



**National Estuarine
Research Reserve
System**

**Nutrient and Chlorophyll
Monitoring Program and
Database Design**

**Date Last Revised:
January, 2012**

Version 1.6



Prepared by
NOAA/NERRS Nutrient Monitoring Committee

I. General Introduction

The National Estuarine Research Reserve System (NERRS) conducts large-scale water quality monitoring for the purposes of increasing understanding of the nation's estuarine waters and contributing to effective coastal zone management. The NERRS System-Wide Monitoring Program (SWMP) tracks short-term variability and long-term changes in coastal ecosystems represented in the reserve system. The initial phase of the reserve's SWMP began in 1996. This phase focused on monitoring a suite of physical water quality and atmospheric information. As part of a recent enhancement to water quality monitoring, the reserve system began monitoring nutrients and chlorophyll levels in 2002. The current monitoring program for nutrients and chlorophyll consists of two separate but complimentary components; they are the monthly grab and the diel sampling programs. This document provides information and guidance for the NERRS nutrient and chlorophyll monitoring program and associated database design.

II. Sampling Protocols

2.1 Monthly Grab Samples: Basic Protocol

- Grab samples are to be taken monthly at the official SWMP long-term continuous monitoring stations (SWMP YSI deployment stations). Reserves interested in collecting grab samples at additional monitoring stations are encouraged to follow these same protocols. A grab sample is defined as a single sample taken at a specific location over a short period of time (typically seconds).

- Grab samples should be reflective of the water mass, as measured by the datasonde, at the long-term continuous monitoring stations. There are three sampling scenarios that can exist at a single, long-term monitoring station. These are:
 - ▶ First, at shallow and well-mixed stations, grab samples can be collected at either the near surface or at the depth of the deployed datasonde (depicted in diagram A, Figure 1).

 - ▶ Second, at stations where the datasonde is sampling either the upper or lower portion of a stratified water mass, grab samples are to be collected at the depth of the deployed datasonde (depicted in diagram B, Figure 1).

 - or

 - ▶ Third, at stations where the datasonde is sampling either the upper or lower portion of a stratified water mass, grab samples are to be collected above and below the thermo/chemocline (depicted in diagram C, Figure 1).

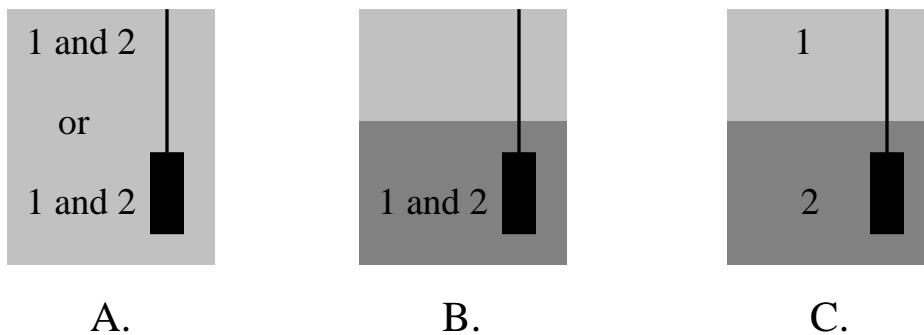
The two accepted methods for grab sample replication are:

► Replicate grab samples (a minimum of 2) may be collected at each long-term continuous monitoring station during each sampling period (denoted as 1 and 2 in Figure 1). Replicate samples are to be taken sequentially. That is, after sample 1 has been collected, sample 2 is collected following a short period of time (seconds or minutes) using the same collection procedure as for sample 1. *Note: If collecting the minimum number of samples, there would be no sample replication with scenario three.*

► Single grab samples may be substituted for replicates IF triplicate grab samples are collected at least every other month at one of the long-term monitoring stations. This station must be randomly chosen. *Note: If collecting the minimum number of samples, scenario three is not feasible with this method. Single grabs would have to be collected at both depths AND both depths must be included in the random triplicate rotation.*

- The method of sample collection (i.e., near surface grab, horizontal or vertical sampler) must be specified within individual reserve water quality sampling protocols and metadata.
- Grab samples at all official SWMP long-term continuous monitoring stations must be taken on the same day. If necessary due to logistical constraints, etc, they may be collected on consecutive days, but sampling days must be consecutive.
- Grab samples are to be taken at, or as near as possible, to slack low-tide conditions; between 3 hours before slack low-water and slack low-water. No distinction need be made between neap and spring tide conditions.
- Efforts should be made to collect samples at approximately monthly (30 day) intervals.
- It is recommended, but not mandatory, that grab samples be collected during periods that are not or minimally impacted by previous storm/precipitation events. As a guide, an antecedent dry period of 72 hours is desirable but may not be practical at all locations throughout the year.
- Clean, amber wide-mouth sample containers are recommended for sample collection. Sample containers are to be rinsed 3 times with ambient water prior to collection of the sample.
- Unless water quality analysis can begin in several hours, samples are to be properly stored (eg. placed on ice). All samples should be filtered immediately after collection or as soon as possible.
- At a minimum, samples are to be analyzed for dissolved inorganic nitrogen (NH_4^+ , NO_3^- , NO_2^-) and phosphorus (PO_4^-) analytes, and the plant pigment chlorophyll a. The NERRS considers these to be tier I analytes. If a reserve can show that NO_2^- is a minor component relative to NO_3^- , $\text{NO}_3^- + \text{NO}_2^-$ can be substituted for individual analysis. Other water quality analyses are encouraged and recommended parameters are presented in Section 4 of this document.

Figure 1. Basic monthly grab sampling scenarios.



2.2 Diel Samples: Basic Protocol

- Samples taken over a diel period are required to be collected monthly at at least one of the official SWMP long-term continuous monitoring stations (SWMP YSI deployment stations).
- The diel monitoring location may be moved to any of the official SWMP long-term stations, but must stay at its new location at least one year before it may be moved again. You must also notify the CDMO and Oversight Committee of your intended move.
- At least 11 samples are to be collected at equal time intervals over one full tidal cycle or 24 hours, whichever is greater, using an ISCO or similar programmable autosampler. Beginning and ending samples are to be collected at the approximate same phase of tide.
- There are two sampling designs that can exist, these are:
 - ▶ First, utilizing a floating platform, samples are to be collected within the photic zone or at a fixed depth of 0.5 meters from the surface.
 - or
 - ▶ Second, samples are to be collected at a fixed depth from the bottom and reflect the water mass sampled by the datasonde.
- No distinction need be made between neap and spring tide conditions.
- Efforts should be made to collect samples at approximately monthly (30 day) intervals.
- It is recommended, but not mandatory, that samples be collected during periods that are not or minimally impacted by previous storm/precipitation events. As a guide, an antecedent dry period of 72 hours is desirable but may not be practical at all locations throughout the year.

- Due to the use of autosamplers, ambient water rinses of the sample containers are not possible. However, autosampler tubing should be rinsed with ambient water prior to a sampling event.
- It is recommended that efforts be taken to decrease sample alteration during the diel sampling interval. This can be accomplished by providing on-site cold storage (refrigerated unit, ice, dry ice), collecting and placing samples in cold storage during some intermittent time period during the diel sampling event, and/or by adding a preservative to sample containers.
- At a minimum, samples are to be analyzed for dissolved inorganic nitrogen (NH_4^+ , NO_3^- , NO_2^-) and phosphorus (PO_4^-) analytes, and the plant pigment chlorophyll a. The NERRS considers these to be tier I analytes. If a reserve can show that NO_2^- is a minor component relative to NO_3^- , $\text{NO}_3^- + \text{NO}_2^-$ can be substituted for individual analysis. Other water quality analyses are encouraged and recommended parameters are presented in Section 4 of this document.

III. General Laboratory Practices and Analytical Procedures

3.1 Glassware and Sample Bottle Care

The following general guidelines are suggested for sample collection containers:

- Sample containers should have a large opening or mouth;
- Sample containers for light sensitive analytes should be amber or opaque;
- Sample containers should be made from hard glass or appropriate plastic that minimize leaching of analytes from the sample container to the water sample and absorption of analytes from the water sample to the container walls; and
- Sample container size (volume) should be sufficient for all analyses, which will be dependent upon laboratory analysis protocols and field conditions.

All sample containers should be cleaned following a standard laboratory protocol that at minimum would include washing with an appropriate detergent (example: Liqui-Nox® contains no phosphate compounds and minimizes formation of residue), acid-washing (i.e., 10% HCl) and multiple (3-6 times) rinsing with distilled-deionized water prior to field use.

3.2 Filters and Filter Treatments

Nutrients

Filtration of nutrient samples serves many purposes, these include:

- Minimizing microbial activity that can affect nutrient concentrations through uptake and release processes;
- Removing microbes that could lyse and thereby release nutrients during the analytical procedure;
- Removing particulates and associated attached nutrients; and
- Removing fine particulates that may cause turbidity interference with colorimetric procedures.

While no claim is made that filtration through a 0.45 µm pore diameter filter is a true separation of dissolved and suspended forms of an analyte, it is a generally accepted technique to make a gross separation between the two fractions. Use of a 0.45 µm membrane filters is recommended for all nutrient samples; recommended filters may include Gelman Supor or Millipore. Membrane filtration is desired for nutrient samples due to the greater likelihood of obtaining a more consistent separation of particle size. Laboratories with historic nutrient databases utilizing other filter types (specifically a glass fiber filter) and pore sizes (0.7-1.2 µm) may be exempt from this requirement. Increased filtration rates of hard to filter samples can be accomplished using a glass fiber prefilter (ex. Whatman type GF/C – 1.2 µm, Gelman type A/E – 1.0 µm) prior to using a 0.45 µm pore diameter membrane filter.

In some cases, such as minimizing filter phosphorus contributions to samples exhibiting low ortho-phosphate concentrations, it may be desirable to pre-rinse or wash membrane filters prior to use. Washing and rinsing procedures include (APHA 1998):

- Soaking 50 filters in 2 L of distilled-deionized water for 24 hours;
- Soaking 50 filters in 2 L of distilled-deionized water for one hour, change water and soak filters for an additional three hours; and
- Running several 100 ml portions (volume dependent of filter diameter size) of distilled-deionized water through filters prior to sample filtration.

Chlorophyll and Pheopigments

Benefits of glass fiber filters over membrane filters for chlorophyll analysis include:

- Assisting in the breaking down of cells during the grinding process;
- Allowing larger volumes of water to be filtered; and
- No precipitate forms after acidification as has been observed with some membrane filters.

Use of a 0.7 – 1.0 um glass-fiber is recommended for all chlorophyll a samples; recommended filters include Whatman type GF/F, or Gelman type A/E. Laboratories with historic chlorophyll databases utilizing other filter types and sizes (0.45-1.2 um) may be exempt from this requirement.

3.3 Sample Preservation

If samples are kept in long-term storage, appropriate preservation techniques must be utilized in order to reduce the effects of volatilization, adsorption and biodegradation. Preservation techniques vary depending on analytes of interest; examples of preservation techniques are presented in Table 1. It is recognized that adequate time, on the order of 5 days, must be allowed for reserves to collect, filter, preserve and ship samples to analytical laboratories. Furthermore, it is recognized that once received at a laboratory, samples may not receive immediate attention. However, in order to assure proper quality control, laboratories are required to complete all analysis within 10-14 days of receiving samples.

3.4 Laboratory Analytical Procedures

Analyte concentrations must be determined using standard or approved methods. All reserves are required to obtain a copy of the Standard Operating Procedures (SOP's) of the contracted laboratory performing water quality analysis. In addition, a copy of the laboratory's SOP must be on file with the NOAA/NERRS Central Data Management Office. For those reserves performing water quality analysis within their own laboratory, an SOP is required and must be developed if not currently available.

Table 1. Water sample preservation techniques by specific water quality parameters of interest.

Variable	Method	Duration	Notes
NH4F	Acidification and cold storage at 4 °C	28 days	
NO3F	Storage at -20 °C	2-3 days	
	Storage at 4 °C	24 hrs	
	Storage at -20 °C	2 weeks	
	Acidification and cold storage at 4 °C	28 days	NO ₃ ⁻ and NO ₂ ⁻ cannot be determined as individual species
NO2F	Freeze at -20 °C or store at 4 °C	1-2 days	
PO4F	Freeze at or below -10 °C		
CHLA	Filter is drawn dry, removed and stored in desiccator at -20 °C	30 days	

IV. Database Design

4.1 Expression of Results

Analyte Concentration Units

Following the International System of Units (SI), analyte concentrations are to be expressed as mg/L or ug/L. In order to assure consistency in reporting values, nutrients are to be expressed as mg/L and chlorophyll as ug/L. Table 2 provides units of expression for phosphorus, nitrogen, carbon, plant pigment, microbial and other parameters of interest. Due to the relatively low concentration of analytes observed in estuarine and coastal waters, nutrient concentrations are to be expressed, at a minimum, to the third decimal place. Chlorophyll a is to be expressed, at a minimum, to one decimal place. Method detection limits must be sufficient to meet this requirement. If a parameter of interest is not listed in Table 2, please contact the NOAA/NERRS Centralized Data Management Office (CDMO) so that a variable name and standard unit of measurement can be assigned.

Table 2. Parameter Titles and Variable Names by Data Category. If a parameter of interest is not listed in Table 2, contact the Centralized Data Management Office (CDMO) so that a variable name and standard unit of measurement can be assigned.

Data Category	Parameter	Variable	Calculation Method	Unit of Measurement
Phosphorus and Nitrogen	Orthophosphate, filtered	PO4F	Determined directly	mg/L as P
	Dissolved Organic Phosphorus	DOP	TDP – PO4F	mg/L as P
	Total Dissolved Phosphorus	TDP	Determined directly	mg/L as P
	Total Phosphorus	TP	Determined directly	mg/L as P
	Particulate Phosphorus	PHOSP	TP - TDP	mg/L as P
	Ammonium, filtered	NH4F	Determined directly	mg/L as N
	Nitrite, filtered	NO2F	Determined directly	mg/L as N
	Nitrate, filtered	NO3F	NO23F - NO2F or determined directly	mg/L as N
	Nitrite + Nitrate, filtered	NO23F	Determined directly	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	NO23F + NH4F or NO2F + NO3F + NH4F	mg/L as N
	Dissolved Organic Nitrogen	DON	TKNF – NH4F or TDN – NH4F – NO23F or TDN – NH4F – NO3F – NO2F or TDN – DIN	mg/L as N
	Total Dissolved Nitrogen	TDN	Determined directly or TKNF + NO23F or TKNF + NO2F + NO3F	mg/L as N
	Total Nitrogen	TN	Determined directly or TDN + PON or TKN + NO23F or TKN + NO2F + NO3F	mg/L as N
	Total Kjeldahl Nitrogen, Whole/Filtered	TKN, TKNF	Determined directly	mg/L as N
	Total Organic Nitrogen	TON	TKN – NH4F or TN – NH4F – NO23F or TN – NH4F – NO2F – NO3F	mg/L as N
Particulate Organic Nitrogen and Particulate Nitrogen	PON	Determined directly or TKN - TKNF	mg/L as N	
Particulate Nitrogen	PN	TN - TDN	mg/L as N	
Urea, filtered	UREA_F	Determined directly	mg/L as N	
Plant Pigments	Chlorophyll a	CHLA_N	Determined directly	µg/L
	Uncorrected Chlorophyll	UncCHLa_N	Determined directly	µg/L
	Phaeophytin	PHEA	Determined directly	µg/L

Data Category	Parameter	Variable	Calculation Method	Unit of Measurement
Carbon	Total Organic Carbon	TOC	Determined directly or DOC + POC	mg/L as C
	Dissolved Organic Carbon	DOC	Determined directly	mg/L as C
	Particulate Organic Carbon and Particulate Carbon	POC	Determined directly or TOC - DOC	mg/L as C
Other Lab Parameters	Silicate, Filtered	SiO4F	Determined directly	mg/L as SI
	Biogenic Silica	SiO2	Determined directly	mg/L as SI
	Sulfate	SO4	Determined directly	mg/L
	Chloride	Cl	Determined directly	mg/L
	Total Suspended Solids	TSS	Determined directly	mg/L
	Total Volatile Solids	TVS	TSS - TFS	mg/L
	Total Fixed Solids	TFS	Determined directly	mg/L
Microbial Parameters	Total Coliforms	TOTCOL	Determined directly	MPN/100ml
	Fecal Coliforms	FECCOL	Determined directly	MPN/100ml
	Escherichia coli	ECOLI	Determined directly	MPN/100ml
	Enterococcus Groups	ENTGRP	Determined directly	MPN/100ml
	Enterococcus faecalis	ENTFEC	Determined directly	MPN/100ml
Field Parameters	Water Temperature	WTEM_N	Determined directly	°C
	Specific Conductance	SCON_N	Determined directly	mS/cm
	Salinity	SALT_N	Determined directly	ppt
	Dissolved Oxygen	DO_N	Determined directly	mg/L
	% Dissolved Oxygen Saturation	DO_S_N	Determined directly	%
	pH	PH_N	Determined directly	SU
	Turbidity – Nephelometer Turbidity Units	TURB_N	Determined directly	NTU
	Water Color - Pt-Co Units	COLOR	Determined directly	PCU
	Total Water Depth	TDEP_N	Determined directly	meters
	Secchi Disk Depth	SECCHI	Determined directly	meters
	Incident Irradiance	IRR0_N	Determined directly	$\mu\text{mol}/\text{m}^2/\text{s}$
	Irradiance at depth 1	IRR1_N	Determined directly	$\mu\text{mol}/\text{m}^2/\text{s}$
	Irradiance at depth 2	IRR2_N	Determined directly	$\mu\text{mol}/\text{m}^2/\text{s}$
	Attenuation of Downwelling Irradiance	Kd_N	Calculated	meters^{-1}
	Air Temperature	ATEM_N	Determined directly	°C
Condition Descriptors (Field parameters available as record comments in the Nutrient QAQC macro)	Cloud Cover		Alphabetic code	See CDMO Manual
	Precipitation type		Alphabetic code	See CDMO Manual
	Tidal Stage		Alphabetic code	See CDMO Manual
	Wave Height		Alphanumeric code	See CDMO Manual
	Wind Direction		Alphabetic code	See CDMO Manual
	Wind Speed		Alphanumeric code	See CDMO Manual

Significant Figures

In order to avoid ambiguity in reporting results and to report only such figures that are justified by the accuracy of laboratory analysis, only significant figures are used in reporting nutrient, chlorophyll and other analyte concentration values. All digits in a reported value are expected to be known to a high degree of accuracy, except for the last digit, which may be in doubt. Such a value is said to contain only significant figures (APHA 1998).

Example: For the reported value of 0.136 mg/L, the laboratory analyst is certain of the 0.13 but may be uncertain as to whether the 6 should be a 5 or 7 because of the uncertainty in the analytical procedure.

In many instances it may be necessary to round off reported values. Rules for rounding off reported values are as follows (APHA 1998):

- Drop digits that are not significant.
- If 6, 7, 8, or 9 are dropped, increase preceding digit by one unit.
Example: 0.0156 becomes 0.016
- If 0, 1, 2, 3, or 4 are dropped, do not alter preceding digit.
Example: 0.0153 becomes 0.015
- If 5 is dropped, round off preceding digit to the nearest even number.
Example: 0.0155 becomes 0.016
Example: 0.0145 becomes 0.014

There are general operating rules for properly expressing calculated values to the correct number of significant figures. If a calculated value is the result of a subtraction or addition operation, the number with the fewest decimal places, not necessarily the fewest significant figures, establishes the number of significant figures that are justified.

Example: The reported value for DIN is 13.37 mg/L as N given an NO₂F concentration of 0.0072 m/L as N, a NO₃F concentration of 12.02 mg/L as N and a NH₄F concentration of 1.345 mg/L as N. Note: Round off all numbers so each has the same number of digits to the right of the decimal point prior to any addition or subtraction operations.

If a calculated value is the result of a multiplication or division operation, round off the calculated value to as few significant figures that are present in the factor with the fewest significant figures.

Example: The reported value for an analyte based on the following calculation, (2.762 ÷ 1.95), is not "1.41641" but "1.42" because "1.95" has only three significant figures.

A zero in a number may or not be significant, depending upon the manner in which it is used. When one or more zeros are used in locating a decimal point, they are not significant. For example, each of the following numbers has two significant figures: 0.063, 0.0063, and 0.00063. When zeros appear between digits in a number, they are significant. However, the quantity 1370

has four significant figures provided the accuracy of the measurement includes the zero as significant. If the digit 7 is estimated then the number has only three significant figures.

Variable Naming Convention

The water quality variable naming convention for the NERRS nutrient and chlorophyll database was developed to address a number of issues, these are:

- While this limitation only held true for initial database development, EQWIN database code names were limited to 8 spaces (this includes variable comment code names). New parameter additions are not constrained to 8 spaces;
- The variable name allows persons to easily differentiate between filtered and whole water samples;
- The variable name allows persons to easily differentiate and select discrete (grab samples) versus continuously monitored datasonde data; and
- Variable code names are designed to make sense and be consistent with other large monitoring programs where possible.

Water quality parameters, variable names, calculation formula if required, and units are presented in Table 2. Field parameters, such as water temperature, salinity, dissolved oxygen, air temperature, irradiance, etc., may provide additional information on environmental conditions at the time of sampling and are also provided in Table 2. Finally, Table 2 lists condition descriptors available as comment codes for insertion directly into the dataset. These descriptors include cloud cover, precipitation, tidal state, wave height, wind direction and wind speed. Existing codes for these descriptors are listed in Table 5. For more information on comment codes, see Section 4.4.

Examples:

TDN denotes Total Dissolved Nitrogen. Note: The term “dissolved” notifies the user that this sample has been filtered.

TN denotes Total Nitrogen. Note: The term “total” without “dissolved” notifies the user that this sample is a whole water sample – it has not been filtered.

NH4F denotes ammonium. Note: The letter “F” notifies the user that this sample has been filtered.

SALT_N denotes salinity. Note: The letter “N” notifies the user that this is a non-continuous measurement versus a datasonde continuously measured salinity value that is denoted by “SAL”.

F_SALT_N denotes the non-continuous salinity measurement flag column. Note: The letters “N” and “F” notify the user that this variable column contains QAQC flags and codes for non-continuously measured salinity values.

4.2 Required and Recommended Water Quality Parameters

Reserves are required to analyze for tier I parameters in both the monthly grab and diel sampling program. Tier I parameters include ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), orthophosphate (PO_4^-), and chlorophyll a. If a reserve can show that NO_2^- is a minor component relative to NO_3^- , $\text{NO}_3^- + \text{NO}_2^-$ can be substituted for individual analysis. If funds allow, additional samples can be collected to provide supplementary information on spatial (vertical and lateral) and temporal variations in nutrient and chlorophyll water quality, and/or the influence of storm-events and/or oceanic inputs. Reserves also have the option to run additional water analysis that may include tier II and other parameters. Recommended tier II parameters include silicate, particulate nitrogen and phosphorus, dissolved total nitrogen and phosphorus, particulate and dissolve carbon, and total suspended solids. Table 2 provides water quality parameters, variable names, calculation method and units of expression for phosphorus, nitrogen, plant pigment, carbon, microbial and other parameters of interest.

4.3 Laboratory Intercomparison Studies

In order to ensure that quality control measures are being performed and to determine the quality of analysis by the various laboratories, the NERRS quality assessment program includes an annual laboratory intercomparison study. Each reserve or participating laboratory is required to participate in this program.

Commercially available known standards for specified nutrient water quality parameters will be sent to participating laboratories during the funding year cycle. Standard concentrations should reflect ambient water quality conditions observed at respective reserves; this may require dilution of some commercially available standards.

4.4 Database Structure

Basic Excel Spreadsheet Structure

A partial representation of a Nutrient and Chlorophyll Monitoring Program excel spreadsheet is depicted in Table 3. The first four columns provide mandatory descriptor information for each sample. Column titles and brief descriptions are as follows:

- First column: Station code “three letter reserve code, two letter sampling site code, data type code” (ex. cbvginut)
- Second column: DateTimeStamp “month/date/year and military time format” (ex. 01/01/2004 14:30 for 2:30 pm on January 1st, 2004). Note: Data should follow chronological order. Exception occurs when the diel and monthly grab sample program overlap on specific dates.
- Third column: Monitoring Program - “1” denotes monthly grab monitoring program sample and “2” denotes monthly diel monitoring program sample.
- Fourth column: Rep - “1” denotes original sample, “2” denotes duplicate sample and “3” represents triplicate sample. S is used to denote a grab sample replicate that occurs at the same station, date, and time as a diel sample.

Table 3. Example Excel spreadsheet for NERRS nutrient and chlorophyll monitoring program.

Station Code	DateTimeStamp	Monitoring Program	Rep	F_Record	PO4F	F_PO4F	NH4F	F_NH4F	NO23F	F_NO23F	CHLA_N	F_CHLA_N
cbmipnut	1/4/2006 12:30	1	1		0.026		0.053		0.307		5.48	
cbmipnut	1/18/2006 14:45	1	1		0.031		0.063		0.362		3.36	
cbmipnut	1/18/2006 14:45	1	2		0.03		0.058		0.347		5.98	
cbmipnut	2/1/2006 10:15	1	1		0.019		0.055		0.502		4.86	
cbmipnut	2/14/2006 12:45	1	1		0.019		0.086		0.362		9.47	
cbmipnut	2/28/2006 10:45	1	1		0.025		0.039		0.369		2.09	
cbmipnut	2/28/2006 10:45	1	2		0.025		0.04		0.362		1.49	
cbmipnut	3/21/2006 14:15	1	1		0.259		0.018		0.097		2.39	
cbmipnut	3/21/2006 14:15	1	2		0.235	<1> (CUS)	0.025		0.102		1.49	
cbmipnut	4/4/2006 14:30	1	1		0.022	<1> (CUS)	0.222		0.665		18.69	
cbmipnut	4/18/2006 14:15	1	1		0.042	<1> (CUS)	0.052		0.181		2.99	
cbmipnut	4/18/2006 14:15	1	2		0.038	<1> (CUS)	0.051		0.192		1.79	
cbmipnut	5/2/2006 13:45	1	1		0.031	<1> (CUS)	0.097		0.433		2.62	
cbmipnut	5/16/2006 11:45	1	1		0.147	<1> (CUS)	0.123		0.552		1.99	
cbmipnut	5/30/2006 11:45	1	1		0.366	<1> (CUS)	0.186		0.942		2.62	
cbmipnut	5/30/2006 11:45	1	2		0.351	<1> (CUS)	0.233		0.903		1.87	
cbmipnut	6/13/2006 11:45	1	1		0.203	<1> (CUS)	0.087		0.521		12.96	
cbmipnut	6/29/2006 10:00	1	1		0.043	<1> (CUS)	0.099		0.185	<-2> (CHB)		
cbmipnut	6/29/2006 10:00	1	2		0.048	<1> (CUS)	0.094		0.181		3.74	
cbmipnut	7/11/2006 11:15	1	1		0.031	<1> (CUS)	0.055		0.296		2.99	
cbmipnut	7/27/2006 10:30	1	1		0.471	<1> (CUS)	0.041		0.723	<-2> (CHB)		
cbmipnut	7/27/2006 10:30	1	2		0.471		0.048		0.688	<-2> (CHB)		
cbmipnut	8/11/2006 11:45	1	1		0.431		0.052		1.11		5.48	
cbmipnut	8/22/2006 8:45	1	1		0.584		0.045		0.447		3.36	
cbmipnut	8/22/2006 8:45	1	2		0.594		0.036		0.459	<-2> (CHB)		
cbmipnut	9/5/2006 8:00	1	1		0.052		0.036		0.251		6.73	
cbmipnut	9/19/2006 9:00	1	1		0.073		0.028		0.372		3.49	
cbmipnut	9/19/2006 9:00	1	2		0.084		0.021		0.364		1.49	
cbmipnut	10/3/2006 10:30	1	1		0.107		0.053		0.35		1.49	
cbmipnut	10/17/2006 8:15	1	1		0.112		0.032		0.232	<-2> (CHB)		
cbmipnut	10/30/2006 14:45	1	1		0.071		0.016		0.18		2.24	
cbmipnut	10/30/2006 14:45	1	2		0.068		0.019		0.18		2.24	

The record flag column (F_Record) is the fifth column and is followed by the variable value and variable flag columns. Variable flag columns follow each variable value column and are denoted by the variable name preceded by an underscore and “F” (ex. F_NH4F). They contain QAQC flags and codes pertinent to that specific sample. The record flag column contains QAQC codes pertinent to the entire sample record. Variable order within the spreadsheet should follow the order of listing in Table 2. There is no need to include a variable’s flag and value column when no analysis for that specific variable was conducted on samples within the database.

QAQC flags and codes are inserted directly into the data file with the CDMO’s NutrientQAQC macro and provide important information that is directly linked to a specific water quality measurement or an entire sample record. QAQC flags and comment codes effectively provide metadata within the data file, thereby reducing metadata reporting requirements. QAQC codes also allow for documentation of environmental conditions observed during sample collection. QAQC flags and codes available for nutrient data are presented in Tables 4 and 5. If a desired code is not listed in Table 5, please contact NOAA/NERRS Centralized Data Management Office (CDMO). If the majority of Reserves are in agreement, a new variable comment code can be assigned.

Table 4. QAQC flags available for use with the nutrient data. Only one flag may be used at a time.

-4	Out of sensor range low data: used during secondary QAQC to indicate a result that is below the minimum detection limit.
-3	Rejected data: Used during secondary QAQC to indicate a rejected value.
-2	Missing data: Used during secondary QAQC where a value is missing (not collected).
-1	Optional SWMP supported parameter: Used to indicate optional data that were not collected.
0	Good data: Used during secondary QAQC on all remaining data.
1	Suspect data: Used during secondary QAQC to indicate a suspect value.
4	Historical: Pre-automated QAQC: Used to indicate data that were submitted to the CDMO prior to the use of the automated primary QAQC system. This flag is only in data that are exported from the CDMO ODIS.
5	Corrected data: Used during secondary QAQC to indicate a value that has been corrected or changed

Table 5. QAQC codes available for use with the nutrient data. One general or sensor error code and one comment code may be applied to each variable value. An unlimited number of record codes may be applied to the entire record.

General errors: Used to document general problems with the sample or sample collection. Cannot be used in combination with a sensor error code.	
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
Sensor errors: Used to document common sensor or parameter specific problems. Cannot be used in combination with a general error code.	
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
Comments: There are two different types of comment codes available for use with the nutrient data	
Parameter or Record Comments: Parameter comments can be used alone or in combination with a general error or sensor error code to further document conditions or a problem with the data. Record comments may be applied to a specific parameter or the entire record by placement in the record flag column (F_Record).	
CAB	algal bloom
CDR	sample diluted and rerun (parameter comment only)
CHB	sample held beyond specified holding time
CIF	Flotsam present in sample vicinity
CIP	ice 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: Can only be applied to entire records in the record flag column to describe conditions during sample collection. These comments are not used in conjunction with flags and an “unlimited” number of comment codes can be applied to the same record.	
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

Reporting of Missing Data, Deleted Data, Calculated Values Less than Zero, Concentrations Lower than Method Detection Limits and Other Comment Codes

- Missing data are denoted by a blank cell “ ” and flagged with a “-2”.
- Rejected data are comment coded with a “-3” and remain in the data file. **No data values are to be removed from the dataset under any conditions** except for the removal of any -9999 values or symbols that may have replaced below MDL values or invalid calculated values.
- Analyte values below method detection limits are reported as the minimum detection limit itself and are flagged -4 (out of sensor range low) and coded with “SBL”.
- If any of the components used to calculate a value are below the MDL, the calculated variable is removed, flagged with a -4, and coded with a “SCB”.

4.5 Metadata Structure

1) Principal investigator(s) and contact persons

- Reserve, Laboratory and other

2) Research objectives

- Monthly Grab
- Diel Sampling Program

3) Research methods

- Monthly Grab Sample Program
- Diel Sampling Program

4) Site location and character

a) Goodwin Islands (37° 13' 07.63" N, 76° 23' 43.85" W)

The Goodwin Islands component of the CBNERRVA is located on the southern side of the mouth of the York River. The Goodwin Islands are a 315 ha (777 acre) archipelago of salt-marsh islands surrounded by inter-tidal flats,

b) York River Bridge (37° 14' 41.60" N, 76° 30' 18.80" W).

The Coleman Bridge station is located in the mid-channel approximately 9 km from the mouth of the York River estuary between Gloucester Point and Yorktown, Virginia. The sampling station is located within the polyhaline region with a mean depth of 21 meters and a tidal range

5) Coded variable definitions

Station Code Names

Goodwin Island (cbvginut), Coleman Bridge (cbvybnut), Catlett Islands (cbvcinut), Clay Bank (cbvcbnut), Taskinas Creek (cbvtcnut), and Sweet Hall Marsh (cbvshnut)

Monitoring Programs

Monthly grab sample program (1), Diel grab sample program (2)

6) Data collection period

• Monthly Grab Sampling

Site	Start Date	Start Time (or rep 1)	End Time (optional - or rep 2))
GI	1/16/11	16:40	
GI	2/14/11	12:50	
.....	
SH	12/22/11	13:25	

• Diel Sampling

Site	Start Date	Start Time	End Date	End Time
TC	1/16/11	14:00	1/17/11	15:00
TC	2/14/11	9:00	2/15/11	10:00
.....		
TC	12/22/11	13:30	12/23/11	14:30

Note: Time is coded based on a 2400 hour clock and is referenced to Eastern Standard Time (EST).

7) Associated researchers and projects

As part of the System Wide Monitoring Program (SWMP), the CBNERR also collects water quality (i.e., nutrients and water parameters using YSI 6600 EDS datasondes) and weather data. All SWMP data is available for download through the Centralized Data Management Office (CDMO), <http://cdmo.baruch.sc.edu/>.

Additional water quality monitoring programs within the York River system include:

- a) USEPA Chesapeake Bay Mainstem and Tributary Monitoring Program. Since 1984, biweekly to monthly water quality sampling at a series of sites located along
- b) VIMS Shoal Survey. Since 1984, biweekly to monthly water quality sampling at a series of sites located along the shoal areas of the lower York River estuary

8) Distribution

NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited.....

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.

10) Parameter Titles and Variable Names by Data Category

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus:	Total Dissolved Phosphorus	TDP	mg/L as P
	Orthophosphate, Filtered	PO4F	mg/L as P
	Dissolved Organic Phosphorus	DOP	mg/L as P
Nitrogen:	Total Dissolved Nitrogen	TDN	mg/L as N
	Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Nitrite, Filtered	NO2F	mg/L as N
	Nitrate, Filtered	NO3F	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
Other Lab Parameters:			
	Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
Field Parameters:			
	Dissolved Oxygen	DO_N	mg/L
	%Dissolved Oxygen Saturation	DO_S_N	%
	Salinity	SALT_N	ppt
	Water Temperature	WTEM_N	°C

11) Measured and Calculated Laboratory Parameters

a) Variables Measured Directly	
Nitrogen species:	NO2F, NO23F, NH4F, TDN
Phosphorus species:	TDP, PO4F
Other:	CHLA_N, PHEA
b) Computed Variables	
NO3:	NO23F-NO2F
DIN:	NO23F+NH4F
DON:	TDN-DIN
DOP:	TDP-PO4F

12) Limits of Detection

Parameter	Variable	Method Detection Limit	Dates in use
Ammonium	NH4F	0.0015 mg/L as N	2010
Nitrate + Nitrite	NO23F	0.0008 mg/L as N	2010

13) Laboratory Methods

Parameter: TDN

- i) Method Summary: The sample is autoclaved in the presence of alkaline potassium persulfate. Following digestion, the sample is then buffered and analyzed for nitrate. It should be noted that this is an adaption of D'Elia's method of 1977.
- ii) Method Reference(s):
 - D'Elia, C.F., P.A. Steudler, and N. Corwin. 1977. Determination of Total Nitrogen in Aqueous Samples using Persulfate Digestion. *Limnology and Oceanography* 22: 760-764.
 - EPA 600/R-97/072 Method 353.4. Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. In: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio 45268.
- iii) Preservation Method: Samples are immediately filtered with a 0.45 µm membrane filter upon return to the laboratory from the field and stored at -20 °C until analysis. Maximum holding time is 28 days.

14) Field and Laboratory QAQC programs

- a) Precision
 - i) Field Variability. CBNERRVA collects two successive grab samples for the monthly grab sample program.
 - ii) Laboratory Variability. The VIMS Analytical Service Center for Nutrients analyzes a laboratory duplicate once for every ten samples.
 - iii) Inter-organizational splits. None
- b) Accuracy
 - i) Sample Spikes. The VIMS Analytical Service Center for Nutrients analyzes a matrix spike once for every ten samples.
 - ii) Standard Reference Material Analysis. None
 - iii) Cross Calibration Exercises. None

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 sensor range low
- 3 Data Rejected due to QAQC
- 2.....

16) QAQC Code Definitions

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

General errors

GCM calculated value could not be determined due to missing data

GCR.....

17) Other Remarks/Notes

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of NO₂F 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.