ACE Basin (ACE) NERR Nutrient Metadata
January-December 2011
Latest Update: December 4, 2023

I. Data Set & Research Descriptors

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2. Research Objectives:

Based on discussions with local Coastal Zone Management (CZM) personnel and our knowledge of land use within the Reserve, the South Edisto River drainage basin appears well suited for studying contrasting hydrographic conditions and land use patterns in the ACE Basin. The Big Bay monitoring station is located near Edisto Beach within a tributary of Big Bay Creek. Surrounded by residential and commercial development and subject to nonpoint source pollution, this station is designated as the "treatment" site. The second station is located near Bailey Island, within a tributary of St. Pierre Creek. Urban development in the immediate area of this station has been sparse to date so this station serves as the "control" site. The third NERR monitoring station is located within a tributary of Fishing Creek on Jehossee Island, and both the South Edisto and North Edisto rivers influence the creek. The island is owned and operated by the U.S. Fish and Wildlife Service and serves as a wildlife refuge for native and migrating birds and many of South Carolina's endangered species. This station will serve as a second "control" site. The fourth NERR monitoring station is situated in Mosquito Creek, a tributary of the Ashepoo River. Surrounded by rural development and agriculture, Mosquito Creek is subject to increased nutrient loading and possibly

herbicides and pesticides. This station will serve as a second "treatment" site.

a) Monthly Grab Sampling Program

In February of 2002, nutrient-monitoring component of SWMP was initiated at the ACE Basin NERR. The monitoring sites are located near the four existing YSI monitoring stations: Big Bay Creek, St. Pierre Creek, Fishing Creek and Mosquito Creek. The objective of the study is to ascertain the annual and seasonal fluctuations in nutrient levels near the data logger sites. Two samples are collected from the station during mid-ebb to slack-low water tide periods each month. The samples are analyzed for ammonia, nitrite + nitrate, orthophosphate, and chlorophyll-a concentrations.

b) Diel Sampling Program

In July 1997, the Reserve staff initiated a diel nutrient study. The objective of the study is to ascertain the tidal fluctuations in nutrient levels near the Big Bay and St. Pierre YSI monitoring stations. Nutrient samples are collected during one complete tidal cycle (24 hr 48 min) each month at each station. The samples are analyzed for ammonium, nitrite + nitrate, ortho-phosphate, and chlorophyll-a concentrations. In February of 2002, St. Pierre Creek was designated as the SWMP diel site.

3. Research Methods

a) Monthly Grab Sampling Program

Water samples are taken monthly at the four NERR data logger stations: Big Bay Creek, St. Pierre Creek, Fishing Creek, and Mosquito Creek. Two samples are collected, consecutively, at a depth of 0.5 meter below the surface, using a water-sampler. The "grab" samples are taken on the same day and between mid-ebb and slack-low water (~ 3 hrs before slack-low water to slack-low water). No distinction is made between neap and spring tide conditions. An effort is made to allow for an antecedent dry period of 72 hours prior to sampling.

All samples are collected in wide-mouth, clear Nalgene sample bottles that are acid washed (10% HCl solution), rinsed (6x) with distilled-deionized water, and dried prior to the sampling day. At each sampling site, sample bottles are rinsed with ambient water prior to sample collection. Samples are returned to the SCDNR/Marine Resources Research Laboratory (MRRI) where they are filtered and frozen by ACE staff. Samples are generally filtered and refrigerated the same day of collection, occasionally the following day. The ACE staff processes the samples for CHLA and the nutrient samples are analyzed by the SC Algal Ecology Laboratory (SCAEL) within MRRI (see Section 13 - *Analytical Methods*).

In-situ measurements of dissolved oxygen (mg/L), salinity (ppt), pH, and air and water temperatures (degrees C) are taken at the time of sample collection and at the same depth as the grab samples. Air and water temperatures, salinity, and pH are measured directly with a thermometer, a refractometer and a pH meter, respectively, and dissolved oxygen level is determined by the Winkler titration. This in-situ data is not included in this dataset but can be obtained from contacting the reserve.

b) Diel Sampling Program

Diel monitoring occurs monthly at the St. Pierre Creek YSI datalogger station. Samples are collected every 2 hours and 4 minutes over one lunar day (24 hr 48 min), using an ISCO auto-sampler. Sample collection begins at the predicted slack-low, and samples are collected at a depth of 0.5 meters below the surface. No distinction is made between neap and spring tide conditions. An effort is made to allow for an antecedent dry period of 72 hours prior to sampling.

All samples are collected in wide-mouth, clear Nalgene sample bottles, which are acid washed (10% HCl solution), rinsed (6x) with distilled-deionized water, and dried prior to the sampling day. Due to the use of the ISCO auto-sampler, ambient water rinses prior to sample collection are not feasible. During the collection period, samples are kept cooled by ice stored in the enclosed ISCO. Within two hours of the last sample collection, samples are removed from the auto-sampler, placed on ice and returned to the SCDNR/Marine Resources Division chemistry (SC Algal Ecology) laboratory for analysis. In the laboratory, samples are processed for nutrient and Chlorophyll-a analyses (see Section 13 - *Analytical Methods*).

4. Site Locations and Character:

ACE Basin National Estuarine Research Reserve is one of the largest undeveloped estuaries on the East Coast. The study area encompasses the Ashepoo, Combahee and South Edisto River basins, which empty into St. Helena Sound. The NERR consists of approximately 150,000 acres of diverse estuarine wetlands providing preserved habitats for fish and wildlife.

Three monitoring stations are tributaries of the South Edisto River and one is in a tributary of both the S. Edisto and Ashepoo rivers, contributing to freshwater input to each site. The average tidal range at all stations is approximately 2.0 m (6.6 feet), with a maximum of 2.8 m (9.2 feet) and a minimum of 1.4 m (4.6 feet). The bottom habitat at each of the four sites consists of mud intermixed with shell hash. The descriptions of the sites are as follow:

Big Bay - GPS coordinates: 32.4941 N and -80.3241 W
This monitoring station is in Big Bay Creek proper, approximately 2 km (1.24 mi) from the mouth of the creek, and is located about 5 m (16.41 ft) from the southern bank of the creek. In 2010, the mean depth at the station was 2.34 m (7.67 ft), and the mean salinity was 30.8 parts per thousand (ppt).

The Big Bay monitoring station is designated as a "treatment" site because it is subject to nonpoint source pollution and has a high density of development. The southern bank of the creek is bordered by residential and commercial development, with little setback from the bordering *Spartina* marsh. For instance, there are over forty private docks, two commercial seafood docks and a marina with 75 slips, three paved boat ramps, and two fueling areas along the southern bank. Docks and bulkheads are constructed of concrete, or creosote, CCA-treated or Wolmanized material. Boat traffic is heavy, especially during the warmer months, and the creek is closed to shellfish harvesting because of the surrounding human activities. The major sources of nonpoint source pollution are surface runoff from lawns, golf courses, and paved ramps that contain fertilizers, pesticides, herbicides and PAHs. All of the high ground along the southern bank is developed (i.e. residential homes, condominiums and restaurants); and maritime plant communities have been replaced by golf courses, lawns and ornamental gardens. Small patches of a few maritime species (i.e. live oak (*Quercus virginiana*), cabbage palmetto (*Sabal palmetto*), and Southern red cedar (*Juniperus silicicola*)) are found along the roads. In contrast, the northern bank is bordered by a wide expanse of *Spartina alterniflora* marsh, and no high ground is present. American oyster (*Crassostrea virginica*) forms a reef along the creek banks, especially the northern side, and on intertidal mud flats within the creek.

Fishing Creek – GPS coordinates: 32.6358 N and -80.3655 W
This monitoring station is in a tributary of Fishing Creek, approximately 1.79 km (1.11 mi) from the mouth of the creek, and is located approximately 5 m (16.41 ft) from the northern bank of the creek. The tributary flows through the eastern half of Jehossee Island, a protected USFWS, and Fishing Creek forms the northeast border of the island. The station is surrounded by extensive *Spartina cynosuroides*

marsh and vast mud flats. The upland area is characterized by slash pine, live oak, and cabbage palmetto. In 2010, the mean depth at the station was 1.77 m (5.81 ft), and the mean salinity was 9.4 parts per thousand (ppt).

Fishing Creek monitoring station is designated as a "control" site because there is no development in the immediate area, and boat traffic is relatively light in the creek. The Wildlife Management Area contains impoundments (formerly rice fields) that are managed as wildlife habitat for endangered fauna and migratory waterfowl. No pesticides or herbicides are applied to the managed wetlands. Water level in the managed wetland is regulated by rice trunks that control the flow of water between the impoundment and the South Edisto River.

Mosquito Creek – GPS coordinates: 32.5558 N and -80.4380 W
This monitoring station is in Mosquito Creek proper (a tributary of both the South Edisto and Ashepoo rivers), approximately 2.51 km (1.56 mi) from the Ashepoo River and 12 km (7.46 mi) from the South Edisto River, and it is about 5 m (16.41 ft) from the southern bank of the creek. In 2010, the mean depth at the station was 3.71 m (12.17 ft), and the mean salinity was 18.2 parts per thousand (ppt).

Mosquito Creek station is designated as a "treatment" site because of the land use practices in the surrounding area. Agriculture fields and impounded wetlands are found upstream of the monitoring station. Ten docks constructed of creosote, concrete and Wolmanized pilings; a public boat landing; a commercial seafood business with three commercial shrimp boats and a fueling area are located about 0.8 km (0.5 mi) downstream of the monitoring station. The major source of nonpoint source pollution to the monitoring station is surface runoff from the impoundments and agricultural lands that contain high levels of nutrients and, at times, herbicides and pesticides. Impoundment trunks open and drain into the creek increasing the nutrient load and possibly introducing herbicides and pesticides. Vegetation in the area includes salt marsh dominated by *Spartina alterniflora* and *Juncus roemerianus*. Upland fringe areas consist of cabbage palmetto, live oaks and pine trees.

St. Pierre - GPS coordinates: 32.5233 N and -80.3568 W
This monitoring station is in a small tributary of St. Pierre Creek, approximately 0.25 km (0.16 mi) from the mouth of the creek, and it is about 5 m (16.41 ft) from the northern bank of the creek. The tributary flows through the southern portion of Bailey Island, and creek forms the eastern border of the island. The monitoring station is surrounded by a wide expanse of *Spartina alterniflora* marsh. Extensive mud flats and oyster reefs fringe the banks. Maritime forest communities comprised of species such as wax myrtles, live oaks, and palmettos dominate the upland areas. In 2010, the mean depth at the station was 2.00 m (8.69 ft), and the mean salinity was 29.7 parts per thousand (ppt).

The St. Pierre station is designated as a "control" site because development in the immediate area was sparse when the station was established on March 3, 1995, and the tributary is subject to relatively light boat traffic. In 1996, the 695-acre island was sold, and the owners partnered with The Nature Conservancy to design a conservation-based development. Four hundred and three acres in the center of Bailey Island were set aside as a nature preserve that is managed by The Nature Conservancy, and number of residential lots on the remaining 292 acres is limited to 67. Access to the island is limited to one bridge and all roads on the island are single lane and made of crushed seashells. In addition, a conservation manual was developed for the property owners that provide specific lot designs and construction guidelines as well as landscaping guidelines to protect the maritime and estuarine habitats.

5. Coded variable definitions:

Each individual sample is given a three-part name code in addition to other codes. The three-part name code gives the Reserve name, station name, and the SWMP program code.

BB = Big Bay
FC = Fishing Creek
MC = Mosquito Creek
SP = St. Pierre

ACEBBNUT = ACE Basin Reserve nutrient data for Big Bay
ACEFCNUT = ACE Basin Reserve nutrient data for Fishing Creek
ACEMCNUT = ACE Basin Reserve nutrient data for Mosquito Creek
ACESPNUT = ACE Basin Reserve nutrient data for St. Pierre

Monitoring Programs:
Monthly grab sample program (1), Diel grab sample program (2)

6. Data collection period:

a) Grab Sampling (Sample Collection Time listed in Eastern Standard Time)
SWMP grab nutrient monitoring began in 2002 for all sites.

Site	Start Date	Rep 1 Time	Start Date	Rep 2 Time
BB	01/05/2011	12:15	01/05/2011	12:16
BB	02/02/2011	11:45	02/02/2011	11:46
BB	03/02/2011	11:00	03/02/2011	11:01
BB	04/13/2011	07:15	04/13/2011	07:16
BB	05/11/2011	08:05	05/11/2011	08:06
BB	06/14/2011	11:15	06/14/2011	11:16
BB	07/13/2011	10:29	07/13/2011	10:30
BB	08/10/2011	10:30	08/10/2011	10:31
BB	09/14/2011	11:45	09/14/2011	11:46
BB	10/12/2011	12:00	10/12/2011	12:01
BB	11/09/2011	13:15	11/09/2011	13:16
BB	12/14/2011	13:00	12/14/2011	13:01

Site	Start Date	Rep 1 Time	Start Date	Rep 2 Time
FC	01/05/2011	13:30	01/05/2011	13:31
FC	02/02/2011	13:00	02/02/2011	13:01
FC	03/02/2011	12:15	03/02/2011	12:16
FC	04/13/2011	09:00	04/13/2011	09:01
FC	05/11/2011	10:00	05/11/2011	10:01
FC	06/14/2011	12:15	06/14/2011	12:16
FC	07/13/2011	11:45	07/13/2011	11:46
FC	08/10/2011	12:15	08/10/2011	12:16
FC	09/14/2011	12:45	09/14/2011	12:46
FC	10/12/2011	13:00	10/12/2011	13:01
FC	11/09/2011	12:15	11/09/2011	12:16
FC	12/14/2011	13:45	12/14/2011	13:46

Site	Start Date	Rep 1 Time	Start Date	Rep 2 Time
MC	01/05/2011	14:45	01/05/2011	14:46
MC	02/02/2011	14:00	02/02/2011	14:01
MC	03/02/2011	13:15	03/02/2011	13:16

MC	04/13/2011	10:15	04/13/2011	10:16
MC	05/11/2011	08:45	05/11/2011	08:46
MC	06/14/2011	13:15	06/14/2011	13:16
MC	07/13/2011	12:45	07/13/2011	12:46
MC	08/10/2011	13:00	08/10/2011	13:01
MC	09/14/2011	13:30	09/14/2011	13:31
MC	10/12/2011	14:00	10/12/2011	14:01
MC	11/09/2011	11:15	11/09/2011	11:16
MC	12/14/2011	14:45	12/14/2011	14:46

Site	Start Date	Rep 1 Time	Start Date	Rep 2 Time
SP	01/05/2011	11:30	01/05/2011	11:31
SP	02/02/2011	11:00	02/02/2011	11:01
SP	03/02/2011	10:15	03/02/2011	10:16
SP	04/13/2011	08:00	04/13/2011	08:01
SP	05/11/2011	07:45	05/11/2011	07:46
SP	06/14/2011	10:30	06/14/2011	10:31
SP	07/13/2011	10:00	07/13/2011	10:01
SP	08/10/2011	09:45	08/10/2011	09:46
SP	09/14/2011	11:00	09/14/2011	11:01
SP	10/12/2011	11:15	10/12/2011	11:16
SP	11/09/2011	14:00	11/09/2011	14:01
SP	12/14/2011	12:15	12/14/2011	12:16

b) Diel Sampling (Sample Collection Time listed in Eastern Standard Time)
SWMP diel nutrient monitoring began in 2002 for the following site.

Site	Start Date	Start Time	End Date	End Time
SP	01/04/2011	01:47	01/05/2011	02:35
SP	02/01/2011	00:43	02/02/2011	01:31
SP	02/28/2011	23:35	03/02/2011	00:23
SP	04/11/2011	20:06	04/12/2011	20:54
SP	05/09/2011	18:44	05/10/2011	19:32
SP	06/14/2011	00:44	06/15/2011	01:32
SP	07/19/2011	04:51	07/20/2011	05:39
SP	08/08/2011	22:15	08/09/2011	23:03
SP	09/13/2011	02:29	09/14/2011	03:17
SP	10/11/2011	01:17	10/12/2011	02:05
SP	11/08/2011	12:37	11/09/2011	13:25
SP	12/12/2011	15:32	12/13/2011	16:20

7. Associated researchers and projects:

Dr. Charles Wenner of SCDNR/Marine Resources Research Institute received funding through the National Marine Fisheries Service in January of 2001 to continue an ongoing survey of red drum (*Sciaenops ocellatus*) in the South Edisto and Combahee River basins, by electrofishing in tidal freshwater and low salinity brackish water. Although red drum is the target species, all species identified to species, measured and weighed.

As part of the System-wide Monitoring Program (SWMP), water quality and weather data are gathered at the ACE NERR in conjunction with the monthly nutrient data collection periods.
Real-time weather and water quality data is gathered 24/7 and is transmitted to the Centralized Data Management Office (CDMO). Near real-time data as well as historic water quality, nutrient, and weather data can be obtained at www.nerrsdata.org.

Information about other studies conducted in the ACE Basin may be obtained from the Research Coordinator.

8. Distribution

According to the Ocean and Coastal Resource Management, Data Dissemination Policy for the NERRS System-wide Monitoring Program as follows:

The National Estuarine Research Reserve retains the right to be fully credited for having collected and process the data. Following academic courtesy standards, the reserve 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. These data sets are 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 or 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.

Suggested 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

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.

The entered values are checked for transcription errors and edited as needed. The data are evaluated to determine whether to flag or delete suspect values. Data are flagged if the values are: 1) above upper limit of range detection, 2) below lower limit of range detection; 3) based on samples held beyond specified holding time; 4) based on samples taken within 72 hours of a rainfall event; and 5) derived on lab analysis from improperly preserved samples. Justin Hart and Amanda Fornal were responsible for these tasks.

The SCDNR/Marine Resources Division Chemistry Lab calculates and reports results in μM. For purposes of consistency in the NERR System, ACE Basin NERR calculates the concentrations as mg/L based on atomic masses of 14.006 and 30.973 for N and P respectively. Therefore, ACE Basin NERR staff multiply the concentrations reported by the chemistry lab by 0.014006, 0.030973 to yield concentrations in mg/L as N and P respectively.

10. Parameter Titles and Variable Names by Data Category

Data Category	Parameter	Variable Name	Units of Measure
i) Phosphorous:	Orthophosphate	PO4F	mg/L as P
ii) Nitrogen:	Nitrite + Nitrate	NO23F	mg/L as N
	Ammonia	NH4F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
iii) Other lab Parameters:			
	Chlorophyll a	CHLA_N	μg/L

Notes:

1. Time is coded based on a 2400 hour clock and is referenced to Eastern Standard Time.
2. Reserves have the option of measuring NO2 and NO3 or they may substitute NO23 for individual analysis if they can show that NO2 is a minor component relative to NO3. Ace NERR staff and the Analytical Laboratory staff determined that separate NO2 and NO3 data were not necessary. The concentration of NO2 is negligible when compared to the concentration of NO3.

11. Measured and Calculated Laboratory Parameters

i) Variables Measured Directly

Nitrogen species	NO23F, NH4F
Phosphorus species	PO4F
Other	CHLA_N

ii) Computed Variables

DIN	NO23F + NH4F

12. Limits of Detection

The Hach/Lachet manufacturer established the Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect. Table 1 lists the MDL values as provided by the SCDNR Algal Ecology Section Charleston Lab from January through July. Table 2 lists the MDL values as provided by the North Inlet NERR Lab for August through December. These values are reviewed and revised periodically.

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

Parameter	Start Date	End Date	MDL in mg/L as N or P
PO4F	1/1/11	12/31/11	0.0010
NH4F	1/1/11	12/31/11	0.0006
NO23F	1/1/11	12/31/11	0.0002

Table 2. Method Detection Limits (MDL) for measured water quality parameters.

Parameter	Start Date	End Date	MDL in µg/L
CHL-A	1/1/11	12/31/11	0.06

13. Laboratory Methods

a) Sampling Preparation Methods:

The supplies used by the ACE Basin NERR to collect and process water samples are: 1) 500-ml wide-mouth clear Nalgene bottles; 2) 1000-ml clear Nalgene ISCO bottles, 3) 20-ml scintillation vials and caps; 4) 15-ml polypropylene centrifuge tubes and caps; 5) borosilicate culture vials; 6) 60-ml filtering apparatus [Norm-Jet plastic syringe, syringe plunger and Pall Gelman Easy-Pressure syringe filter holder with 25 mm pore size]; 7) 25 mm glass microfibre filter paper, 8) pump pipettor (variable volume: 0.5-5 ml) and plastic pipette tips, 8) hypochlorite-phenol solution; and 9) 90% acetone solution.

Prior to sample collection, the nalgene bottles, scintillation vials and caps, and filtering apparatus are acid-washed with 10% hydrochloric acid solutions, rinsed (6x) with distilled-deionized water, and dried. The dried bottles are capped, and the filtering apparatus is stored in a plastic re-sealable bag.

b) Filtering Process:

As described below the samples are filtered by NERR staff within four hours of collection. First, one 25 mm filter is placed in a filter holder using clean tweezers to prevent contamination. Gently agitate the sample bottle to suspend the particulates and "seed" the filter syringe with the sample water by filling it completely and then discarding water. Next, attach the filter holder to syringe and add 50 ml of sample water into the filter apparatus (syringe with attached filter holder). Position the filter apparatus over a scintillation vial and insert the filter plunger into syringe and slowly push down on the plunger. Samples are not forced through the filter. Seed both scintillation vials with the sample water by filling them with filtered water and then discarding the water. After filtering the 50 ml, remove the filter holder from the syringe, cover it and set it aside. (If sediments and other solids in the sample prevented the filtration of the entire 50 ml, note the volume that was filtered on laboratory sheet and discard unfiltered portion.)

Using a clean filtering apparatus, the filtering process is repeated, not discarding the filtered water collected in the scintillation vials. If samples are not going to be analyzed within 24 hours of filtering, three drops of hypochlorite-phenol solution are added to the NH_4 scintillation vial to preserve the sample until it is analyzed. After filtering the 50 ml, remove the filter holder from the syringe, set holder aside and cover. (If sediments and other solids in the sample prevented the filtration of the entire 50 ml, note the volume that was filtered on laboratory sheet and discard unfiltered portion.) Place vials in tray and set aside.

Next, examine the two filters. If the color and coverage of particulates on the two filters are similar, place them in centrifuge tubes (one filter per tube) filled with 10 ml of 90% acetone and cover tubes with foil. If the density and coverage of particulates on one filter is noticeably lighter than the other filter, cover filters and repeat the filtering process until two filters of similar color and coverage are obtained.

After filtering all of the samples, place the scintillation vials and centrifuge tubes in refrigerator set at 4ºC. Acid wash the filtering apparatus (syringe, syringe plunger and filter holder) and sample bottles with a 10% HCl solution, then rinse them six times with distilled-deionized water, and allow them to air-dry.

Nutrient samples are usually processed the next day and almost always within the allowed NERRS hold time, but may be frozen if need be. CHLA samples are generally analyzed 18-24 hours after filtering.

c) Analytical Methodology:

Nitrogen and phosphorus chemistry is determined with a Lachat™ QuikChem 8000 Flow Injection Nutrient Analyzer equipped with a data logger. A 0.7 μm (nominal pore size) glass fiber filter is used to separate the dissolved and particulate constituents of the sample. The filtered water is then run through the autoanalyzer. The autoanalyzer is calibrated at the beginning of an analysis run. Calibration is done by injecting standards. The system will then prepare a calibration curve by plotting sample response versus standard concentration. The data logger calculates the sample concentrations based on the regression equation and store the values in a temporary file. At the end of the analysis run, the temporary file is transferred to a computer that stores the concentrations in a file.

A Turner Model 450 Fluorometer, equipped with a 440 nm filter, is used to determined chlorophyll-a values. The fluorometer is calibrated regularly and the calibration is checked with solid chlorophyll standard before and after the analysis run. Corrected chlorophyll-a readings are calculated using the before and after acidification fluorescence readings. The fluorometer is calibrated regularly and a solid chlorophyll standard is used to check the calibration before and after the analysis run.

Corrected chlorophyll-a readings are calculated using the before and after acidification fluorescence readings, the flourometer's calibration constant and acid ratio, the volume of sample filtered and the volume of acetone used to break down the chlorophyll from the filter paper. The following formula is used:

((((calibration constant)*(acid ratio/(acid ration – 1))*(before acidification – after acidification))))*(volume of acetone-volume filtered)

i. **Parameter: NH_4**

Method reference: QuikChem® Method No. 31-107-06-1-B (2001)

Range: 0.355 - 42.836 μM N/L as NH_4

Method Descriptor: The fixed filtrate (<0.7 μm) is used in the procedure to determine the ammonia concentration. This method is dependent upon the Berthelot Reaction, during which a blue colored compound, closely related to indophenol, forms when an ammonium salt solution is added to sodium phenoxide, followed by the addition of sodium hypochlorite (Glibert and Loder 1977). A solution of potassium sodium tartrate and sodium citrate is added

to the sample stream to eliminate the precipitation of the hydroxides of calcium and magnesium.

Preservation Method: The water is initially filtered through a 25-mm glass filter, fixed with three drops of a hypochlorite-phenol solution if analysis will not occur within 24 hours, and stored at 4ºC up to 14 days. Prior to analysis, the filtrate (25 mm) is passed through a 0.7 μm filter to separate the dissolved and particulate constituents of the sample.

ii. Parameter: NO2, NO3, and NO23

Method Reference: QuikChem® Method No. 31-107-04-1-D (2000)

Range: 0.356 - 0.999 μM N/L as NO_3 and/or NO_2

Method Descriptor: The filtrate (<0.7 μm) is used in the procedure to determine the NN chemistry. The combined nitrate-nitrite (NO_3 + NO_2) value is obtained by passing a sample through a copper-cadmium reductor column that reduces the nitrate(NO_3) to nitrite(NO_2), and the nitrite is obtained by passing a sample through the auto-analyzer machine without the column. The nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-napthylethylenediamine dihydrochloride to form a reddish-purple azo dye. The dye absorbs at 540 nm. The nitrate value is obtained by subtracting the nitrite value from the combined nitrate and nitrite value.

Preservation Method: Water is initially filtered through 25-mm glass filter and stored at 4ºC up to 14 days. Prior to analysis, the filtrate (25 mm) is passed through a 0.7 μm filter to separate the dissolved and particulate constituents of the sample.

iii. Parameter: PO_4

Method Reference: QuikChem® Method No. 31-115-01-1-H (2001)

Range: 0.161 - 0.12.914 μM N/L as PO_4

Method Descriptor: The filtrate (<0.7 μm) is used in the procedure to determine the OP chemistry. The QuikChem® Method is a modification of the Murphy and Riley (1962) single solution method. The phosphomolybdate blue complex formed during the reaction is read at a wavelength of 880 nm to determine the value.

Preservation Method: Water is initially filtered through 25-mm glass filter and stored at 4ºC up to 14 days. Prior to analysis, the filtrate (25 mm) is passed through a 0.7 μm filter to separate the dissolved and particulate constituents of the sample.

iv. Parameter: CHLA

Method Reference: Modification of EPA Method 445.0 (EPA/600/R-92/121)

Method Descriptor: The extract is used in the procedure to determine the chlorophyll-a chemistry. Within a 24-hour period the samples are centrifuged at 3000 rpm for 10 minutes and then 5 ml are transferred to culture tubes, using a pump pipettor. The extraction is read at 440 nm wavelength, and then the sample is acidified with 0.1 ml (two drops) of 0.1 N HCl solution and re-read at the same wavelength.

Preservation Method: The 25-mm glass filters are placed in centrifuge tubes (one filter/tube) filled with 10 ml of 90% acetone solution and stored at 4ºC for 18-24 hours. Samples have been stored for up to 72 hours at 4ºC without any noticeable difference in values.

14. QA/QC Programs

a) Precision:

i) **Field Variability** - Grab samples are collected monthly at each of the four monitoring site. A water-sampler is used to collect two consecutive samples at a depth of 0.5 meter below the surface. The grab samples are taken on the same day and between mid-ebb and slack-low water (~ 3 hrs before slack-low water to slack-low water). Grab samples do not have replicates.
Diel samples are collected monthly in St. Pierre Creek near the YSI datalogger station. Samples are collected every 2 hours and 4 minutes over one lunar day (24 hr 48 min), using an ISCO auto-sampler. Sample collection begins at the predicted slack-low, and samples are collected at a depth of 0.5 meters below the surface. Diel samples do not have replicates.

ii) **Laboratory Variability -** No replications

iii) **Inter-organizational splits -** No splits: all samples are analyzed by the same lab

b) **Accuracy:**

i) **Sample Spikes -** The lab does not run sample spikes but does run known standards and blank checks (DI water) during the analysis.

ii) **Standard Reference Material Analysis -** Our lab is not an EPA lab, so they do not receive samples.

iii) **Cross Calibration Exercises -** ACE Basin NERR does not participate in the cross calibration exercises.

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

1) Data Blanket Statement:

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 NO23F 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.

2) Missing Data <-2>

Chl-a diel St. Pierre data are missing or were not recorded [GDM] for the following date for unknown reasons.
02/01/2011 – 15:11

3) Precipitation Blanket Statement:

The Reserve is over 72,846 ha, and it encompasses most of the estuarine portion of the 320,000-ha ACE Basin watershed, extending 27.14 km northward from the mouth of St. Helena Sound to its inland boundary at the defunct *SCCL* railroad. Due to the immense size of the Reserve it is not uncommon to observe heavy rainfall in one area of the Reserve but not in another area. However, we do assume that rain occurred at all the nutrient monitoring stations if rain was recorded by the Reserve weather station.

4) Suspect Data <1>

December grab and diel samples were collected Dec 12-14, 2011. They were not analyzed for nutrients until January 3, 2012. It is likely that these samples were frozen and processed within the allowable hold time for frozen samples, but we can not confirm that they were frozen and therefore have flagged them suspect and coded as held too long <1> [GSM] (CHB).

5) References:

Gilbert, P.M. and Loder, T.C. (1977). Automated Analysis of Nutrients in Seawater: A Manual of

Techniques. Woods Hole Oceanographic Institution. Publication Number WHOI-77-47. Woods Hole, Massachusetts

Murphy, J., and Riley, J.P. (1962). A modified single solution method for the determination of phosphate in natural waters. Anal. Chem. Acta. 27: 31-36.