

SAP NERR Nutrient Metadata
January 2013 - December 2013
Latest Update: 5/12/14

Note: This is a provisional metadata document; it has not been authenticated as of its download date. Contents of this document are subject to change throughout the QAQC process and it should not be considered a final record of data documentation until that process is complete. Contact the CDMO (cdmosupport@belle.baruch.sc.edu) or Reserve with any additional questions.

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons – List the Reserve staff members responsible for the implementation and collection of the nutrient data. List the Laboratory staff members responsible for processing of the samples and data output. Include name, title, mailing address, phone number, and email address for the Research Coordinator, SWMP technician(s), person(s) responsible for data management, and laboratory contact.

a) Reserve Contact

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c) Other Contacts and Programs

none

2) Research objectives – Describe briefly the nature of the monitoring program resulting in this data set (monitoring along land use, vertical, salinity or habitat gradients).

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 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 – Detail the specifics of sample collection, collection intervals, sample processing, QAQC of the equipment and analyzers.

- a) Monthly Grab Sampling Program

Monthly grab samples were taken at four stations within the Duplin River estuary from January to December 2012. 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 um 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°C . 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 22 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 – Describe your NERR site in general and the sampling sites associated with each YSI data logger / nutrient collection. Include the following in your description for each sampling location. If certain characteristics apply to all sample sites or the entire Reserve they may be discussed in an overview:

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. 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. 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 – Explain the station code names and monitoring program codes.

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 – List the date and time each sample was collected. For grab samples include replicate times or a general statement about the time frame for replicate collection. For diel samples, include start and end times for the sampling session. Specify the date that SWMP nutrient monitoring first began for each monitoring site.

Diel sampling for 2013 began at 12:35:00 on January 22, 2013 at the Lower Duplin site. Grab sampling commenced on January 23, 2013 for all sites. Start times for each site are as follows: 10:45:00 at the Hunt Dock site, 11:30:00 at the Lower Duplin site, 11:58:00 at the Cabretta site, and 12:45 at the Dean Creek site.

Diel Sampling

Site	Start Date	Start Time	End Date	End Time
LD	01/22/2013	1235	01/23/2012	1235
LD	02/19/2013	1023	02/20/2013	1023
LD	03/19/2013	1002	03/20/2013	1002
LD	04/23/2013	1434	04/24/2013	1434
LD	05/20/2013	1217	05/21/2013	1217
LD	06/17/2013	1044	06/18/2013	1044
LD	07/15/2013	0830	07/16/2013	0830
LD	08/19/2013	1405	08/20/2013	1405
LD	09/16/2013	1352	09/17/2013	1352
LD	10/14/2013	1310	10/15/2013	1310
LD	11/13/2013	1100	11/14/2012	1100
LD	12/16/2013	1300	12/17/2013	1300

Grab Sampling

Site	Start Date	Start Time	End Date	End Time
CA	01/23/2013	1158	01/23/2013	1208
CA	02/20/2013	1142	02/20/2013	1149
CA	03/20/2013	1155	03/20/2013	1206
CA	04/24/2013	1424	04/24/2013	1432
CA	05/21/2013	1220	05/21/2013	1232
CA	06/18/2013	1136	06/18/2013	1142
CA	07/16/2013	1103	07/16/2013	1110
CA	08/20/2013	1506	08/20/2013	1513
CA	09/17/2013	1310	09/17/2013	1315
CA	10/15/2013	1525	10/15/2013	1532
CA	11/14/2013	1020	11/14/2013	1025

CA	12/17/2013	1140	12/17/2013	1147
LD	01/23/2013	1130	01/23/2013	1136
LD	02/20/2013	1104	02/20/2013	1112
LD	03/20/2013	1114	03/20/2013	1123
LD	04/24/2013	1216	04/24/2013	1240
LD	05/21/2013	1125	05/21/2013	1142
LD	06/18/2013	1040	06/18/2013	1045
LD	07/16/2013	0946	07/16/2013	0953
LD	08/20/2013	1346	08/20/2013	1354
LD	09/17/2013	1211	09/17/2013	1222
LD	10/15/2013	1255	10/15/2013	1301
LD	11/14/2013	1050	11/14/2013	1052
LD	12/17/2013	1002	12/17/2013	1007
HD	01/23/2013	1045	01/23/2013	1054
HD	02/20/2013	1030	02/20/2013	1037
HD	03/20/2013	1034	03/20/2013	1043
HD	04/24/2013	1113	04/24/2013	1128
HD	05/21/2013	1028	05/21/2013	1040
HD	06/18/2013	0953	06/18/2013	1003
HD	07/16/2013	0903	07/16/2013	0911
HD	08/20/2013	1302	08/20/2013	1311
HD	09/17/2013	1036	09/17/2013	1044
HD	10/15/2013	1221	10/15/2013	1229
HD	11/14/2013	1000	11/14/2013	1002
HD	12/17/2013	1201	12/17/2013	1211
DC	01/23/2013	1245	01/23/2013	1253
DC	02/20/2013	1220	02/20/2013	1229
DC	03/20/2013	1240	03/20/2013	1250
DC	04/24/2013	1525	04/24/2013	1537
DC	05/21/2013	1310	05/21/2013	1324
DC	06/18/2013	1224	06/18/2013	1230
DC	07/16/2013	1220	07/16/2013	1227
DC	08/20/2013	1612	08/20/2013	1618
DC	09/17/2013	1350	09/17/2013	1351
DC	10/15/2013	1442	10/15/2013	1449
DC	11/14/2013	1105	11/14/2013	1107
DC	12/17/2013	1032	12/17/2013	1035

7) Associated researchers and projects (link to other products or programs) – Describe briefly other research (data collection) that correlates or enhances the nutrient data. At a minimum, mention the SWMP MET and WQ datasets.

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 –

The following excerpt is from the Ocean and Coastal Resource Management Data Dissemination Policy:

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 for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature, including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal Resource Management, National Ocean Service, National Oceanic and Atmospheric Administration. 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.

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 <http://cdmo.baruch.sc.edu/>. Data are available in text tab-delimited format.

II. Physical Structure Descriptors

9) Entry verification – This section explains how data acquisition, data entry, and data verification (QAQC) were performed before data were sent to the CDMO to be archived into the permanent database. Describe how your Reserve receives data from the analytical laboratory, how it is entered into Excel, and how it is verified. If your Reserve converts nutrient values to attain the required units of measurement, note that here and detail your process. List who was responsible for these tasks and include the following statement:

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 – Only list those parameters that are reported in the data. See Table 2 in the “Nutrient and Chlorophyll Monitoring Program and Database Design” SOP version 1.6 (January 2012) for a full list of available parameters.

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

Microbial:

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 – This section lists all measured and calculated variables. Only list those parameters that are collected and reported, do not list field parameters. See Table 2 in the “Nutrient and Chlorophyll Monitoring Program and Database Design” SOP version 1.6 (January 2012) document for a full list of directly measured and computed variables.

- a) **Parameters measured directly**
- Nitrogen species: NH₄, NO₂, NO₃
- Phosphorus species: PO₄F
- Other: CHLA
- b) **Calculated parameters**
- NO₃ NO₂₃-NO₂
- DIN NO₂₃+NH₄

12) Limits of detection – This section explains how the laboratory determines the minimum detection limit (MDL). List the method detection limits used and dates they were in use. You may copy this data from the MDL sheet created in the NutrientQAQC macro.

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.'13
Nitrite	NO ₂ F	0.139	0.001	0.004	Jan.'08 – Dec.'13
Nitrite + Nitrate	NO ₂₃ F	0.126	0.001	0.004	Dec.'01 – Dec.'13
Orthophosphate	PO ₄ F	0.087	0.001	0.002	Dec.'01 – Dec.'13
Chl-a	CHLA			0.0	Dec.'01 – June'07
Chl-a	CHLA	0.6849	0.0053	0.0168	June '07 – Aug. '08
Chl-a	CHLA	0.7987	0.0094	0.0295	Aug. '08 – Dec. '13

13) Laboratory methods – This section lists the laboratory and reference method, the method reference, a brief description of method and a brief description of the sample preservation method used *for each parameter that is directly determined*.

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 are 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 um polycarbonate filters. Filtered sample is subjected to cadmium reduction column to reduce nitrate to nitrite. The sample nitrite is then determined by diazotizing 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 are 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 are 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: Nitrate is calculated from NO₃F minus NO₂F results.

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 are 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 QAQC 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 – This section details the primary and secondary QAQC flag definitions.

QAQC flags provide documentation of the data and are applied to individual data points by insertion into the parameter's associated flag column (header preceded by an F_). QAQC flags are applied to the nutrient data during secondary QAQC to indicate data that are out of sensor range low (-4), rejected due to QAQC checks (-3), missing (-2), optional and were not collected (-1), suspect (1), and that have been corrected (5). All remaining data are flagged as having passed initial QAQC checks (0) when the data are uploaded and assimilated into the CDMO ODIS as provisional plus data. The historical data flag (4) is used to indicate data that were submitted to the CDMO prior to the initiation of secondary QAQC flags and codes (and the use of the automated primary QAQC system for WQ and MET data). This flag is only present in historical data that are exported from the CDMO ODIS.

- 4 Outside Low Sensor Range
- 3 Data Rejected due to QAQC
- 2 Missing Data
- 1 Optional SWMP Supported Parameter
- 0 Data Passed Initial QAQC Checks
- 1 Suspect Data
- 4 Historical Data: Pre-Auto QAQC
- 5 Corrected Data

16) QAQC code definitions – This section details the secondary QAQC Code definitions used in combination with the flags above.

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

General errors

GCM	Calculated value could not be determined due to missing data
GCR	Calculated value could not be determined due to rejected data
GDM	Data missing or sample never collected
GQD	Data rejected due to QA/QC checks
GQS	Data suspect due to QA/QC checks

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

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 – Use this section for further documentation of the research data set. Include any additional notes regarding the data set in general, circumstances not covered by the flags and comment codes, or specific data that were coded with the CSM “See Metadata” comment code. You may include the metadata worksheets here if so desired. You may also include information on major storms or precipitation events that could have affected the data recorded at the sample sites.

You are encouraged to include a table detailing sample hold times if your laboratory provides this information. If your lab does not, you should encourage them to do so as this may soon become a requirement.

Include the following excerpt:

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.

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 2013 samples.

Month	Station ID	Dilution factor	Analyte
January	Dean Creek (Grab 1)	2	PO ₄
February	Dean Creek (Grab 1 and 2)	10	PO ₄
March	Dean Creek (Grab 1 and 2)	5	PO ₄
April	Dean Creek (Grab 1 and 2)	2	PO ₄
June	Cabretta Creek (Grab 1 and 2)	2	PO ₄
June	Dean Creek (Grab 1 and 2)	5	PO ₄
July	Dean Creek (Grab 1 and 2)	10	PO ₄
August	Cabretta Creek (Grab 1 and 2)	2	PO ₄
August	Dean Creek (Grab 1 and 2)	5	PO ₄
October	Dean Creek (Grab 1 and 2)	2	PO ₄
November	Cabretta Creek (Grab 2)	2	PO ₄
November	Dean Creek (Grab 1 and 2)	2	PO ₄

Additional notes:

- NO₂ results and calculated NO₃ results for February 2013 were rejected due to air spikes in raw NO₂ peaks affecting final values.
- PO₄ results for March 2013 were flagged as 'suspect data' with code <1>. Lab results were showing sample matrix effects presumably due to the use of distilled water rather than deionized water (laboratory grade water system out of commission), thus causing a large refractive index (negative peak) in the data peaks, resulting in negative values for PO₄. The other analytes (NH₄, NO₂+NO₃, NO₂) did not exhibit this effect.

- NH4 results for October 2013 were flagged as ‘suspect due to QA/QC’ with code <0> (GQS) since the calibration check standard (100 ug N/L) fluctuated outside of acceptable range of 90-110 ug/L (in chronological order, check standard results were as follows: 88.0, 91.6, 89.3, 90.3, 93.7 ug/L NH4 as N).

- **Comment Code, <0> [CHB]:**

Samples for the following months were held beyond the specified holding times for all parameters:

- January 2013
- March 2013
- August 2013
- September 2013
- October 2013
- November 2013
- December 2013