

SAP NERR Nutrient Metadata
January 2011 - December 2011
Latest Update: June 12, 2015

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

a) Reserve Contact

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c) Other Contacts and Programs

none

- 2) Research objectives** – The nutrient monitoring program is designed upon spatial deployment across a wide variety of marsh types with differing fresh and marine water mixing. These differing dynamics allow scientists and researchers to select from both a wide variety of research sites as well as tailor research programs to specific tidal dynamics and utilize the Reserves SWMP data acquisitions to the maximum extent. Additionally, from a long-term trend perspective the variety of marsh types and hydrology being monitored will allow for a better understanding of the different effects of sea-level rise upon marsh type. Due to a lack of residential development and very low human activity within the watersheds of the sites, they serve as a proxy for reference conditions with the various marsh and associated hydrology types for the creeks and river stations. All of the sites selected have very little anthropogenic nutrient influences. The following brief descriptions are associated with each nutrient monitoring site. For more detail please refer to the site descriptors located under section (4) of this document and/ or contact the Research Coordinator at the SAP NERR for detailed information of any/all sites.

Lower Duplin: Located at the mouth of the Duplin River with large, rapid and near-complete hydraulic exchange with Doboy Sound within each diurnal cycle. Typical of a high salinity, well mixed estuary site.

Hunt Dock: Located on the upper Duplin with relatively high hydraulic retention requiring an estimated 6-7 diurnal events to complete a total hydraulic exchange. Rainfall may drop salinity precipitously in the basin depending on tidal height, duration and volume of precipitation.

Cabretta Creek: Located on the eastern side of Sapelo Island with direct exchange with the Atlantic Ocean. Creek is typical of high salinity, high oceanic exchange and near complete hydraulic exchange

with each diurnal event. Creek is extremely buffered from rainfall (event driven) fluctuations in salinity.

Dean Creek: Located on the southern end of Sapelo is the primary drainage of the inter-dune (located amid primary and secondary dune systems) meadow. This site is highly susceptible to very high salinity fluctuations associated with rainfall events on both seasonal and short-term, event driven scales. Tidal exchange is complete at each diurnal event and exchange water genesis is the Doboy Sound.

The Duplin River is a tidal basin with no freshwater influence within its headwaters apart from surficial aquifer weeping from the perched lens of water associated with Sapelo Island. This nutrient monitoring effort is tied into the Georgia Coastal Ecosystems, Long-Term Ecological Research (GCE-LTER) initiative and the University of Georgia Marine Extension Service water quality database whose collection and analysis of the water samples facilitates the database. This long-term data set is being developed to provide information on estuarine water mixing within the well-studied Duplin River basin in addition to providing a long-term characterization of water quality as related to nutrient loading within the Duplin River.

- a) The **monthly grab** sampling program focuses on documentation of baseline reference nutrient trends within a wide array of local marsh systems with differing hydrology.
- b) The **diel** sampling program focuses on short-term temporal variability over a lunar tidal cycle.

3) Research methods –

a) Monthly Grab Sampling Program

Monthly grab samples were taken at four stations within the Duplin River estuary from January to December 2011. Bottom water samples were taken at the Lower Duplin (LD), Hunt Dock (HD), Cabretta Creek (CA) and Dean Creek (DC) stations using a Niskin style sampling bottle. All grab samples were taken sequentially in duplicate beginning near the time the last diel sample was collected by the ISCO sampler (this time corresponds to low tide at the end of the tidal cycle). Chronological collection times for each of the four sites varied as two teams of people were conducting the actual sampling. Typically, the field crew would sample at the Hunt Dock site and then split into two groups, one group of two remaining onboard the research vessel to sample at the Lower Duplin site (and process the Diel samples), while the other group drove inland to Cabretta Creek and Dean Creek. At the time of sample collection, latitude, longitude, time and depth were recorded. All grab samples were collected from the Niskin bottle into an acid-washed (10% HCl) polypropylene beaker for filtering. Two filter towers were set up, one acid-washed tower with a 0.45 μ m polycarbonate filter for nutrient filtering and one clean tower with a GF/F filter for chlorophyll filtering. A small amount of sample was used to rinse the nutrient filter tower equipped with a filter and then the filtrate was discarded. The tower was then filled to the 250-mL mark. The chlorophyll tower with the GF/F filter was also filled to the 250-mL mark (or 500-mL mark if a larger filtration apparatus was used) and the two towers were connected by a small piece of tubing. The vacuum pump was turned on to pull the sample through each filter and then the vacuum was released. The nutrient sample tower was disconnected and an acid-washed 250-mL polypropylene bottle was rinsed and filled with the filtrate. Space was left in the sample bottle for expansion during freezing at approximately -18 degC. If the first 250 or 500 milliliters went through the chlorophyll filter easily, the filtrate was discarded and an additional 50, 100, 250 or 500 milliliters was filtered, depending on suspended sediment load, to concentrate the sample onto the filter. The chlorophyll filter was then removed with tweezers and placed face up

in a petri dish, wrapped in aluminum foil and labeled with the volume filtered and sample information. The chlorophyll filter towers were rinsed between replicate grabs with distilled water and the nutrient filter tower was acid-washed and DI water rinsed between samples. Nutrient and chlorophyll filtering between grabs took approximately 10 minutes to complete. At the Cabretta and Dean Creek sites, a vacuum hand pump was used rather than a mechanical pump, which is available only on the research vessel. The depths at these two sites were estimated as sampling took place from a bridge. Samples were immediately placed on ice, in the dark and returned to the laboratory within six hours. Once in the laboratory, samples were frozen and processed within the specified times (unless flagged) for nutrient and chlorophyll-a concentrations.

b) Diel Sampling Program

WWW Tide and Current Predictor for Wolf Island, South End was used to estimate low tide. As close to an early, low, neap tide as possible was selected each month for sampling. The ISCO sampler was deployed at the Lower Duplin (LD) site on the day previous to the grab sampling date chosen for that particular month with the sample line suction tube placed 1.5 feet below the surface of the water. The ISCO sampler collected the first diel sample at the low tide predicted for the following day and continued collecting samples every two hours for the next 24 hours, representing a full tidal cycle and a total of 13 samples, ending at low tide when grab sampling began. The ISCO was turned off at the end of the collection period and the samples were secured with caps upon arriving at the site. The samples were filter processed either in the field after completion of grab sampling at Lower Duplin or back in the laboratory, weather depending. The filtration process for the diel samples follows the same process as for grab samples described above. High-density polypropylene bottles were used to store the samples after filtration. Polypropylene bottles and filter towers were soaked in 10% HCl in preparation for the fieldwork, and then triple rinsed with distilled water. A squeeze bottle was used to acid wash (then rinse with distilled water) beakers and filter towers in the field between filtering of each sample.

4) Site location and character –

The Sapelo Island National Estuarine Research Reserve is located on the Southeastern Atlantic coast of the United States in McIntosh County, Georgia. The study area encompasses the Duplin River estuary, a tidally flushed drainage system flowing into Doboy Sound from the north and two inland creeks, Cabretta and Dean Creek. The Duplin River watershed occupies most of the Reserve, which also contains various forest types, sand dunes, a section of ocean beach and minor developed areas. The Duplin River estuary covers 3,300 acres between Sapelo Island and the mainland in McIntosh County. It drains a tidal bay and an extensive network of salt marshes about 6 miles long, into which there is little upland run-off. Diverse estuarine wetlands provide extensive and complex habitat types for fish and wildlife. The island contains several small, interior brackish and freshwater marshes fed by surficial aquifer expression (interdune meadow of Nannygoat beach: south end) and anthropogenic upland ditches and dikes produced in the early 19th century (north end). The upland forests are composed of several diverse habitats including long leaf pine/slash pine forests, climax maritime forests, small amounts of pond cypress bays and naturally regenerated loblolly pine forests which are timbered on a 70 year selectively cut harvest rotation. There are no current studies on pollutants in this area. Sapelo Island is typically considered a pristine environment, with minimal pollutant input.

Latitude and Longitude-

Lower Duplin: Lat: 31 25' 4" N, Long: 81 17' 46" W

Hunt Dock: Lat: 31 28' 43" N, Long: 81 16' 23" W

Cabretta Creek: Lat: 31 26 37.3" N, Long: 81 14 23.7" W

Dean Creek: Lat: 31 23 22.5" N, Long: 81 16 44.2" W

Water Quality site descriptions-

Salinities at all Duplin River sites vary according to localized rainfall and associated runoff. The upper Duplin River site (Hunt Dock) experiences slightly lower salinities associated with rainfall events (2 -3ppt) as compared to the lower Duplin River site. Average salinities range from 15 ppt to 30 ppt depending on seasonal or event rainfall. Average tidal range of diurnal tidal cycle is approximately 2.5 meters twice daily. Due to high turbidity, all Duplin River sites are lacking any persistent submerged aquatic vegetation and have an unconsolidated sandy/mud bottom (soft sediment) typical of southeastern near-ocean estuaries. Marsh sediments are relatively pristine and free of pollutants based on sediment analysis conducted in 1996 by C. Alexander, Skidaway Institute of Oceanography. Watershed is dominated by oceanic tidal influences associated with Doboy Sound. Depths are as follows: Lower Duplin (LD) ranges from 1.5 meters to 6.0 meters depending on tide, and the Hunt Dock site maximum depth is 4.27 meters.

Cabretta Creek is fed directly from waters of the Atlantic Ocean. Cabretta experiences a maximum tidal range of approximately 4.3 meters. Average mean low water depth at the sample site is approximately 3.25 meters. Salinity ranges, with exception to major, long-term precipitation events, from 15-36 ppt, seasonally. The station is located on a small (one-lane), wooden, roadway bridge spanning Cabretta Creek, located on the island's extreme eastern side. The benthos is composed primarily of sand substrate with small, intertidal oyster reef conglomerate communities. Adjacent to the site is extensive, intertidal, bank stabilization (armoring) in the form of woven rip-rap fencing and granite rocks. This manipulation is slowly becoming stabilized via oyster reef community colonization. The adjacent marshes are dominated by *Spartina alterniflora* with occasional *Juncus roemerianus* in the nearby fringe community habitat. The creek has very little adjacent uplands due to: 1) the low elevational gradient and 2) the area's geologically recent accretion genesis (Holocene) resulting in sandy soils; of which neither condition allows for extensive floral colonization or stabilization.

The Dean Creek site is located on a recently rebuilt steel bridge spanning Dean Creek, in close proximity to the adjacent Nannygoat Beach causeway. Dean Creek is a small tidal basin fed from the waters of Doboy Sound, which is located on Sapelo Island's south end. With exception to short duration local or long duration regional precipitation events, the creek's salinity normally ranges between 20 and 30 ppt. The benthic community consists of a sandy-mud substrate with occasional small, intertidal oyster reef community and mean tidal amplitude of approximately 8 feet. Average mean low water depth at the sample site is approximately 1 meter, but fluctuates due to bank erosion. The small creek feeds approximately 150 acres of *Spartina alterniflora* dominated salt marsh, which is interspersed with small 0.5-1 acre hammocks and salt pans. Fringe community components range from Loblolly pine forests with a sub-canopy of Yaupon holly to Wax myrtle and Sable Palm.

5) Coded variable definitions –

LD = Lower Duplin; HD = Hunt Dock; CA = Cabretta Creek; DC = Dean Creek.

Each individual sample is given a 3 part name code in addition to other codes. The 3 part name code, "sapldnut" for example, gives the reserve name (sap = Sapelo), station name (LD = Lower Duplin, etc), and SWMP program code (nut = nutrient monitoring program).

Sampling Site codes:

sapldnut – Sapelo Island nutrient data for Lower Duplin

saphdnut – Sapelo Island nutrient data for Hunt Dock
 sapcanut – Sapelo Island nutrient data for Cabretta Creek
 sapdcnut – Sapelo Island nutrient data for Dean Creek

The monitoring codes are set as “1” to indicate grab samples and “2” to indicate diel samples. Replicates are also given specific codes. Grab samples in which duplicate field samples are taken utilize a “1” for the first sample and a “2” for the second sample. Subsequent lab splits of each field rep are labeled with an “S”. Diel samples are always labeled with a “1” for the first lab replicate and an “S” for the second lab replicate. Only one actual sample is taken at each interval with the ISCO sampler.

6) Data collection period –

Diel sampling for 2011 began at 14:35:00 on January 18, 2011 at the Lower Duplin site. Grab sampling commenced on January 19, 2011 for all sites. Start times for each site are as follows: 13:47:00 at the Hunt Dock site, 14:25:00 at the Lower Duplin site, 16:12:00 at the Cabretta site, and 15:25 at the Dean Creek site.

Diel Sampling

Site	Start Date	Start Time	End Date	End Time
LD	01/18/2011	1435	01/19/2011	1435
LD	02/14/2011	1227	02/15/2011	1227
LD	03/14/2011	1158	03/15/2011	1158
LD	04/11/2011	1030	04/12/2011	1030
LD	05/11/2011	1058	05/12/2011	1058
LD	06/08/2011	0925	06/09/2011	0325
LD	07/11/2011	1309	07/12/2011	1309
LD	08/22/2011	1018	08/23/2011	1018
LD	09/20/2011	0937	09/21/2011	0937
LD	10/24/2011	1437	10/25/2011	1437
LD	11/09/2011	1433	11/10/2011	1433
LD	12/05/2011	1151	12/06/2011	1151

Grab Sampling

Site	Start Date	Start Time	End Date	End Time
CA	01/19/2011	1612	01/19/2011	1623
CA	02/15/2011	1400	02/15/2011	1408
CA	03/15/2011	1320	03/15/2011	1331
CA	04/12/2011	1420	04/12/2011	1434
CA	05/12/2011	1227	05/12/2011	1236
CA	06/09/2011	1111	06/09/2011	1123
CA	07/12/2011	1218	07/12/2011	1226
CA	08/23/2011	1110	08/23/2011	1119
CA	09/21/2011	1111	09/21/2011	1117
CA	10/25/2011	1411	10/25/2011	1420
CA	11/10/2011	1342	11/10/2011	1347
CA	12/06/2011	1308	12/06/2011	1318
LD	01/19/2011	1425	01/19/2011	1438
LD	02/15/2011	1313	02/15/2011	1326
LD	03/15/2011	1234	03/15/2011	1242

LD	04/12/2011	1250	04/12/2011	1301
LD	05/12/2011	1122	05/12/2011	1130
LD	06/09/2011	1028	06/09/2011	1037
LD	07/12/2011	1139	07/12/2011	1146
LD	08/23/2011	1037	08/23/2011	1044
LD	09/21/2011	1018	09/21/2011	1028
LD	10/25/2011	1305	10/25/2011	1312
LD	11/10/2011	1242	11/10/2011	1252
LD	12/06/2011	1206	12/06/2011	1213
HD	01/19/2011	1347	01/19/2011	1358
HD	02/15/2011	1228	02/15/2011	1238
HD	03/15/2011	1156	03/15/2011	1205
HD	04/12/2011	1010	04/12/2011	1021
HD	05/12/2011	1041	05/12/2011	1051
HD	06/09/2011	0948	06/09/2011	1000
HD	07/12/2011	1101	07/12/2011	1110
HD	08/23/2011	1005	08/23/2011	1012
HD	09/21/2011	0940	09/21/2011	0952
HD	10/25/2011	1231	10/25/2011	1240
HD	11/10/2011	1157	11/10/2011	1208
HD	12/06/2011	1128	12/06/2011	1138
DC	01/19/2011	1525	01/19/2011	1536
DC	02/15/2011	1439	02/15/2011	1449
DC	03/15/2011	1417	03/15/2011	1424
DC	04/12/2011	1512	04/12/2011	1525
DC	05/12/2011	1328	05/12/2011	1337
DC	06/09/2011	1150	06/09/2011	1158
DC	07/12/2011	1301	07/12/2011	1310
DC	08/23/2011	1148	08/23/2011	1154
DC	09/21/2011	1148	09/21/2011	1201
DC	10/25/2011	1453	10/25/2011	1500
DC	11/10/2011	1453	11/10/2011	1500
DC	12/06/2011	1408	12/06/2011	1417

7) Associated researchers and projects

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

For a complete viewing of associated projects visit the following website and search the collaborators links:

<http://gce-lter.marsci.uga.edu/lter/>

http://www.uga.edu/marine_advisory/

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 –

A Lachat QuikChem 8000 FIA+ is used to analyze nutrient concentrations. The instrument is calibrated daily for each parameter to be tested using a series of working standards. Once the calibration run is complete and satisfactory ($r \geq 0.99500$ up to 1.0000), the samples are set up for analysis. A set of mid-range check standards is used before the sample run, after approximately every 10 samples and at the end of the run to ensure the instrument is in control. The check standards must remain within + or – 10% of their original value during the entire run. Also, a blank sample is run and then spiked with each analyte to a known concentration, which must come out within + or – 10% as well. An external standard independent of calibration standards is processed with each set of samples. Once the run is complete, the raw data is reviewed on the computer attached to the Lachat QuikChem 8000 FIA+ instrument, and the timing is checked to ensure proper integration of sample peaks. Once this is completed, the data is exported via network to another computer. Here the raw file is imported into an Excel spreadsheet and calculations are performed to obtain the appropriate unit. Orthophosphate values are converted from μM to mg P/L by a conversion factor of 0.031. Nitrate and nitrite values are converted from μM to mg N/L using a factor of 0.014. Ammonia values are converted from $\mu\text{g N/L}$ to mg N/L by dividing the raw result by 1000. The data file for each month is saved and the results are copied into a comprehensive file with all results. A data quality management (DQM) report is filed with the results.

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.

This data was entered and reviewed by Katy Austin Smith, Research Professional II and Lab Manager at the University of Georgia Marine Extension Service.

Unit conversion equations:

$\text{NO}_3 \mu\text{M} * 0.014 \rightarrow \text{mg/L as N}$

$\text{NO}_2 \mu\text{M} * 0.014 \rightarrow \text{mg/L as N}$

$\text{PO}_4 \mu\text{M} * 0.031 \rightarrow \text{mg/L as P}$

$\text{NH}_4 \mu\text{g/L as N} / 1000 \rightarrow \text{mg/L as N}$

10) Parameter titles and variable names by category

Required NOAA/NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisks “*”.

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

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_N

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, have been established by the UGA Marine Extension Service Laboratory. The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a low concentration sample. Table 1 presents the current MDLs; these values are reviewed and revised periodically.

Table 1. Method Detection Limits (MDL) for measured water quality parameters.

Parameter	Variable	Mean Conc.	Std. Dev.	MDL	Dates in use
		mg/L as N or P		mg/L as N or P	
Ammonium	NH ₄ F	0.047	0.001	0.003	Dec.'01 – Dec.'11
Nitrite	NO ₂ F	0.139	0.001	0.004	Jan.'08 – Dec.'11
Nitrite + Nitrate	NO ₂ 3F	0.126	0.001	0.004	Dec.'01 – Dec.'11
Orthophosphate	PO ₄ F	0.087	0.001	0.002	Dec.'01 – Dec.'11
Chl-a	CHLA_N			0.0	Dec.'01 – June'07
Chl-a	CHLA_N	0.6849	0.0053	0.0168	June '07 – Aug. '08
Chl-a	CHLA_N	0.7987	0.0094	0.0295	Aug. '08 – Dec. '11

13) Laboratory methods –

a) Parameter: NH₄F

QuikChem Method: 31-107-06-1-E

Method Reference: U.S. EPA 1983. USEPA-600/4-79-020. Method 350.1.

Standard Methods 4500-NH₃ H.

Method Descriptor: Samples were filtered with a 0.45 µm membrane filter and subjected to hypochlorite, which in the presence of phenol, catalytic amounts of nitroprusside and excess hypochlorite, yields indophenol blue, which measured at 630 nm is proportional to the original ammonia concentration.

Preservation Method: Samples filtered and stored frozen (-18 degC).

Holding Time: 2-3 days

b) Parameter: NO₂3F

QuikChem Method: 31-107-04-1-C

Method Reference: U.S. EPA 1974. Method 353.2.

Standard Methods 4500-NO₃ F.

Method Descriptor: Samples were filtered with 0.45 µm polycarbonate filters. Filtered sample is subjected to cadmium reduction column to reduce nitrate to nitrite. The sample nitrite is then determined by diatizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured at 520 nm and is proportional to the original nitrate + nitrite concentration. The NO₂F concentration (below) is subtracted from this result to give NO₃F.

Preservation Method: Samples filtered and stored frozen (-18 degC).

Holding Time: 2 weeks

c) Parameter: NO₂F

QuikChem Method: 31-107-04-1-C

Method Reference: U.S. EPA 1974. Method 353.2.

Standard Methods 4500-NO₃ F.

Method Descriptor: Samples were filtered with 0.45 um polycarbonate filters. Nitrite in a filtered sample is measured by closing off the cadmium reduction column so that the nitrate is not converted and the sample follows through the same chemistry as with NO₃F to yield the original nitrite concentration.

Preservation Method: Samples filtered and stored frozen (-18 degC).

Holding Time: 1-2 days

d) Parameter: NO₃F

QuikChem Method: 31-107-04-1-C

Method Reference: U.S. EPA 1974. Method 353.2.

Standard Methods 4500-NO₃ F.

Method Descriptor: Nitrate is calculated from NO₃F minus NO₂F results.

Preservation Method: Samples filtered and stored frozen (-18 degC).

Holding Time: 2 weeks

e) Parameter: DIN

Method: DIN is calculated by adding the NH₄F and NO₃F results together.

f) Parameter: PO₄F

QuikChem Method: 31-115-01-3-A

Method Reference: U.S. EPA 1978. Method 365.1.

Standard Methods 4500-P E.

Method Descriptor: Samples were filtered with 0.45 um polycarbonate filters. Filtered sample is subjected to ammonium molybdate and antimony potassium tartrate under acidic conditions to form a yellow complex. This complex is reduced with ascorbic acid to form a blue complex, which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

Preservation Method: Samples filtered and stored frozen (-18 degC).

Holding Time: 30 days

g) Parameter: CHLA

APHA Standard Methods: 10200 H.

Method Reference:

Method Descriptor: Suspended sediment and other material in a water sample is concentrated onto a 47 mm GF/F filter under low vacuum. The sample is stored in a petri dish wrapped in aluminum foil in an airtight plastic bag kept on ice while in the field. The samples are then kept frozen and in the dark until analysis. The acetone extraction method is used to extract the chlorophyll over 2-24 hours and a spectrophotometer is used to obtain readings, which are calculated into a final result.

Preservation Method: Filters are stored frozen (-18 degC).

Holding Time: 28 days

14) Field and Laboratory QA/QC programs – This section describes field variability, laboratory variability, the use of inter-organizational splits, sample spikes, standards, and cross calibration exercises.

a) **Precision**

- i) **Field variability** – Field replicates are successive grab samples. Duplicate grabs are collected. Samples are filtered and placed on ice before the next sample is grabbed (usually about 10 minutes between grabs).
- ii) **Laboratory variability** – All samples are analyzed in duplicates.
- iii) **Inter-organizational splits** – Samples were analyzed by one lab.

b) **Accuracy**

- i) **Sample spikes** – A blank sample is spiked with each set for each analyte to obtain a 100% recovery (+ or – 10%). One or two sample unknowns are spiked with each set for each analyte to obtain a 100 % recovery (+ or – 20% under ideal conditions).
- ii) **Standard reference material analysis** – NERR QA/QC sample analyzed December 2011; External Standard (‘Simple Nutrients’ ERA catalog #739 purchased from Environmental Resource Associates and analyzed with each sample set beginning August 2008 through December 2011).
- iii) **Cross calibration exercises** – None. External standard (independent of calibration standards) processed with each run to ensure calibration accuracy.

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
GQS	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
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Cloud cover

CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)

CFY	foggy
CHY	hazy
CCC	cloud (no percentage)

Precipitation

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

Tide stage

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

Wave height

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

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest

Wind speed

WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots

WS4 > 30 to 40 knots
WS5 > 40 knots

17) Other remarks/notes –

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

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.

Samples that have been diluted and rerun are coded <0> (CDR). This happens frequently with PO₄ results as those values above the upper limit of the linear range (upper limit 2.2 uM or 0.0682 mg P/L) are diluted, rerun and the appropriate dilution factor applied to the raw data, thus yielding a final result analyzed within the linear range. The following table highlights dilutions that were performed on 2011 samples.

Month	Station ID	Dilution factor
January	Cabretta Creek (Grab 1 and 2)	2
January	Dean Creek (Grab 1 and 2)	2
February	Dean Creek (Grab 1 and 2)	10
March	Dean Creek (Grab 1 and 2)	5
April	Dean Creek (Grab 1 and 2)	5
May	Cabretta Creek (Grab 1)	2
May	Dean Creek (Grab 1 and 2)	5
June	Cabretta Creek (Grab 1 and 2)	2
June	Dean Creek (Grab 1 and 2)	10
July	Cabretta Creek (Grab 1 and 2)	2
July	Dean Creek (Grab 1 and 2)	5
August	Cabretta Creek (Grab 1 and 2)	2
August	Dean Creek (Grab 1 and 2)	10
August	Hunt Dock (Grab 1 and 2)	2
September	Diel 1, 2, 5-13	2
September	Cabretta Creek (Grab 1 and 2)	2
September	Dean Creek (Grab 1 and 2)	10

September	Lower Duplin (Grab 1 and 2)	2
October	Cabretta Creek (Grab 1 and 2)	2
October	Dean Creek (Grab 1 and 2)	5
November	Cabretta Creek (Grab 1 and 2)	2
November	Dean Creek (Grab 2)	2
December	Cabretta Creek (Grab 1 and 2)	2
December	Dean Creek (Grab 1 and 2)	5

Some February and December NH₄F and NO₂F samples were marked suspect and coded CHB because they were held beyond the time allowed by SWMP protocols, however these samples remained frozen prior to analysis and laboratory staff believe that they should be reliable for up to 6 months.

In June 2011, the power at Marsh Landing dock was interrupted and only samples 1-10 were collected for the month's diel samples.

In September 2011, the ammonia result from the diel sample collected at 17:37 was rejected as it was a negative value and inconsistent with typical results. This was likely due to an analytical error. DIN was rejected as a result as well.

A group of chlorophyll results from September 2011, those diel samples collected from 23:37 to 7:37, were flagged with <1> [SRD], replicate values differ substantially. The negative values in this group are erroneous, they have been flagged as rejected and were likely due to an analytical error.