

Reserve Name: Jobos Bay (JOB) NERR Nutrient Metadata
Months and year the documentation covers: January-December 2011
Latest Update: May 12, 2016

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons

a) Reserve Contact

Jobos Bay National Estuarine Research Reserve
PO Box 159
Salinas, PR 00704-0159
Ph. 787-853-4617
Fx. 787-853-4618

Angel Dieppa, Research Coordinator
Ph. 787-853-4617, ext. 1004
Email. adieppa@gmail.com, adieppa@drna.gobierno.pr

Sebastian Garcia
Ph. 787-717-1355
Email. sgarcia076@gmail.com

Enid Malavé, Chemist
Ph. 787-853-4617, ext. 1005
Email. emalave1@gmail.com, emalave@jbnerr.org

b) Laboratory Contact

Carol Pollard
Laboratory Manager
Virginia Institute of Marine Science
PO Box 1346
Gloucester Point, VA 23062
Email. jlopez@vims.edu
Ph: 804-684-7213
Fx: 804-684-7614

2) Research objectives

The main objective of this monitoring program is to understand the nutrients dynamics within the bay that may come from the watershed affecting the health of the estuary. Inorganic nutrients, particularly nitrogen and phosphorus are naturally found in mangrove and estuarine habitats. They can be significantly increased by human activities reaching the system through non-point source run-off or direct discharge. Eutrophication is defined as gradual accumulation of nutrients and organic biomass accompanied with an increase in photosynthesis and a decrease in the average deep of the water column caused by the accumulation of sediment.

a) Monthly grab sampling program

The objective of this study is to provide baseline information on inorganic nutrients and chlorophyll levels in the Jobos Bay estuary. It will also assess nutrients and chlorophyll levels in areas within the reserve that may be receiving impact from human activities from surroundings areas or may act as a habitat gradient in the Bay. In order to compare these with physical (abiotic) water quality parameters, monitoring sites were established at the four YSI's data-sonde stations.

b) Diel sampling program

The diel sampling program objective is to quantify the temporal variability of important nutrients and sediment loading in the water column as a function of tidal forcing.

See the Site Location and Character section for more information on the chosen sample sites.

3) Research methods

a) Monthly Grab Sampling Program

Monthly grab samples are taken at the four data-sonde stations. Grab samples are taken on the same day at or as near as possible to slack low-tide conditions. Efforts are made to collect samples at approximately monthly intervals. Samples are not influenced by previous storm events. Grab samples are reflective of the water mass sampled by the data-sonde. Because we have shallow and well-mixed water on our stations, two surface grab samples are collected that are reflective of the data-sonde sampling area. Replicate (N=2) samples were collected by hand at an approximate depth of 30 cm.

Grab samples are taken in duplicate (two separate samples collected in different bottles); this will result in a total of eight samples. All samples were collected in amber, Nalgene™ sample bottles that were previously acid washed (10%) rinsed (3x) with distilled-deionized water, dried and followed by rinsing (3x) of ambient water prior to collection of the sample. Samples were immediately placed on ice, in the dark and returned to the laboratory. All samples are filtered immediately after collection using a vacuum pump. Membrane filters are used for nutrient samples and GF/F are used for Chlorophyll samples. All samples were immediately placed on ice again, in the dark and sent to Virginia Institute of Marine Sciences (VIMS) laboratory next day shipment. Field parameter data (water temperature, specific conductivity, salinity, dissolved oxygen, pH and turbidity) readings were also taken at the time of grab sample collection and are available by contacting the Reserve directly.

b) Diel Sampling Program

Diel samples are taken in long-term data-sonde station 9. Twelve samples are collected at 2 hour intervals using an ISCO auto-sampler model 6712. Suction line is set to sample at 0.5 meters, and is covered with a mesh to avoid clogging with organic debris. Efforts are made to collect samples at approximately monthly (30 days) interval. Samples are not influenced by previous storm events; an antecedent dry period of 72 hours is desirable but may not be practical at all locations throughout the year. Sampling depth follows the following designs; samples are

collected at a fixed depth from the bottom, generally 0.5 meters, and reflect the water mass sampled by the data-sonde. This device automatically samples 1000 ml of water every 2 hrs. A field blank consists of DI water placed in the bottle rack and left open during the diel sampling. All samples are pumped into polyethylene sample bottles that were previously acid washed (10%), rinsed (3x) with distilled-deionized water and dried. At the end of the 24 hr period, the 12 samples are kept in the dark and returned to the laboratory for immediate processing. All samples are filtered immediately after collection. Nutrient filtered samples are placed in 250 ml Nalgene bottles and Chl-a filters in amber (empty) vials, stored in a cooler (dark) on ice packs and sent to Virginia Institute of Marine Sciences (VIMS) laboratory.

4) Site location and character

The Jobos Bay National Estuarine Research Reserve (JBNERR) is located on the southern coastal plain of the island of Puerto Rico, a reserve within the West Indies geographical area. JBNERR is composed of two major areas: (1) Mar Negro, located on the western margin of the Bay, and (2) Cayos Caribe (a chain of 17 tear-shaped islets located to the southeast) and Cayos Barca (a chain of 7 tear-shaped islets located to the southwest boundaries) both with a back-reef system. The Mar Negro area comprises the bulk of the Reserve, and consists of mangrove forests and a complex system of lagoons and channels interspersed with salt and mud flats. Coral reefs and sea grass beds, with small beach deposits and upland areas fringe Cayos Caribe and Cayos Barca mangrove islands.

Station number nine (9), was chosen as the impacted site due to its vicinity to agricultural lands at the north, collects water quality data in a site associated with runoff from littoral and basin mangrove areas. This lagoon has an average depth of 1.5 meters and water regime is subject to high concentrations of tannin pigments associated to red mangroves. Station is characterized by a low water exchange due to a low circulation pattern. The tidal range varies from 12 to 18 inches in the vicinity of the monitoring station. The salinity at the vicinity of the monitoring station varies from 30 ppt to 42 ppt. Fresh water input consists of rain water, runoff and groundwater flux, that source of water has not been quantitatively determined. This sampling station is located in the most inland lagoon northeast of Mar Negro, closest to the Thermoelectric Power Plant. It is subjected to runoff and agrochemicals from agricultural activities within the northern boundary of the Reserve. Information compiled from historical environmental documents, indicate that station nine (9) was used as a disposal site for residues of the previously operating sugar mill operation, and therefore might have high organic input into the sediments. From all four water quality monitoring station, this has the lowest dissolved oxygen values during the year. A thick layer of fine sediments with a high content of organic material covers the bottom. Benthic vegetation is scarce with few brown and green algae present at this site, but is dominated by nitrogen fixing cyanobacteria *Microcoleus lyngbyaceus*.

The station 9 platform was located at 17°56'34.87"N and 66°14'18.64"W until 09/02/2010 12:00PM, then it was relocated to 17° 56' 35.0" N and 66° 14' 18.9" W approximately 65.0 meters from original position. The relocation was due to sedimentation issues and the construction of a new telemetry station. This station has been subject of several studies indicating the presence of relatively high level of copper and pesticides compared to other stations.

Station number ten (10), located in a mangrove lagoon area towards the southwestern section of Mar Negro is considered the reference or non-impacted site. Station is characterized by a low water exchange due to a low circulation pattern. The tidal range varies from 12 to 18 inches. The salinity at the vicinity of the monitoring station varies from 0.0 ppt to 41.7 ppt. Fresh water input consists of rain water, limited runoff and groundwater flux, the amount of water has not been determined. This lagoon has an average depth of 1.5 meters and water regime is subject to high concentrations of tannin pigments associated to red mangroves. The bottom is covered with a layer of fine sediments with organic material, followed by a layer of calcareous material mainly from shells and oysters. Benthic vegetation is scarce but we can find sea grasses (*Thalassia testudinum* and *Halophila decipiens*), calcareous green algae (*Halimeda sp.*), green algae (*Caulerpa sp.*, *Udotea sp.*) and brown algae (*Dictyota sp.*) among others. The station is located at 17° 56' 19.00"N, 66° 15' 27.85"W.

Station number nineteen (19) is located in main bay of Jobos Bay. It is surrounded by sea grass beds dominated by *Thalassia testudinum* but may find *Syringodium filiforme*, *Halodule wrightii* and *Halophila decipiens*. Typical macroalgal assembles consist of calcareous green algae (*Halimeda sp.*), green algae (*Caulerpa sp.*, *Udotea sp.* and others) and brown algae (*Dictyota sp.*) among others. Bottom sediments are silt to muddy with some influence from mangrove islands to the west. This station is close to the Power Plant navigation channel, used by barges to bring oil and gas into the Power Plant pier. This area is exposed to barge standings and sediment re-suspension. Oil spills are always a threat. The tidal range varies from 12 in. to 18 in. in the vicinity of the monitoring station. Average depth is 1.5 meters. Fresh water input in the vicinity of the station may come from rain events and groundwater but the amount has not been determined. The salinity at the vicinity of the monitoring station range 34-36 ppt. Station is located at 17° 56' 34.49"N, 66° 13' 43.77"W.

Station number twenty (20) is located adjacent to Cayos Caribe reef system. The sonde is deployed over seagrass beds dominated by *Thalassia testudinum* and bottom sediments are silt to muddy with some influence from mangrove islands to the south. Water streams coming from the reef platform may bring to this station an indication of water conditions behind the coral reef platform. These waters are part of the main marine current coming from the eastern side of Jobos Bay that runs along the coast, getting in contact with sensitive areas like agricultural fields, a coal power plant, an oil refinery Phillips Core (shut down in 2005) and other industries. The tidal range varies from 12 in. to 18 in. in the vicinity of the monitoring station. Average depth is 2 meters. Fresh water input in the vicinity of the station comes by runoff from Punta Pozuelo peninsula in Guayama and from rain events. The salinity at the vicinity of the monitoring station range 34-36 ppt. Station is located at 17° 55' 49.14"N, 66° 12' 41.30"W.

5) Code variable definitions –

Station Code Names:

job09nut – Jobos Bay Station 9 nutrient data

job10nut – Jobos Bay Station 10 nutrient data

job19nut – Jobos Bay Station 19 nutrient data
 job20nut – Jobos Bay Station 20 nutrient data

Monitoring Programs:

Monthly grab sample program (1)

Diel grab sample program (2)

6) Data collection period –

Diel:

Site	Start Date/ Time	Stop Date/ Time
9	1/18/2011 10:00	1/19/2011 8:00
9	2/15/2011 10:00	2/16/2011 8:00
9	3/15/2011 10:00	3/16/2011 8:00
9	4/12/2011 10:00	4/13/2011 8:00
9	5/18/2011 10:00	5/19/2011 8:00
9	6/15/2011 11:30	6/16/2011 9:30
9	7/13/2011 10:00	7/14/2011 8:00
9	8/16/2011 10:00	8/17/2011 8:00
9	9/12/2011 10:00	9/13/2011 8:00
9	10/17/2011 10:00	10/18/2011 8:00
9	11/21/2011 10:00	11/22/2011 8:00
9	12/12/2011 10:00	12/13/2011 8:00

Grab:

Site	Start Date/ Time	Stop Date/ Time
9	1/19/2011 10:19	1/19/2011 10:20
9	2/15/2011 9:50	2/15/2011 9:51
9	3/16/2011 9:50	3/16/2011 9:51
9	4/13/2011 9:50	4/13/2011 9:51
9	5/19/2011 9:48	5/19/2011 9:49
9	6/16/2011 10:52	6/16/2011 10:53
9	7/14/2011 9:40	7/14/2011 9:41
9	8/16/2011 9:25	8/16/2011 9:26
9	9/13/2011 9:51	9/13/2011 9:52
9	10/18/2011 10:05	10/18/2011 10:06
9	11/22/2011 10:05	11/22/2011 10:06
9	12/13/2011 10:05	12/13/2011 10:06

Site	Start Date/ Time	Stop Date/ Time
19	1/19/2011 10:42	1/19/2011 10:43
19	2/15/2011 9:15	2/15/2011 9:16
19	3/16/2011 9:15	3/16/2011 9:16
19	4/13/2011 9:15	4/13/2011 9:16
19	5/19/2011 11:50	5/19/2011 11:51
19	6/16/2011 11:25	6/16/2011 11:26
19	7/14/2011 9:06	7/14/2011 9:07
19	8/16/2011 10:06	8/16/2011 10:07
19	9/13/2011 8:49	9/13/2011 8:50
19	10/18/2011 9:12	10/18/2011 9:13
19	11/22/2011 9:12	11/22/2011 9:13
19	12/13/2011 9:12	12/13/2011 9:13

**Grab
(CONT):**

Site	Start Date/ Time	Stop Date/ Time
10	1/19/2011 9:39	1/19/2011 9:40
10	2/15/2011 10:20	2/15/2011 10:21
10	3/16/2011 10:20	3/16/2011 10:21
10	4/13/2011 10:20	4/13/2011 10:21
10	5/19/2011 10:09	5/19/2011 10:10
10	6/16/2011 11:10	6/16/2011 11:11
10	7/14/2011 10:25	7/14/2011 10:26
10	8/16/2011 9:45	8/16/2011 9:46
10	9/13/2011 9:17	9/13/2011 9:18
10	10/18/2011 9:43	10/18/2011 9:44
10	11/22/2011 9:43	11/22/2011 9:44
10	12/13/2011 9:43	12/13/2011 9:44

Site	Start Date/ Time	Stop Date/ Time
20	1/19/2011 9:51	1/19/2011 9:52
20	2/15/2011 10:35	2/15/2011 10:36
20	3/16/2011 10:35	3/16/2011 10:36
20	4/13/2011 10:35	4/13/2011 10:36
20	5/19/2011 10:38	5/19/2011 10:39
20	6/16/2011 10:27	6/16/2011 10:28
20	7/14/2011 8:51	7/14/2011 8:52
20	8/16/2011 10:28	8/16/2011 10:29
20	9/13/2011 8:32	9/13/2011 8:33
20	10/18/2011 10:28	10/18/2011 10:29
20	11/22/2011 10:28	11/22/2011 10:29
20	12/13/2011 10:28	12/13/2011 10:29

7) Associated researchers and projects

As part of the SWMP long-term monitoring program, JB NERR also monitors Meteorological and Water Quality data which may be correlated with this Nutrient dataset. These data are available online at <http://cdmo.baruch.sc.edu/>.

The JBNERR water quality monitoring data has been incorporated into the Puerto Rico Environmental Quality Board (EQB) Integrated Report 303(d)/305(b) of the Federal Clean Water Act. This document consists of a water quality inventory and list of impaired waters and it's used by the Environmental Protection Agency (EPA) to inform Congress of the progress made at the national level towards the achievement of the statutory water quality goals and purposes established by the Federal Clean Water Act. SWMP data has been incorporated in the Conservation Effects Assessment Project (CEAP), a collaborative study of USDA, NOAA and JBNERR that pretends to implement best management practices in agricultural lands to improve water quality within the aquifer and Jobos Bay. Also, the Caribbean Regional Association for the Caribbean Regional Integrated Coastal Ocean Observing System (CaRICOOS) integrated and monitors Real Time data from our SWMP stations.

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:

National Estuarine Research Reserve System (NERRS). 2012. System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; *accessed* 12 October 2012.

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

Samples are pre-processed at JBNERR laboratory. This consists of filtration of samples and storing in a cooler with ice-packs for overnight delivery to VIMS. Analysis results were sent from the VIMS Laboratory in digital and hardcopy format.

Files consisted of sampling station ID, date, replicate number, and parameter values expressed in unit concentrations. Nutrients results are reported by VIMS in mg/L and pigments in ug/L. The CDMO rounding macro is applied to the data after unit conversion calculations. Data are double-checked to insure correct data transfer.

Data is reported with the number of decimal places that conserves the laboratory number of significant figures, i.e., four decimal places for all nutrients and two decimals for CHLA, PHEA.

Sebastian Garcia (SWMP technician) entered and double-checked 2011 sampling dates, locations, times, field parameters, and replicates from the original field data sheets provided by SWMP technician, Enid Malave. Missing data are verified through inspection of field logs, inserted into the data files, and denoted by a blank space. VIMS laboratory reports any value below the MDL as the <MDL value, ie. <0.0002 for NO₂. When entering those values below the method detection limit (MDL) are left in blank. The same convention is used for the NERRS system. All data is processed by CDMO Nutrient QAQC Excel macro described below.

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 category

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:	*Orthophosphate	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L

Notes:

1. Time is coded based on a 2400 clock and is referenced to Standard Time.
2. Reserves have the option of measuring either NO2 and NO3 or they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3.

11) Measured or calculated laboratory parameters

a) Parameters measured directly

Nitrogen species: NH4F, NO2F, NO23F
 Phosphorus species: PO4F
 Other: CHLA, PHEA

b) Calculated parameters

NO3F NO23F-NO2F
 DIN NO23F+NH4F

12) Limits of detection

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, has been established by the VIMS Nutrient Analytical Laboratory. The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. These values are reviewed and revised periodically.

Parameter	Start Date	End Date	MDL
PO4F	1/18/11	12/13/11	0.0015 mg/L
NH4F	1/18/11	12/13/11	0.0054 mg/L

NO2F	1/18/11	12/13/11	0.0002 mg/L
NO23F	1/18/11	12/13/11	0.0010 mg/L
CHLA_N	01/18/11	11/22/11	0.10 ug/L
CHLA_N	12/12/11	12/13/11	0.50 ug/L
PHEA	01/18/11	11/22/11	0.10 ug/L
PHEA	12/12/11	12/13/11	0.50 ug/L

13) Laboratory methods

i) Parameter: NH₄F

VIMS Laboratory Method:

EPA or other Reference Method:

Method Reference: US.EPA 1974. Methods for Chemical Analysis of Water and Wastes pp.168-174

Method Descriptor: Samples were filtered with a 0.45 µm membrane filter.

Preservation Method: Samples are stored at 4°C up to 24 hours, followed by freezing @ 20°C.

Summary of Method:

Automated Continuous flow, segmented stream, no bubble gating. Dual wavelength detection and matrix correction.

Chemistry:

Alkaline phenol and hypo chlorite react with ammonia to form indophenols blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.

Reaction is heat catalyzed at 37°C. The range is 0.001-2.0 mg/L.

Interferences:

Alkalinity over 500mg/L

Acidity over 100 mg/L

Ca and Mg ions will precipitate unless complexed

Color intensity is pH dependent

ii) Parameter: NO₂F

VIMS Laboratory Method:

EPA or other Reference Method: 353.4

Method Reference: US.EPA 1994. USEPA 600/R-97/072. Method 353.4

Method Descriptor: Samples were filtered with a 0.45 µm membrane filter.

Preservation Method: Samples are stored at 4°C up to 24 hours, followed by freezing @ 20°C.

Summary of Method:

Automated continuous flow, segmented stream, no bubble gating. Dual wavelength detection and matrix correction.

Chemistry:

An adaptation of the diazotization method. Under acidic conditions, nitrite ion reacts with sulfanilamide to yield a diazole compound, which couples with N-1 naphthylenediamine dihydrochloride to form a soluble dye, which is measured colorimetrically. The range is 0.001 to 0.050 mg/L.

Interferences:

NCl₃ false positive

These metal ions cause precipitation at high concentrations:

Sb +3, Au +3, Bi +3, Fe +3, Pb +2, Hg +2, Ag +, PtCl₆-2, VO₃-2

Cupric ion may catalyze decomposition of diazole compound.

iii) Parameter: NO₃ F

VIMS Laboratory Method:

EPA or other Reference Method: 353.4

Method Reference: US.EPA 1994. USEPA 600/R-97/072. Method 353.4

Method Descriptor: Samples were filtered with a 0.45 µm membrane filter.

Preservation Method: Samples are stored at 4°C up to 24 hours, followed by freezing @ -20°C.

Summary of Method:

Automated continuous flow, segmented stream, no bubble gating. Dual wavelength detection and matrix correction.

Chemistry:

Nitrate is reduced to nitrite by a copper/cadmium reductor column. The nitrite ion then reacts with sulfanilamide to form diazole compound. This compound then couples with n-1-naphthylenediamine dihydrochloride to form a reddish/purple azo dye. The color development chemistry is the same as that used in nitrite, Method #5. Range is 0-1.2 mg/L.

Interferences:

High concentrations of Fe, Cu (>10 mg/L)

Oil and Grease will coat Cd column

Residual Chlorine oxidizes Cd column

Sulfates will consume Cd column in the formation of S -2

iv) Parameter: PO₄ F

VIMS Laboratory Method:

EPA or other Reference Method: 365.5

Method Reference: US.EPA 1994. USEPA 600/R-97/072. Method 365.5

Method Descriptor: Samples were filtered with a 0.45 µm membrane filter.

Preservation Method: Samples are stored at 4°C up to 24 hours, followed by freezing @ -20°C.

Summary of Method:

Automated continuous flow, segmented stream, no bubble gating. Dual wavelength detection and matrix correction.

Chemistry:

Ammonium molybdate and antimony potassium tartrate react in a sulfuric acid environment to form an antimony-phospho-molybdo complex, which is reduced to a blue colored complex by ascorbic acid. Reaction is heat catalyzed at 40 °C. Range is 1-50 ppb.

Interferences:

Fe +3 at concentrations greater than 50 mg/L

SiO₂ at conc.>10mg/L positive interference- not naturally present

Hydrogen sulfide

Mercuric Chloride (used as preservative by some)

v) Parameter: CHLA_N and PHEA

VIMS Laboratory Method:

EPA or other Reference Method: 445.0

Method Reference: US.EPA 1997. USEPA 600/R-97/072. Method 445.0

Method Descriptor: Samples were filtered with a 0.47 µm membrane filter, placed dry in an amber vial and stored with ice packs. They were kept in the dark and extracted at VIMS using 90% acetone.

Preservation Method: Samples are stored at 4°C up to 24 hours, followed by freezing @ -20°C.

Summary of Method:

The two methods for determining Chlorophyll a given here are with 1) a scanning spectrophotometer and 2) a Turner Design fluorometer. The method used requires filtering a known quantity of water through a glass fiber filter. This filter is later ground with a tissue grinder made of Teflon/glass. Approximately 2-3 mL's of 90% acetone are added to the filter before grinding. Acetone is also used to wash the filter in to 17 x 150 test tube with tight fitting cap. The sample is steeped at least 2 hours and not exceeding 24 hours at 4 °C, in the dark. The samples are centrifuged and read on spectrophotometer or fluorometer. If the samples cannot be read within that time period, storage in the freezer at -20 °C for a few days is acceptable. If pheophytin measurements are desired, the sample is acidified and read again.

14) Field and Laboratory QAQC programs**a) Precision****i) Field variability**

Two successive true replicate grab samples are collected for the monthly grab samples at each of the four stations ensuring that replicate samples are collected at the same depth. They are collected successively by hand within the same minute.

ii) Laboratory variability –10% of samples are replicated and RPD should not exceed 20% except in specific circumstances which are defined**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 Standard reference material analysis – This will result from samples sent out from EPA to each lab. 10% of samples are spiked acceptable range is 80-120% recovery except in specific circumstances which are defined.

ii) 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 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

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 |
| QGS | Data suspect due to QA/QC checks |

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

- | | |
|-----|---|
| CAB | Algal bloom |
| CDR | Sample diluted and rerun |
| CHB | Sample held beyond specified holding time |
| CIP | Ice present in sample vicinity |
| CIF | Flotsam present in sample vicinity |
| CLE | Sample collected later/earlier than scheduled |
| CRE | Significant rain event |

CSM	See metadata
CUS	Lab analysis from unpreserved sample

Record comments

CAB	Algal bloom
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample

Cloud cover

CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)
CFY	foggy
CHY	hazy
CCC	cloud (no percentage)

Precipitation

PNP	none
PDR	drizzle
PLR	light rain
PHR	heavy rain
PSQ	squally
PFQ	frozen precipitation (sleet/snow/freezing rain)
PSR	mixed rain and snow

Tide stage

TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide

Wave height

WH0	0 to <0.1 meters
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.6 meters
WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east

ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest
<i>Wind speed</i>	
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 the method detection limit itself rather than a measured value. For example, if the measured concentration of NO₃F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the Reserve submitting the data.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2007-2010 were also flagged/coded, but either reported as the measured value or a blank cell. Any 2007-2011 nutrient/pigment data downloaded from the CDMO prior to November of 2011 will reflect this difference.

Replicate grab sample values for NO₂3 often varied greatly and in fact matched replicate values for other stations more closely. These differences were quite alarming, but an error in sample labeling or processing/contamination could not be found. As a result, these NO₂3 data and calculated NO₃ and DIN data were flagged 1 SRD CSM, or if below minimum detection limits, -4 SBL/SCB CSM. These data should be used with caution.