxides and carbonates occurs in seawater, but these ions may be held in solution by complexing them with EDTA. The indophenol blue measured at 630 nm is proportional to the original ammonia concentration.
- iii) <u>Preservation Method</u>: Sample is filtered through a 0.45 um disposable disk filter and stored at –20°C until analyzed.

## b) Parameter: NO23F

i) Method Reference: Westco Scientific Instruments, SmartChem Discrete Analyzer. SmartChem

Method #375-100D. Method is based on USEPA 353.3.

Armstrong, F.A., Stearns, C.R., and Strickland, J.D.H. (1967) The measurement of upwelling and subsequent biological processes by means of the Technicon AutoAnalyzer and associated equipment. *Deep Sea Research* 14:381-389.

- ii) Method Description: Nitrate is 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 resulting diazonium ion is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting pink dye absorbs at 520 nm. The procedure is the same for the nitrite analysis minus the cadmium column. Nitrate concentrations are obtained by subtracting nitrite values, which have been previously analyzed, from the nitrite + nitrate values.

  Though the method is written for seawater and brackish water, it is also applicable to non-saline sample matrixes. The method is calibrated using standards prepared in deionized water. Once calibrated, samples of varying salinities (0 to 35 ppt) may be analyzed. The determination of background absorbance is necessary only for samples which have color absorbing at 540 nm. The salt effect is less than 2%.
- iii) <u>Preservation Method</u>: Sample is filtered through a 0.45 um disposable disk filter and stored at -20°C until analyzed.

## c) Parameter: PO4F

i) <u>Method Reference</u>: Westco Scientific Instruments, SmartChem Discrete Analyzer. SmartChem Method #410-200E.

Method is based on USEPA 365.2. Bernhardt, H. and Wilhelms, A. (1967) The continuous determination of low-level iron, soluble phosphate, and total phosphate with the AutoAnalyzer. *Technicon Symp.* 1:386.

- ii) Method Description: Ammonium molybdate and antimony potassium tartrate reacts in an acid medium with phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color produced is proportional to the phosphate concentration in the sample. Though there is a density difference between seawater and reagent water the bias is less than 2%. Though the method is written for seawater and brackish water it is also applicable to non-saline sample matrixes. The method is calibrated using standards prepared in deionized water. Once calibrated, samples of varying salinities (0 to 35 ppt) may be analyzed. The determination of background absorbance is necessary only for samples, which have color absorbing at 880 nm.
- iii) <u>Preservation Method</u>: Sample is filtered through a 0.45 um disposable disk filter and stored at -20°C until analysis.

#### d) Parameter: TDN

i) <u>Method Reference</u>: Shimadzu Scientific Instruments Inc., TOC-V with TNM-1 Nitrogen Module. High Temperature Catalytic Oxidation with chemiluminescent detection.

Merriam, J.L., W.H. McDowell, W.S. Currie (1996) A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. Soil Science Society of America Journal, 60(4) 1050-1055.

- ii) Method Description: A precisely measured aliquot of filtered sample is injected and combusted on a catalyst at 720°C. All fixed N is converted to Nitric Oxide (NO) and then coupled with ozone (O<sub>3</sub>) producing Nitrogen Dioxide\* (NO<sub>2</sub>\*) which is measured chemiluminescently.
- iii) <u>Preservation Method</u>: Sample is filtered through a 0.45 um disposable disk filter and stored at -20°C until analyzed.

## e) Parameter: DOC

- i) <u>Method Reference</u>: Shimadzu Scientific Instruments Inc., TOC-V: High Temperature Catalytic Oxidation: USEPA Method 415.1.
- ii) Method Description: Organic carbon in a sample is converted to carbon dioxide by catalytic combustion or wet chemical oxidations. The carbon dioxide formed is measured directly by an infrared detector. The amount of carbon dioxide is directly proportional to the concentration of carbonaceous material in the sample.
- iv) <u>Preservation Method</u>: Sample is filtered through a 0.45 um disposable disk filter and stored at -20°C until analyzed.

## f) Parameter: POC/PON

- i) <u>Method Reference</u>: Carbon, Nelson et al, 1996. Total carbon, organic carbon, and organic matter. Soil Sci Soc Am; Nitrogen, Bremner et al., 1996. Nitrogen total. Methods of Soil Analysis.
- ii) Method Description: An accurately measured amount of particulate matter is combusted at 950C using an elemental analyzer (Elementar Unicube). The combustion products are passed over a copper reduction tube. Carbon dioxide, water vapor, and nitrogen are homogeneously mixed at a known volume, temperature, and pressure. The mixture is released into a series of thermal conductivity detectors/traps, measuring in turn by difference, hydrogen (as water vapor), C (as CO2) and N (as N2).
- iii) Preservation Method: Dried at 60°C.

The GRB Reserve staff were responsible for processing the following parameters.

#### g) Parameter: TSS

- i) <u>Method Reference</u>: JEL SOP 1.06; adapted from Standard Methods for the Examination of Water and Wastewater. 2540 B. pp. 2-55-56.
- ii) Method Description: Whatman GF/C 47mm filters are combusted at 400°C for 4 hours. Filters are weighed and stored in a desiccator until analysis. Sample water (280 ml or less under high sediment load) is vacuum filtered through the filters. Filters are placed in a drying oven at 60°C for 24 hours. Filters are weighed again to determine TSS.

#### h) Parameters: CHLA

i) <u>Method Reference</u>: EPA Method 445.0, Revision 1.2. In Vitro Determination of Chlorophyll-a and Pheophytin-a in Marine and Freshwater Algae by Fluorescence. September 1997.

Welschmeyer, Nicholas A. (1994) Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and phaeopigments. Limnology and Oceanography, 39 (8).

- ii) Method Description: Sample water (64 ml) is vacuum filtered through a 25mm Whatman GF/F glass microfiber filter, which is then folded in half, wrapped in foil, and placed in liquid nitrogen. For analysis, filters are removed and placed in centrifuge tubes. Ten milliliters of 90% acetone are added and the contents are mixed using a vortexer. Samples are frozen at -20°C for 24 hours in the dark. Samples are brought to room temperature and then centrifuged for 5 minutes at 1500 rpm. Approximately three milliliters of sample are transferred to a culture tube and fluorescence is determined using a Turner Trilogy fluorometer, using a non-acidified module.
- iii) Method Preservation: The filter is stored in liquid nitrogen until processing. Samples are run within one month of collection.

Jackson Estuarine Laboratory (Stephen Jones) was responsible for microbial analysis.

#### i) Parameters: ECOLI, ENTERO, FECCOL

i) <u>Method Description</u>: Water samples are filtered through membrane filters and the organisms caught on the filters are grown to colonies on indicator specific media and conditions. The colonies showing the indicator-specific reaction on the agar media are enumerated following appropriate incubation times.

Please contact the Reserve for detailed methods.

#### 14) Field and Laboratory QAQC programs

#### a) Precision

- i. **Field Variability** GBNERR collects triplicate grab samples at a randomly selected station every month and collects one set of triplicates per month during the diel sampling. This helps to determine water mass variability.
- ii. Laboratory Variability none
- i. **Inter-organizational splits** Inter-laboratory comparison completed during 2018 between laboratories analyzing NERRS nutrient samples for analytes NO23F, NO2F, PO4F.

#### b) Accuracy

- ii. Sample Spikes blanks
- iii. Standard Reference Material Analysis see lab protocols
- iv. Cross Calibration Exercises none

## 15) QAQC flag definitions – This section details the primary and secondary 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** This section details the secondary QAQC Code definitions used in combination with the flags above.

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

#### General errors

GCM	Calculated value could not be determined due to missing data
GCR	Calculated value could not be determined due to rejected data

GDM Data missing or sample never collected GQD Data rejected due to QA/QC checks
GQS Data suspect due to QA/QC checks

GSM See metadata

#### Sensor errors

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

#### **Parameter Comments**

anneuer C	Offinients
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

CAD Algai blobii	CAB	Algal bloom
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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. 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 changed to the method detection limit itself rather than a measured value. For example, if the measured concentration of NO23F was 0.005 mg/L as N (MDL=0.008), 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 MDLs is missing, suspect, or rejected and the data is needed, contact the Research Coordinator at the Reserve submitting the data.

Note: The way MDL values are handled in the NERRS SWMP dataset was changed in November 2011. Data from 2007-2010 that fell below the MDL 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.

Data flagged as missing <-2> or not collected <-1> were usually caused by acute weather events, safety concerns that occurred during a sampling effort (i.e., not an event that caused the rescheduling of an entire trip), or loss of sample resulting from equipment failure.

No physical ("water quality") parameters are included in this dataset for the diel sample program because these data can be obtained via download from the Lamprey River station (grblrwq) at <a href="www.nerrsdata.org">www.nerrsdata.org</a>. It is recommended that users utilize the Advanced Query System (<a href="www.nerrsdata.org/aqs">www.nerrsdata.org/aqs</a>) to merge these nutrient and water-quality data into one file.

While basic and notable weather information was inserted into the F\_Record column for all grab samples, it is recommended that users of these data refer to the GRBNERR's meteorological dataset from the Greenland Meteorological station (grbglmet) for weather information. The meteorological dataset can be accessed online at the CDMO home page <a href="http://cdmo.baruch.sc.edu/">http://cdmo.baruch.sc.edu/</a> or <a href="www.nerrsdata.org/">www.nerrsdata.org</a>. It is recommended that users utilize the new Advanced Query System (<a href="www.nerrsdata.org/aqs">www.nerrsdata.org/aqs</a>) to merge nutrient, weather, and water-quality data into one file.

If discrepancies between replicate grab samples are observed, they are flagged in the dataset with an "[SRD]" (denoting "Replicate values differ substantially") code in the dataset. It is up to the user to retain or discard these data during analyses.

#### Sample hold times for 2024

Inorganic nutrient samples are held at -20°C. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30 days) at -20°C and allows an additional 5 days for collecting, processing, and shipping samples. Samples held beyond that time are flagged suspect <1> and coded (CHB). If measured values were below the MDL, <-4> [SBL] (CHB) flagging/coding was applied. For all calculated concentrations, e.g. DIN, if one or more of the analytes used for the calculation were coded (CHB), the final solution was flagged suspect <1> and coded "see metadata" (CSM).

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 are flagged suspect and coded (CHB) in the data set.

#### 18) Remarks on (GSM/CSM) coded data

## Oyster River <1> [GSM] (CAB)

The chlorophyll-a grab sample collected on 11/05/2024 07:55 was anomalous. The concentration was 106.11  $\mu$ g/L which is extremely high for any of our sites. Field logs noted that the river water was very yellow. After the sample was processed, the filter was a deep pink color. The sample was run through a spectrophotometer by another lab and there was a peak in fluorescence in the 400-500 nm range, in addition to high chlorophyll peaks. We could not determine the species that was causing the fluorescence. Despite the unusual concentration, we believe the sample represents real environmental conditions.

#### All sites

The majority of the NH4 and NO3+NO2 grab and diel samples collected between August 4 and September 10, 2024 were held for longer than 28 days. The UNH Water Quality Lab's Smartchem Discrete Analyzer was out of service and it took an extended time to receive a part necessary for its repair.

#### **Nutrient Sample Holding Times Table**

Site/Sample Type	Collection Date	PO4†	NH4†	NO3 + NO2†	POC/PON
GB grab	01/19/2024	03/12/2024*	02/08/2024	02/07/2024	02/27/2024
GB grab	02/27/2024	03/14/2024	03/28/2024	03/28/2024	04/16/2024
GB grab	03/27/2024	04/11/2024	05/03/2024*	04/11/2024	06/03/2024
GB, LR, OR, SQ grabs	04/15/2024	05/06/2024	05/03/2024	05/06/2024	06/03/2024
LR diel samples	04/29 - 04/30/2024	05/06/2024	05/03/2024	05/06/2024	
GB, LR, OR, SQ grabs	05/13/2024	06/20/2024*	06/10/2024	06/12/2024	Filters lost
LR diel samples	05/29 - 05/30/2024	06/20/2024	06/06/2024	06/14/2024	
GB, LR, OR, SQ grabs	06/10/2024	07/01/2024	07/01/2024	06/28/2024	10/16/2024
LR diel samples	06/25 - 06/26/2024	07/08/2024	07/02/2024	07/21/2024	
GB, LR, OR, SQ grabs	07/09/2024	07/18/2024	07/22/2024	07/21/2024	02/03/2025

LR diel samples	07/25 - 07/26/2024	08/05/2024	08/05/2024	08/02/2024	
Ert dier sampres	07723 0772072021	00/03/2021	00/02/2021	00/02/2021	
GB, LR, OR, SQ grabs	08/05/2024	08/27/2024	10/14/2024*	10/29/2024*	02/05/2025
LR diel samples	08/29 - 08/30/2024	09/09/2024	10/14/2024*	11/06/2024*	
GB, LR, OR, SQ grabs	09/09/2024	10/05/2024	10/30/2024*	10/05/2024	02/11/2025
LR diel samples	09/25 - 09/26/2024	10/15/2024	10/20/2024	10/15/2024	
GB, LR, OR, SQ grabs	10/21/2024	10/31/2024	11/05/2024	11/22/2024	02/11/2025
LR diel samples	10/29 - 10/30/2024	11/18/2024	11/21/2024	11/22/2024	
GB, LR, OR, SQ grabs	11/05/2024	11/18/2024	11/21/2024	11/22/2024	04/15/2025
LR diel samples (1A, 1C, 6, 9-13)	11/25 - 11/26/2024	12/10/2024	12/09/2024	12/10/2024	
LR diel samples (1B, 1-5, 7, 8)	11/25 - 11/26/2024	12/10/2024	12/09/2024	01/21/2025*	
GB, LR, OR, SQ grabs	12/09/2024	12/17/2024	12/17/2024	12/17/2024	04/22/2025
LR diel samples	12/17 - 12/18/2024	01/10/2025	01/06/2025	01/10/2025	

<sup>\*</sup>Sample held longer than allowed by NERR protocol. Samples flagged as suspect or rejected.

## **Chlorophyll Sample Holding Times Table**

	1	Date Analyzed
Site/Sample Type	Collection Date	CHLA_N
GB grab	01/19/2024	01/20/2024
GB grab	02/27/2024	02/28/2024
GB grab	03/27/2024	03/28/2024
GB, LR, OR, SQ grabs	04/15/2024	05/15/2024
LR diel samples	04/29 - 04/30/2024	05/15/2024
GB, LR, OR, SQ grabs	05/13/2024	05/15/2024
LR diel samples	05/29 - 05/30/2024	06/28/2024
GB, LR, OR, SQ grabs	06/10/2024	06/28/2024
LR diel samples	06/25 - 06/26/2024	06/28/2024
GB, LR, OR, SQ grabs	07/09/2024	08/08/2024
LR diel samples	07/25 - 07/26/2024	08/08/2024
GB, LR, OR, SQ grabs	08/05/2024	08/08/2024
LR diel samples	08/29 - 08/30/2024	09/18/2024
GB, LR, OR, SQ grabs	09/09/2024	09/18/2024
LR diel samples	09/25 - 09/26/2024	10/25/2024
GB, LR, OR, SQ grabs	10/21/2024	10/25/2024

<sup>†</sup>Parameters with 28 day holding times

POC/PON calculated only on grab samples

LR diel samples	10/29 - 10/30/2024	11/26/2024
GB, LR, OR, SQ grabs	11/05/2024	11/26/2024
LR diel samples	11/25 - 11/26/2024	12/20/2024
GB, LR, OR, SQ grabs	12/09/2024	12/20/2024
LR diel samples	12/17 - 12/18/2024	12/20/2024