Great Bay Estuary (GRB) NERR Nutrient Metadata May 2020 through December 2020

Latest Update: June 13, 2021

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

1) Principal Investigator(s) and Contact Persons

a) Principal Investigator

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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 physico-chemical 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 boat. Oyster River and Lamprey River are usually sampled from a floating dock close to the location of the water quality datalogger. Historically, two replicate samples were collected at each station at a depth of approximately 0.5 m 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 at least every other month. The station replicated is chosen randomly. 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 (3x) with deionized water and dried. Filled bottles are capped and stored in a dark cooler for the remainder of the sampling cruise. Upon arrival to the laboratory, dissolved nutrients, chlorophyll, and particulate samples are filtered and preserved immediately. Dissolved nutrients are frozen at -20C and then transferred to the analytical laboratory at the UNH main campus. Chlorophyll samples are wrapped in aluminum foil and preserved in liquid nitrogen. Particulate samples are oven-dried for 24 hours at 60C, then stored in a dessicator 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 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 Datalogger. Care is taken to conduct individual casts during times of consistent solar irradiance. Measurements are made at 0.1 meters and then every 0.25 meters to a depth of 2 meters. Where possible, eight or more readings are taken per cast. The light attenuation coefficient for PAR (Kd) is obtained by computing the linear regression of sample depth vs. ln (PAR) then taking the absolute value of the inverse of the slope of the regression. Values for Kd are considered robust if the r² of the regression is >0.95 and values failing this test are not included in the dataset. At Oyster River, it is not possible to do the light attenuation measurement 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. Wind speed and direction are estimated. A compass is used to verify direction if necessary.

b) Diel Sampling Program

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

Historically, this device automatically collected two 850 ml water samples one minute apart every 2 hours and 30 minutes for 22.5 hours such that 10 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 3 samples of the deployment are a triplicate set taken within 2 minutes of each other. A total of 15 time points is sampled. An effort is made to begin sampling at low tide although this is not always possible. Instead, 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 km². 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 mid Great Bay, and in the Lamprey, Oyster and Squamscott Rivers.

Site #1 Great Bay (GB)

Location: Central area of Great Bay proper.

Coordinates are 43° 04′ 20″ N latitude and 70° 52′ 10″ W longitude. Salinity range: 5-32 ppt (seasonally); 0-5 ppt from high to low tide.

Temperature range: -1° C to 24° C (seasonally); 0-3 (from high to low tide)

Depth: 6.5 meters at MLW Tidal height: 2.7 meters

Bottom type: Mud and rock channel bottom

Tidal velocity: maximum 50 cm/sec

Watersheds: Squamscott, Lamprey and Winnicut Rivers plus smaller streams.

High tide influence from Little Bay and associated rivers

Pollutant influence: Clean reference site

Site #2 Squamscott River (SO)

Location: Mid channel of the Squamscott River at the Boston and Maine Railroad Bridge, Stratham, NH.

Coordinates are 43° 02' 30" N latitude and 70° 55' 20" W longitude

Salinity range: 0-30 ppt (seasonally); 5-20 ppt from high to low tide.

Temperature range: -1° C to 27° C (seasonally); difference of 0-5° between high and low tide

Depth: 3.5 meters at MLW Tidal height: 2.7 meters

Bottom type: Mud/oyster channel bottom Tidal velocity: maximum 50 cm/sec

Watersheds: Exeter River, adjacent marshes

Pollutant influence: Urban stormwater, agriculture, two municipal wastewater treatment plants,

residential septic systems

Site #3 Lamprey River (LR)

Location: West bank of the tidal portion of the Lamprey River, approximately 300 m downstream of the dam at Route 108 in Newmarket, NH.

Coordinates are 43° 04' 48" N latitude and 70° 56' 04" W longitude.

Salinity range: 0 - 27 ppt (seasonally); difference of up to 15 ppt between high and low tides. Temperature range: -1° C to 27° C (seasonally); difference of up to 5° C between high and low tides.

Depth: 3.5 meters Tidal height: 2.7 meters Bottom type: Mud/rock

Tidal velocity: maximum 40 cm/sec

Watershed: Lamprey River

Pollutant influence: Urban stormwater, adjacent marina, upstream and downstream wastewater

treatment plants, upstream agriculture

Site #4 Oyster River (OR)

Location: In the center channel of the tidal portion of the Oyster River, approximately 300 meters downstream of the head of tide dam adjacent to Jackson's Landing in Durham, NH.

Coordinates are 43.134° N latitude and 70.911° W longitude

Salinity range: 0 –32 ppt (seasonally); difference of up to 15 ppt between high and low tides Temperature range: -1° C to 27° C (seasonally); difference of up to 5° C between high and low tides

Depth: 0.3 meters at MLW, 3 meters at highest high tides

Tidal height: 2.7 meters (maximum)

Bottom type: Mud

Tidal velocity: maximum 40 cm/sec

Watershed: Oyster River

Pollutant influence: Urban stormwater, mooring field and crew dock, downstream wastewater treatment plant, upstream agriculture, residential on-site sewage disposal.

GRB NERR nutrient/pigment monitoring stations:

Station	SWMP	Station Name	Location	Active	Reason	Notes
Code	Status			Dates	Decommissioned	
GB	P	Great Bay	43° 04' 20" N,	07/1995 —	NA	NA
			70° 52' 10" W	present		
T.D.	D	T D.	420 0 41 4011 NI	05/1000	NIA	NT A
LR	P	Lamprey River	43° 04' 48" N,	05/1998 –	NA	NA
			70° 56' 04" W	present		
OR	P	Oyster River	43° 08' 02" N,	06/2000 -	NA	NA
			70° 54' 40" W	present		

SQ	P	Squamscott River	43° 02' 30" N,	07/1997 –	NA	NA
			70° 55' 20" W	present		

5) Coded Variable Definitions

GRB = Great Bay NERR Nut = nutrients

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

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 May through December.

Grab Sampling

Station grbgb	Station grblr	Station grbor	Station grbsq
Sample Date and	Sample Date and	Sample Date and	Sample Date and
Time	Time	Time	Time
05/11/2020 09:55	05/11/2020 10:31	05/11/2020 09:08	05/11/2020 09:35
06/09/2020 09:35	06/09/2020 10:26	06/09/2020 09:40	05/11/2020 09:36
07/07/2020 08:56	06/09/2020 10:27	07/07/2020 08:40	05/11/2020 09:37
08/24/2020 10:11	06/09/2020 10:28	07/07/2020 08:41	06/09/2020 09:15
08/24/2020 10:12	07/07/2020 07:35	07/07/2020 08:42	07/07/2020 08:21
08/24/2020 10:13	08/24/2020 11:15	08/24/2020 09:00	08/24/2020 09:50
09/21/2020 09:05	09/21/2020 10:07	09/21/2020 09:07	09/21/2020 09:22
10/19/2020 08:25	09/21/2020 10:08	10/19/2020 07:00	10/19/2020 08:00
11/02/2020 07:52	09/21/2020 10:09	10/19/2020 07:01	11/02/2020 07:38
11/02/2020 07:53	10/19/2020 09:00	10/19/2020 07:02	12/07/2020 11:30
11/02/2020 07:54	11/02/2020 08:15	11/02/2020 07:35	12/07/2020 11:31
12/07/2020 11:53	12/07/2020 12:20	12/07/2020 11:35	12/07/2020 11:32

Diel Sampling Station grblr

Start Date and Time End Date and Time

05/31/2020 12:21	06/01/2020 13:06
06/15/2020 10:01	06/16/2020 10:50
07/16/2020 10:59	07/17/2020 11:48
09/13/2020 09:44	09/14/2020 10:28
09/24/2020 07:07	09/25/2020 07:51
10/21/2020 10:51	10/22/2020 11:35
11/19/2020 10:54	11/20/2020 11:38
12/03/2020 09:16	12/04/2020 10:00

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 www.nerrsdata.org.

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 http://www.ciceet.unh.edu/. A spatially explicit non-exhaustive list and description of additional programs can be found at http://www.gulfofmaine.org/esip/map/.

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.

8) Distribution

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

Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2020.

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 www.nerrsdata.org. 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 Tom Gregory (NERR Research Scientist) in the form of an Excel spreadsheet. The data are then transferred to a process workbook that also contains TSS and chl 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	Units of Measure
Phosphorus:			
	*Orthophosphate, Filtered	PO4F	mg/L as P
Nitrogen:			
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	*Ammonium, Filtered	NH4F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Dissolved Organic Nitrogen	DON	mg/L as N
	Total Dissolved Nitrogen	TDN	mg/L as N
	Particulate Organic Nitrogen	PON	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA N	μg/L
	Pheophytin	PHEA	μg/L
Other Lab Parame	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	ey 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^{-1}

Notes:

- 1. Time is coded based on a 24:00 clock and is referenced to 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 no longer reports NO2 and NO3 separately.

11) Measured and Calculated Laboratory Parameters

The following parameters are reported in the 2020 nutrient dataset for GRB

a) Variables Measured Directly

Nitrogen species: NH4F, NO23F, TDN

Phosphorus species: PO4F

Other: TSS, CHLA N, PHEA, DOC, POC, PON

FECCOL, ECOLI, ENTERO

b) Computed Variables

DIN: NO23F + NH4F

DON: TDN - NH4F - N023F

GRB Reserve uses DON values provided by University of New Hampshire Water Quality Analytical Laboratory. We do not calculate DON using the Nutrient QAQC Excel macro.

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 2020. (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 Limits for CHLA N and PHEA were determined by GRB Reserve staff.

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

Parameter	Start Date	End Date	MDL	Revisited
CHLA_N	01/01/2020	12/31/2020	$0.33~\mu g/L$	11/19/2020
PHEA	01/01/2020	12/31/2020	0.46 μg/L	11/19/2020
NH4F	01/01/2020	12/31/2020	$0.005~\mathrm{mg/L}$	

NO23F	01/01/2020	12/31/2020	0.005 mg/L
PO4F	01/01/2020	12/31/2020	0.001 mg/L
TSS	01/01/2020	12/31/2020	1.0 mg/L
DOC	01/01/2020	12/31/2020	0.10 mg/L
POC	01/01/2020	12/31/2020	0.004 mg/L
PON	01/01/2020	12/31/2020	0.0024 mg/L
TDN	01/01/2020	12/31/2020	0.050 mg/L

13) Laboratory Methods

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

a) Parameter: NH4F

- Method Reference: 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 –20C 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 less 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 salinites (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 –20C until analyzed.

c) Parameter: PO4F

- i) Method Reference: 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 –20C until analysis.

d) Parameter: TDN

- i) Method Reference: 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 (O₃) producing Nitrogen Dioxide* (NO₂*) which is measured chemiluminescently.
- iii) <u>Preservation Method</u>: Sample is filtered through a 0.45 um disposable disk filter and stored at –20C 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.
- iii) <u>Preservation Method</u>: Sample is filtered through a 0.45 um disposable disk filter and stored at –20C 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 975C using an elemental analyzer. 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 to 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 60C.

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

g) Parameter: TSS

- i) Method Reference: 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 400C for 4 hours. Filters are weighed and stored in a dessicator until analysis. Sample water (280 ml) is vacuum filtered through the filters. Filters are placed in a drying oven at 60C for 24 hours. Filters are weighed again to determine TSS.

h) Parameters: CHLA and PHEA

- i) <u>Method Reference</u>: EPA Method 445.0. In Vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence.
- ii) Method Description: Sample water (64 ml) is vacuum filtered through a 25mm Whatman GF/C glass microfiber filter which is then 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 tube is mixed using a vortexer. The samples are frozen for 24 hours in the dark. Samples are brought to room temperature and then centrifuged for 5 minutes at 1500rpm. Three milliliters of sample are transferred to a culture tube and fluorescence is determined using a Turner Trilogy fluorometer. Two drops of 10% hydrochloric acid are added to the culture tube and the sample is run again in the fluorometer.
- iii) Method Preservation: The filter is stored in liquid nitrogen until further processing.

Jackson Estuarine Laboratory (Stephen Jones) was responsible for microbial analysis. Please contact the reserve for detailed methods.

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.

14) Field and Laboratory QAQC programs

a) Precision

- i. **Field Variability** GBNERR collects triplicate grab samples at a randomly selected station every month and also collects one set of triplicates per month during the diel sampling. This helps to determine water mass variability.
- ii. Laboratory Variability none
- iii. Inter-organizational splits none

b) Accuracy

- i. Sample Spikes blanks
- ii. Standard Reference Material Analysis see lab protocols
- iii. 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 OAOC
- 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 erro	rs
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
	11
Parameter (Comments
CAB	Algal bloom
CDR	Sample diluted and rerun
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample
Record con	nments
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 cov	ver
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)
Precipitat	ion
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 0.008 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 <-1> were generally lost as a result of our inability to access a station as a result of acute weather events or 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.

Remarks on (CSM) coded data:

Great Bay

05/11/2020 09:55 <0> (CSM)

The orthophosphate value was unusually high (0.069 mg/L). Field logs note that the two preceding days had 20-25 mph winds, with gusts up to 40 mph. This may have caused a lot of turbulence at this site which is in the middle of Great Bay.

12/07/2020 11:53 <0> (CSM)

The dissolved organic carbon value was unusually high (5.115 mg/L). Field logs note that in the days leading up to the collection there had been winds up to 40 mph. In addition, 36 hours previously, it had rained two inches and then snowed.

Lamprey River

05/31/2020 12:21 – 06/01/2020 13:06 [GSM]

 $06/15/2020\ 10:01 - 06/16/2020\ 10:50\ [GSM]$

 $07/16/2020\ 10:59 - 07/17/2020\ 11:48\ [GSM]$

At the beginning of the 2020 field season, our Hach Sigma autosampler broke. We were forced to borrow a Teledyne Isco 6712 autosampler from Wells National Estuarine Research Reserve for our first three deployments.

For the May deployment, we used an existing program in the sampler that collected water every two hours and fifteen minutes, for a total of 12 samples. We did not collect a triplicate at the beginning of the diel cycle as we typically do.

For the June and July deployments, we collected a triplicate at the beginning of the diel cycle and then collected water every two hours and fifteen minutes, for a total of 14 samples.

Starting on 09/13/2020, we returned to our standard collection interval.

12/03/2020 09:16 – 12/04/2020 10:00 <0> (CSM)

During this diel sampling, all dissolved organic carbon values were unusually high. Two to three days before this sampling, 2 inches of rain had fallen and there had been winds up to 30 mph.

12/07/2020 12:20 <0> (CSM)

The dissolved organic carbon value was unusually high (8.275 mg/L). Field logs note that in the days leading up to the collection there had been winds up to 40 mph. In addition, 36 hours previously, it had rained two inches and then snowed.

Oyster River

09/21/2020 09:07 <1> (CSM)

Total suspended solids (95.4 mg/L), particulate nitrogen (0.374 mg/L), particulate carbon (3.382 mg/L), chlorophyll-a (15.4 ug/L), and pheophytin (6.1 ug/L) values were unusually high. Sample was collected at dead low tide at a very shallow site. Staff waded into the water and may have disturbed the sediments during collection.

12/07/2020 11:35 < 0 > [GSM] (CIP)

Dissolved organic carbon (8.454 mg/L) and nitrate + nitrite as N (0.266 mg/L) values were unusually high. Field logs note that in the days leading up to the collection there had been winds up to 40 mph. Thirty-six hours previously, it had rained two inches and then snowed. In addition, this sample was collected at dead low and the water was very shallow and fresh. There was ice floating on the surface.

Squamscott River

12/07/2020 11:30-11:32 <0> (CSM)

The dissolved organic carbon values were unusually high (8.340, 9.251, 8.501 mg/L). Field logs note that in the days leading up to the collection, there had been winds up to 40 mph. In addition, 36 hours previously, it had rained two inches and then snowed.

Sample Holding Times Table

Site/Sample Type	Collection Date	PO4†	NH4†	NO3 + NO2†	POC/PON
GB, LR, OR, SQ grabs	5/11/2020	6/12/2020	6/22/2020*	7/2/2020*	6/18/2020
LR diel samples (Samples 1-11)	5/31 - 6/01/2020	6/17/2020	7/6/2020*	8/19/2020*	
LR diel sample (Sample 12)	5/31 - 6/01/2020	6/17/2020	7/6/2020*	2/23/2021*	
GB, LR, OR, SQ grabs	6/09/2020	8/19/2020*	7/6/2020	8/19/2020*	7/07/2020
LR diel samples	6/15 - 6/16/2020	8/19/2020*	7/6/2020	8/19/2020*	
GB, LR, OR, SQ grabs	7/07/2020	8/19/2020*	8/26/2020*	8/25/2020*	12/07/2020
LR diel samples	7/16 - 07/17/2020	8/19/2020*	8/26/2020*	8/19/2020*	
GB, LR, OR, SQ grabs	8/24/2020	9/28/2020*	9/25/2020	9/28/2020*	12/09/2020
LR diel samples	9/13 - 9/14/2020	10/05/2020	10/01/2020	11/18/2020*	
GB, LR, OR, SQ grabs	9/21/2020	10/05/2020	10/01/2020	11/18/2020*	12/18/2020
LR diel samples	9/24 - 9/25/2020	9/29/2020	9/29/2020	9/28/2020	
GB, LR, OR, SQ grabs	10/19/2020	11/05/2020	11/04/2020	11/18/2020	1/04/2021
LR diel samples	10/21 - 10/22/2020	12/2/2020*	12/2/2020*	12/4/2020*	
GB, LR, OR, SQ grabs	11/02/2020	12/02/2020	12/02/2020	12/04/2020	1/04/2021
LR diel samples	11/19 - 11/20/2020	12/02/2020	12/02/2020	12/10/2020	
LR diel samples	12/3 - 12/04/2020	12/21/2020	12/21/2020	12/22/2020	
GB, LR, OR, SQ grabs	12/07/2020	12/21/2020	12/21/2020	12/22/2020	1/06/2021

^{*}Sample held longer than allowed by NERR protocol. Samples flagged as suspect or rejected.

[†]Parameters with 28 day holding times

Chlorophyll Sample Holding Times Table

		Date Analyzed
Site/Sample Type	Collection Date	CHLA, PHEA
GB, LR, OR, SQ grabs	05/11/2020	05/15/2020
LR diel samples	05/31 - 06/01/2020	06/12/2020
GB, LR, OR, SQ grabs	06/09/2020	06/12/2020
LR diel samples	06/15 - 06/16/2020	07/22/2020*
GB, LR, OR, SQ grabs	07/07/2020	07/22/2020
LR diel samples	07/16 - 07/17/2020	07/22/2020
GB, LR, OR, SQ grabs	08/24/2020	09/23/2020
LR diel samples	09/13 - 09/14/2020	09/23/2020
GB, LR, OR, SQ grabs	09/21/2020	09/23/2020
LR diel samples	09/24 - 09/25/2020	10/22/2020
GB, LR, OR, SQ grabs	10/19/2020	10/22/2020
LR diel samples	10/21 - 10/22/2020	11/20/2020
GB, LR, OR, SQ grabs	11/02/2020	11/20/2020
LR diel samples	11/19 - 11/20/2020	12/11/2020
LR diel samples	12/3 - 12/04/2020	12/11/2020
GB, LR, OR, SQ grabs	12/07/2020	12/11/2020

^{*}Sample held longer than allowed by NERR protocol. Samples flagged as suspect or rejected.