

ACE Basin (ACE) National Estuarine Research Reserve Nutrient Metadata
January-December 2016
Latest Update: December 7, 2020

I. Data Set and Research Descriptors

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2) Research objectives –

Long-term water quality monitoring in the ACE Basin provides a unique opportunity to increase understanding of how various environmental factors influence estuarine processes. Based on discussions with local Coastal Zone Management (CZM) personnel and ACE Basin NERR staff knowledge of land use within the Reserve, the South Edisto River drainage basin was selected because it is well suited for studying contrasting hydrographic conditions and land use patterns.

The SWMP program began on March 3, 1995 in two tributaries of the South Edisto River, Big Bay Creek and St. Pierre Creek. In October 2002, monitoring stations were established in Fishing Creek and in Mosquito Creek, also tributaries of the South Edisto River. On January 1, 2015 the Edisto Island station replaced the Big Bay Creek station (which was discontinued) as a primary SWMP station. It is also located in Big Bay Creek, approximately 1.27 km upstream from the former Big Bay station, with similar water quality and influences.

The two major objectives of the ACE Basin monitoring program are to: 1) compare water quality conditions in shallow creeks along a salinity gradient and at different levels of development in the South Edisto River watershed and 2) track changes to the saltwater demarcation line in the South Edisto River as a result of prolonged drought, extraction of river water, and sea level rise. The two “treatment” sites are Edisto Island and Mosquito Creek, where boat traffic is moderate to heavy and residential and commercial development is medium to dense. St. Pierre Creek and Fishing Creek, where boat traffic is light and development is sparse, are designated as “control” sites. The four sites are located along a salinity gradient ranging from the polyhaline (Edisto Island & St. Pierre Creek) to mesohaline (Mosquito

Creek) to oligohaline (Fishing Creek). See *Section 5 - Site Location and Character* for detailed descriptions of the sites.

a) Monthly Grab Sampling Program

In February of 2002, the monthly grab nutrient-monitoring component of SWMP was initiated at the ACE Basin NERR. The objective of the study is to ascertain the annual and seasonal fluctuations in nutrient levels at the water quality monitoring sites. Two samples are collected from each monitoring station between mid-ebb to slack-low tide periods each month. The samples are analyzed for ammonium, nitrite + nitrate, ortho-phosphate and chlorophyll-a concentrations.

b) Diel Sampling Program -

In July 1997, the Reserve staff initiated a nutrient diel study at the Big Bay and St. Pierre monitoring stations; in 2002, St. Pierre Creek was designated as the SWMP diel site, and diel monitoring at the Big Bay site was discontinued. The objective of the study is to track the tidal fluctuations in nutrient levels during a complete diurnal tidal cycle (24 hr 48 min). Samples are collected once each month by an ISCO sampler, and samples are analyzed for ammonium, nitrite + nitrate, ortho-phosphate, and chlorophyll-a concentrations.

3) Research methods –

a) Monthly Grab Sampling Program

Water samples are taken monthly at the four NERR water quality stations: Edisto Island, 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 or by hand. The “grab” samples are taken on the same day and between mid-ebb and slack-low tide (within 3 hours before slack-low tide). No distinction is made between neap and spring tide conditions or between morning and afternoon tides.

All samples are collected in wide-mouth, clear polypropylene bottles that are acid washed (10% HCl solution), rinsed (6x) with distilled or 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 immediately removed from natural light and placed on ice, then returned to the laboratory. In the laboratory, samples are processed for nutrient and chlorophyll-a analyses (see *Section 13 - Analytical Methods*).

b) Diel Sampling Program

Diel monitoring occurs monthly at the St. Pierre Creek water quality station. Thirteen water 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 are collected at a depth of 0.5 meters below the surface. No distinction is made between neap and spring tide conditions.

All samples are collected in clear polypropylene bottles, which are acid washed (10% HCl solution), rinsed (6x) with distilled or 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. When retrieved, samples are removed from the auto-sampler and placed on ice. In the laboratory, samples are filtered through 25-mm glass fiber filter within three hours of sample retrieval, and then stored at 4°C (see *Section 13 - Analytical Methods* for more details of analyses).

4) Site location and character –

All ACE Basin NERR historical nutrient/pigment monitoring stations:

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
aceeinut	P	Edisto Island	32.5040 N, 80.3247 W	01/01/2015 - current	NA	NA
acefcnut	P	Fishing Creek	32.63593 N, 80.36556 W	03/01/2002 - current	NA	NA
acemcnut	P	Mosquito Creek	32.5558 N, 80.4380 W	03/01/2002 current	NA	NA
acespnut	P	St. Pierre	32.52800 N, 80.36144	01/01/2002 - current	NA	NA
acebbnut	P	Big Bay	32.4941 N, 80.3241 W	02/01/2002 - 12/31/2014	Privately owned dock no longer structurally sound	Station replaced by Edisto Island

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.

The South Edisto River has a drainage area of approximately 394,176 ha, encompassing the area between Four Holes Swamp and St. Helena Sound. The river receives considerable input of freshwater with an average annual streamflow of 74 m³/s. The official saltwater-freshwater demarcation line on the river lies at river mile 20; however, during periods of very low flow, the saltwater interface can intrude to river mile 32, which is approximately 12 river miles from the inland boundary of the reserve. Salt marshes of smooth cordgrass (*Spartina alterniflora*) dominate the wetlands in the polyhaline and mesohaline, while waterfowl impoundments are the dominant land cover in the oligohaline and limnetic waters.

The average tidal range in the South Edisto River is approximately 2.0 m (6.6 ft), with a maximum of 2.8 m (9.2 ft) and a minimum of 1.4 m (4.6 ft). The bottom habitat at all stations consists of mud that is intermixed with dead shell hash at the saltwater sites.

Monitoring Stations

Three of the four stations (Edisto Island, Fishing Creek, and St. Pierre Creek) are in tributaries of the South Edisto River and one station (Mosquito Creek) is in a tributary of both the South Edisto and Ashepoo rivers. The descriptions of the sites are as follow:

Edisto Island (EI) – GPS coordinates: 32.5040 N and -80.3247 W

On January 1, 2015, Edisto Island water quality station replaced the Big Bay station as a primary station. The Edisto Island station is approximately 1.27 km (0.68 nautical miles) upstream of the previous site (Big Bay) and is located on a dock at the Edisto Beach State Park. Water quality data was collected at both stations for 8 months and the overall results were very similar. Edisto Island station is also designated as a "treatment" site because of its proximity to developed areas. In 2015, the mean depth at the station was 2.48 m (8.1 ft.), and the mean salinity was 29.30 parts per thousand (ppt).

The eastern bank of the Big Bay creek, at the new station, is bordered by *Spartina alterniflora* and *Salicornia virginica*. The high ground is dominated by maritime forest, characterized by live oak (*Quercus virginiana*), slash pine (*Pinus taeda*), and cabbage palmetto (*Sabal palmetto*). A marsh island with no high ground

borders the western bank; while American oyster (*Crassostrea virginica*) forms a reef along both creek banks. Boat traffic is heavy, especially during the warmer months, and the creek is closed to shellfish harvesting because of the surrounding human activities. Nonpoint sources of pollution, including fertilizers, pesticides, herbicides and PAHs, to the monitoring station are surface runoff from lawns, golf courses, and paved ramps. Docks and bulkheads are constructed of concrete or wood treated with creosote, CCA-treated, or Wolmanized process.

Fishing Creek (FC) – GPS coordinates: 32.63593 N and -80.36556 W

This monitoring station is in a tributary of Fishing Creek, approximately 2 km (1.08 nautical miles) 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 Wildlife Management Area (WMA) protected by the 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 2015, the mean depth at the station was 2.35 m (7.71 ft.), and the mean salinity was 8.79 parts per thousand (ppt).

The 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 WMA 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 wetlands. Water level in the wetland is regulated by rice trunks that control the flow of water between the impoundment and the South Edisto River.

Mosquito Creek (MC) – GPS coordinates: 32.5558 N and -80.4380 W

This monitoring station is in Mosquito Creek (a tributary of both the South Edisto and Ashepoo rivers), approximately 2.51 km (1.36 nautical miles) from the Ashepoo River and 12 km (6.48 nautical miles) from the South Edisto River, and it is approximately 5 m (16.41 ft.) from the southern bank of the creek. In 2015, the mean depth at the station was 3.61 m (11.84 ft.), and the mean salinity was 14.15 psu.

The 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. Approximately fifteen docks constructed of creosote, concrete, Wolmanized or CCA treated wood; a public boat landing; a commercial seafood business with commercial shrimp boats and a fueling dock are located approximately 1.00 km (0.54 nautical miles) downstream of the monitoring station. The major contributor of nonpoint source pollution to the monitoring station is surface runoff from the impoundments and agricultural lands that may 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 Creek (SP) – GPS coordinates: 32.52800 N and -80.36144 W

This monitoring station is in a small tributary of St. Pierre Creek, approximately 0.25 km (0.13 nautical miles) from the mouth of the creek, and it is approximately 5 m (16.41 ft.) from the northern bank of the creek. The tributary flows through the southern portion of Bailey Island, and the 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 (*Morella cerifera*), live oaks (*Quercus virginiana*), and palmettos dominate the upland areas. In 2015, the mean depth at the station was 1.82 m (5.97 ft.), and in 2015 the mean salinity was 27.35 parts per thousand (ppt).

The St. Pierre Creek 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 the 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 3-part name code in addition to the date of grab sample collection or start date of diurnal sample collection. The name code gives the Reserve 3-letter code, station 2-letter code and SWMP program 2-letter code.

Sampling Station:	Site code:
Edisto Island	EI
Fishing Creek	FC
Mosquito Creek	MC
St. Pierre	SP

3 Part Name Codes:

aceeinut = ACE Basin Edisto Island nutrient samples
 acefcnut = ACE Basin Fishing Creek nutrient samples
 acemcnut = ACE Basin Mosquito Creek nutrient samples
 acespnut = ACE Basin St. Pierre Creek nutrient samples

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)

The SWMP grab sample program began in 2002 for St. Pierre Creek, Big Bay Creek, Fishing Creek, and Mosquito Creek. In 2015, the Edisto Island station replaced Big Bay Creek which was decommissioned.

Site	Sample Date	Rep 1 Time	Rep 2 Time
EI	01/13/2016	12:30	12:31
EI	02/10/2013	12:30	12:31
EI	03/09/2016	12:15	12:16
EI	04/06/2016	11:15	11:16
EI	05/18/2016	09:15	09:16
EI	06/15/2016	09:15	09:16
EI	07/13/2016	08:15	08:16
EI	08/17/2016	10:15	10:16
EI	09/28/2016	11:05	11:06
EI	10/26/2016	10:02	10:03
EI	11/16/2016	12:40	12:41
EI	12/14/2016	11:43	11:44

Site	Sample Date	Rep 1 Time	Rep 2 Time
FC	01/13/2016	13:45	13:46
FC	02/10/2013	13:45	13:46
FC	03/09/2016	12:45	12:46
FC	04/06/2016	12:00	12:01

FC	05/18/2016	10:15	10:16
FC	06/15/2016	08:30	08:31
FC	07/13/2016	06:45	06:46
FC	08/17/2016	11:00	11:01
FC	09/28/2016	10:20	10:21
FC	10/26/2016	08:55	08:56
FC	11/16/2016	13:45	13:46
FC	12/14/2016	12:21	12:22

Site	Sample Date	Rep 1 Time	Rep 2 Time
MC	01/13/2016	16:45	16:46
MC	02/10/2013	14:00	14:01
MC	03/09/2016	13:45	13:46
MC	04/06/2016	13:00	13:01
MC	05/18/2016	11:15	11:16
MC	06/15/2016	10:45	10:46
MC	07/13/2016	09:45	09:46
MC	08/17/2016	11:45	11:46
MC	09/28/2016	11:55	11:56
MC	10/26/2016	10:45	10:46
MC	11/16/2016	15:36	15:37
MC	12/14/2016	14:27	14:28

Site	Sample Date	Rep 1 Time	Rep 2 Time
SP	01/13/2016	13:00	13:01
SP	02/10/2013	13:00	13:01
SP	03/09/2016	12:00	12:01
SP	04/06/2016	11:15	11:16
SP	05/18/2016	09:30	09:31
SP	06/15/2016	07:45	07:46
SP	07/13/2016	06:15	06:16
SP	08/17/2016	10:30	10:31
SP	09/28/2016	09:44	09:45
SP	10/26/2016	08:15	08:16
SP	11/16/2016	12:50	12:51
SP	12/14/2016	11:40	11:41

b) Diel sampling (sample collection time listed in Eastern Standard Time)

The SWMP diel sample program began in 2002 for the St. Pierre Creek site.

Site	Start Date	Start Time	End Date	End Time
SP	01/11/2016	15:28	01/12/2016	16:16
SP	02/09/2016	02:31	02/10/2016	03:19
SP	03/08/2016	01:21	03/09/2016	02:09
SP	04/04/2016	11:43	04/05/2016	12:31
SP	05/16/2016	23:00	05/17/2016	23:48
SP	06/13/2016	21:28	06/14/2016	22:16
SP	07/11/2016	20:46	07/12/2016	21:34
SP	08/16/2016	00:22	08/17/2016	01:10
SP	09/26/2016	23:13	09/28/2016	00:01
SP	10/24/2016	21:53	10/25/2016	22:41
SP	11/14/2016	14:01	11/15/2016	14:49
SP	12/12/2016	12:50	12/13/2016	13:38

7) Associated researchers and projects –

As part of the System-wide Monitoring Program (SWMP), ACE Basin NERR is also monitoring 15-minute meteorological and water quality data, which may be correlated with the nutrient/pigment dataset. These data are available at www.nerrsdata.org. Information about other studies conducted in the ACE Basin may be obtained from the ACE Basin NERR Research Coordinator.

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:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; *accessed* 12 October 2016.

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. Amanda Fornal and Meghan Miller are 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 staff calculate the concentrations as mg/L based on atomic masses of 14.006 and 30.973 for N and P, respectively. Concentrations reported from the chemistry lab are multiplied by 0.014006 and 0.030973 to yield concentrations in mg/L for N and P, respectively. CHLA_N sample concentrations are an average of two replicate subsamples per grab and diel sample, and are calculated in and reported as $\mu\text{g/L}$.

10) Parameter titles and variable names by category –

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:	*Orthophosphate	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:			
	*Chlorophyll-a	CHLA_N	$\mu\text{g/L}$

Notes:

1. Time is coded based on a 2400 clock and is referenced to Standard Time.
2. Reserves have the option of measuring either the NO_2 or NO_3 parameter or they may substitute $\text{NO}_2 + \text{NO}_3$ combined value if they can demonstrate that NO_2 is a minor component relative to NO_3 . ACE NERR staff and the Analytical Laboratory staff have determined that separate NO_2 and NO_3 data were not necessary because the concentration of NO_2 is negligible when compared to the concentration of NO_3 .

11) Measured or calculated laboratory parameters –

a) Parameters measured directly

Nitrogen species:	NH4F, NO23F
Phosphorus species:	PO4F
Other:	CHLA_N

b) Calculated parameters

DIN	NO23F+NH4F
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12) Limits of detection –

The MDLs for NH4, NO23, and PO4 were calculated by analyzing 10 replicate aliquots of stock standards for each parameter. The following equation was then used $\text{MDL} = St(n-1, 1-\alpha=0.99)$. Where, $t(n-1, 1-\alpha=0.99)$ is the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom; n is the number of replicates; and S is the standard deviation of the replicate analysis.

The MDL for chlorophyll a is calculated the same way, except using seven replicate aliquots of ambient water.

Table 1 lists the MDL values from January through December. These values are reviewed and revised annually.

Parameter	Start Date	End Date	MDL	Provided by	Currentness
NO23F	01/01/2016	12/31/2016	0.0021	MRD Algal Group	2016
NH4F	01/01/2016	12/31/2016	0.002	MRD Algal Group	2016
PO4F	01/01/2016	12/31/2016	0.0006	MRD Algal Group	2016
CHLA_N	01/01/2016	03/31/2016	0.06	ACE Basin NERR	2015
CHLA_N	04/01/2016	07/31/2016	0.02	MRD Algal Group	2016
CHLA_N	08/01/2016	12/31/2016	0.06	ACE Basin NERR	2016

13) Laboratory methods –

a) Sampling preparation methods:

The supplies used by the ACE Basin NERR to collect and process water samples are: 1) 1000-ml wide-mouth clear polypropylene bottles; 2) 1000-ml clear polypropylene ISCO bottles, 3) 20-ml scintillation vials and caps; 4) 15-ml polypropylene centrifuge tubes and caps; 5) 20 mL borosilicate culture vials; 6) 60-ml filtering apparatus [polypropylene syringe, syringe plunger and syringe filter holder with 25mm pore size]; and 7) 25 mm glass microfiber filter paper.

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

b) Filtering Process:

The samples were filtered by ACE NERR staff within four hours of collection. A 25 mm diameter 0.7 μm (nominal) pore size glass fiber filter was used to separate the dissolved and particulate constituents of the sample. While wearing gloves one filter was placed in a filter holder using clean forceps to prevent contamination. The sample bottle was gently agitated by 10 inversions to suspend the particulates. The filter syringe was “seeded” with the sample water by rinsing it with sample water. The filter holder was attached to the syringe and 50 ml of agitated sample water was added to the filter apparatus (syringe with attached filter holder). The filter apparatus was positioned over a scintillation vial and filter plunger inserted and slowly pushed upon. Both scintillation vials were seeded with the sample water by filling them with filtered water and then discarded. After filtering the 50 ml, the filter holder was removed from the syringe, covered it and set aside. If sediments and other solids in the sample prevented the filtration of the entire 50 ml, the volume filtered was recorded on a laboratory sheet and the unfiltered portion discarded.

Using a clean filtering apparatus, the filtering process was repeated as above, with the filtered water retained in two scintillation vials. The samples contained in the scintillation vials were placed in a 4°C freezer and moved to a -20°C within 24 hours. They were analyzed within 28 days for dissolved inorganic nutrient concentrations.

The two filters were examined for similar color and coverage of particulates. If similar, then each filter was placed in a labeled centrifuge tube filled with 10 ml of 90% acetone. The tube was capped and covered with foil. If the density and coverage of particulates on one filter was noticeably different than the duplicate filter, both filters were discarded and the filtering process was repeated until two filters of similar color and coverage were obtained. After filtering all of the samples, the centrifuge tubes were placed in a refrigerator set at 4°C and analyzed within 24 hours for chlorophyll *a*.

c) Analytical Methodology:

Nitrogen and phosphorus chemistry was determined with a Lachat™ QuikChem 8000 Flow Injection Nutrient Analyzer equipped with a data logger during 2016. The filtered water was then run through the autoanalyzer. At the beginning of each analysis, the autoanalyzer was calibrated by injecting

calibration standards. The autoanalyzer was calibrated at the beginning of each analysis run. Calibration was done by injecting standards. The autoanalyzer and data logger system prepared a calibration curve by plotting sample response versus standard concentration. The filtered water was then run through the autoanalyzer. The data logger calculated the sample concentrations based on the regression equation and stored the values in a temporary file. At the end of the complete analysis run, the temporary file was then transferred to a computer.

During 2016, chlorophyll chemistry was determined by the acidification and the non-acidification method. The acidification method was performed with a Turner 10-AU-005-CE, and the non-acidification method with the TD-700 fluorometer. The 10-AU-005-CE fluorometer was equipped with Turner Acidification Optical Kit (Daylight White Lamp), while the TD-700 fluorometer was equipped with Turner Non-Acidification Optical Kit (Blue Mercury Vapor Lamp that optimally excite chlorophyll-a at 436nm and minimally excite other interfering compounds), to determine chlorophyll-a values. Both fluorometers were checked with a solid chlorophyll standard before and after every analysis run.

The Turner 10-AU-005-CE fluorometer was used for January-March and August-December, and the following formula was used to calculate chlorophyll-a:
$$(((\text{calibration constant}) \times (\text{acid ratio} / (\text{acid ratio} - 1))) \times (\text{fluorescence before acidification} - \text{fluorescence after acidification}))) \times (\text{volume of acetone} / \text{volume filtered})$$

The Turner TD-700 fluorometer was used for April-July, and the following formula was used to calculate chlorophyll-a: $\text{Fluorescence} \times (\text{volume of acetone} / \text{volume filtered})$

a) Parameter: NH₄

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

Range: 0.355 - 42.836 μM N/L as NH₄

Method Descriptor: The fixed filtrate (<0.7 μm) is used in the procedure to determine the ammonium 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 (Gilbert 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: Water was initially filtered through 25-mm (0.7 μm pore size) glass filter and stored at 4°C up to 24 hours. Samples were relocated to a freezer within 24 hours freezer within 24 hours where they were stored at ≤ -20°C for up to 28 days.

Gilbert, P. and T. Loder: Automated analysis of nutrients in seawater. Technical report WHOI-11-41, 46 pp. Woods Hole, MA: Woods Hole Oceanogr. Inst. 1977

b) 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 NO₃ and/or NO₂

Method Descriptor: The fixed filtrate (<0.7 μm) is used in the procedure to determine the Nitrate and Nitrite concentrations. The combined nitrate-nitrite (NO₃ + NO₂) value is obtained by passing a sample through a copper-cadmium reductor column that reduces the nitrate(NO₃) to nitrite(NO₂), 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 diazonium ion. This compound then couples with N-(1-naphthylethyl) enediamine dihydrochloride to form a reddish-purple azo dye. The dye absorbs at 540 nm. The nitrate concentration is obtained by subtracting the nitrite value from the combined nitrate and nitrite value.

Preservation Method: Water was initially filtered through 25-mm glass filter (0.7 µm pore size) and stored at 4°C up to 24 hours. Samples were relocated to a freezer within 24 hours where they were stored at ≤ -20°C for up to 28 days.

c) Parameter: PO₄

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

Range: 0.161 - 0.12.914 µM N/L as PO₄

Method Descriptor: The fixed filtrate (<0.7 µm) was used in the procedure to determine the orthophosphate concentration. The QuikChem® Method was a modification of the Murphy and Riley (1962) single solution method. Ammonium molybdate and antimony potassium tartrate reacts in an acid medium with phosphate to form an antimonyphospho-molybdate complex. This complex was reduced to an intensely blue colored complex by ascorbic acid. The phosphomolybdate blue complex formed during the reaction is read at a wavelength of 880 nm to determine the value.

Preservation Method: Water was initially filtered through 25-mm (0.7 µm pore size) glass filter and stored at 4°C up to 24 hours. Samples were relocated to a freezer within 24 hours where they were stored at ≤ -20°C for up to 28 days.

d) Parameter: CHLA_N

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

Method Descriptor: The extract was used in the procedure to determine the chlorophyll-a chemistry. Within a 24-hour period the samples were brought to room temperature, centrifuged at 3000 rpm for 10 minutes and then 5 ml were transferred to culture tubes, using a pump pipettor. During January to March and August to December, the extraction was read at 440 nm wavelength, and then the sample was acidified with 0.1 mL (two drops) of 0.1 N HCl solution and re-read at the same wavelength on a Turner 10-AU-005-CE fluorometer. During April to July, the extraction was read at 436 nm wavelength on a Turner TD-700.

Preservation Method: The 25-mm (0.7 µm pore size) glass filters were placed in 15 mL centrifuge tubes (one filter/tube) filled with 10 ml of 90% acetone solution and stored in the freezer at ≤ -20°C for 18-24 hours.

14) Field and Laboratory QAQC programs –

a) Precision:

- i) Field Variability** - Grab samples were collected monthly at each of the four monitoring sites. A water-sampler or hand collection was used to collect two consecutive samples at a depth of 0.3-0.5 meter below the surface. The grab samples were taken on the same day and between mid-ebb and slack-low water (~ 3 hrs before slack-low water to slack-low water).
Diel samples were collected monthly in St. Pierre Creek near the water quality station. Samples were collected every 2 hours and 4 minutes over one lunar day (24 hr 48 min), using an ISCO auto-sampler. Sample collection began at the predicted slack-low, and samples were collected at a depth of 0.5 meters below the surface. Diel samples do not have replicates.
- ii) Laboratory Variability** - One replication for grab/diel NH₄F, NO₂3F, and PO₄F; two filter replicates for CHLA_N.
- iii) Inter-organizational splits** - No splits: all samples were analyzed by the same laboratory.

b) Accuracy:

- i) Sample Spikes** - The laboratory does not run sample spikes but does run known standards and blank checks (DI water) during the analysis.
- ii) Standard Reference Material Analysis** - Our laboratory is not an EPA lab, so they do not receive samples.
- iii) Cross Calibration Exercises** - ACE Basin NERR has participated in the cross calibration exercises but one has not been conducted since 2011.

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
GSM	See metadata

Sensor errors

SBL	Value below minimum limit of method detection
SCB	Calculated value could not be determined due to a below MDL component
SCC	Calculation with this component resulted in a negative value
SNV	Calculated value is negative
SRD	Replicate values differ substantially
SUL	Value above upper limit of method detection

Parameter Comments

CAB	Algal bloom
CDR	Sample diluted and rerun

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

Record comments

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

Cloud cover

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

Precipitation

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

Tide stage

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

Wave height

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

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast

S	from the south				
SSW	from the south southwest				
SW	from the southwest				
WSW	from the west southwest				
W	from the west				
WNW	from the west northwest				
NW	from the northwest				
NNW	from the north northwest				
<i>Wind speed</i>					
WS0	0 to 1 knot				
WS1	> 1 to 10 knots				
WS2	> 10 to 20 knots				
WS3	> 20 to 30 knots				
WS4	> 30 to 40 knots				
WS5	> 40 knots				

17) Other Remarks/Notes –

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

Variable	Method	Duration
Ammonium (NH4F)	Storage at 4°C Freeze at ≤ -20 °C	24 hrs 28 days
Nitrate + Nitrite (NO23F)	Storage at 4°C Freeze at ≤ -20 °C	24 hrs 28 days
Orthophosphate (PO4F)	Storage at 4°C Freeze at ≤ -20 °C	24 hrs 28 days
Chlorophyll-a (CHLA_N)	Storage at 4°C	24 hr

Sample hold times

01/13/2016	01/14/2016	01/14/2016	01/14/2016	01/14/2016
02/10/2916	02/11/2016	02/11/2016	02/11/2016	02/11/2016
03/09/2016	03/10/2016	03/10/2016	03/10/2016	03/10/2016
04/06/2016	04/07/2016	04/07/2016	04/07/2016	04/07/2016
05/18/2016	05/20/2016	05/20/2016	05/20/2016	05/19/2016
06/15/2016	06/28/2016	06/28/2016	06/28/2016	06/16/2016
07/13/2016	07/27/2016	07/27/2016	08/10/2016	07/14/2016
08/17/2016	08/16/2016	08/16/2016	08/16/2016	08/18/2016
09/28/2016	10/13/2016	10/13/2016	10/13/2016	09/29/2016
10/26/2016	10/28/2016	10/28/2016	11/07/2016	10/27/2016
11/16/2016	11/18/2016	11/18/2016	11/23/2016	11/17/2016
12/14/2016	12/16/2016	12/16/2016	12/16/2016	12/15/2016
ISCO Samples				
01/13/2016	01/14/2016	01/14/2016	01/14/2016	01/14/2016
02/10/2916	02/11/2016	02/11/2016	02/11/2016	02/11/2016
03/09/2016	03/10/2016	03/10/2016	03/10/2016	03/10/2016
04/06/2016	04/07/2016	04/07/2016	04/07/2016	04/07/2016
05/18/2016	05/20/2016	05/20/2016	05/20/2016	05/19/2016
06/15/2016	06/28/2016	06/28/2016	06/28/2016	06/16/2016
07/13/2016	07/27/2016	07/27/2016	08/10/2016	07/14/2016
08/17/2016	08/16/2016	08/16/2016	08/16/2016	08/18/2016
09/28/2016	10/13/2016	10/13/2016	10/13/2016	09/29/2016
10/26/2016	10/28/2016	10/28/2016	11/07/2016	10/27/2016
11/16/2016	11/18/2016	11/18/2016	11/23/2016	11/17/2016
12/14/2016	12/16/2016	12/16/2016	12/16/2016	12/15/2016

Nutrient Equipment History

Turner 10-AU-005-CE Fluorometer

1994 - Fluorometer (S/N: 0057 LRXX) was purchased in **April**.

2004 - Fluorometer was sent to Turner designs for a standard repair in **November**.

2012 - Fluorometer was calibrated in **July**.

2013 - Fluorometer was calibrated in **May**.

2014 - Fluorometer was sent in Turner designs for a standard repair in **October**.

2014 - Calibration during **December** but was not successful, so unit was re-set to default settings.

2016 - Fluorometer was calibrated in **July**.

2016 - Solid standard was replaced in **August**.

Turner TD-700 Fluorometer

2015 - Fluorometer was calibrated in **May**.

2016 - Fluorometer was calibrated in **June**.

Data Editing/Flagging Notes: Organized by Sample type, and Code

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. Therefore, we do not assume that rain occurred at all the nutrient monitoring stations if rain was recorded by the Reserve weather station.

Significant Weather Event	Date Started	Date Ended	Max Wind Speed
Hurricane Hermine	August 28, 2016	September 3, 2016	80 mph
Tropical Storm Julia	September 13, 2016	September 19, 2016	40 mph
Hurricane Matthew	September 28, 2016	October 9, 2016	160 mph

From 02/05/2016 at 00:00 to 02/18/2016 at 23:45, water quality was affected by a significant rain event. A decrease in salinity values were attributed to the high streamflow in the South Edisto River caused by the record rains during early-mid February.

From 09/01/2016 at 00:00 to 09/03/2016 at 23:45, water quality was affected by Hurricane Hermine.

From 09/14/2016 at 00:00 to 09/15/2016 at 23:45, water quality was affected by Tropical Storm Julia.

From 10/07/2016 at 00:00 to 10/08/2016 at 23:45, water quality was affected by Hurricane Matthew.

Grab Samples: (Monitoring Program 1)

Edisto Island

Rejected Data (Flag <-3>)

Missing Data (Flag <-2>)

Suspect Data (Flag <1>)

The differences in field replicates for the identified parameter during the following sampling events were suspect. The percent difference between field replicates was greater than 50. The values are flagged as <1> [SRD] (CSM).

Ammonium	06/15/2016 (0.0494 and 0.0185 mg/L)
Nitrate+Nitrite	06/15/2016 (0.0279 and 0.0163 mg/L)
Dissolved Inorganic Nitrogen	06/15/2016 (0.077 and 0.035 mg/L)

Passed Initial QAQC Checks (Flag <0>)

The ortho-phosphate values (0.0579 and 0.0581 mg/L) during the November 16 sampling event were not suspect because the values also spiked at the St. Pierre site during this sampling event. The values are flagged as <0> (CSM).

Fishing Creek

Rejected Data (Flag <-3>)

Missing Data (Flag <-2>)

Suspect Data (Flag <1>)

The nitrate+nitrite values (0.1460 and 0.1550 mg/L) during the April 6 sampling event were suspect due to the values were approximately two times the other values for that year at Fishing Creek. A similar spike was not observed at any of the other sites. Potential cause for this is unknown. The values are flagged as <1> [GQS] (CSM).

The differences in field replicates for the identified parameter during the following sampling events were suspect. The percent difference between field replicates was greater than 50. The values are flagged as <1> [SRD] (CSM).

Ortho-phosphate	04/06/2016 (0.0256 and 0.0096 mg/L)
Nitrate+Nitrite	10/26/2016 (0.0130 and 0.0271 mg/L)

Passed Initial QAQC Checks (Flag <0>)

Mosquito Creek

Rejected Data (Flag <-3>)

Missing Data (Flag <-2>)

Suspect Data (Flag <1>)

The nitrate+nitrite values (0.2739 and 0.2369 mg/L) during the July 13 sampling event were suspect due to the values were approximately an order of magnitude higher than the other values for that year at Mosquito Creek. A similar spike was not observed at any of the other sites. Potential cause for this is unknown. The values are flagged as <1> [GQS] (CSM).

The differences in field replicates for the identified parameter during the following sampling events were suspect. The percent difference between field replicates was greater than 50. The values are flagged as <1> [SRD] (CSM).

Nitrate+Nitrite	03/09/2016 (0.0201 and 0.0355 mg/L)
Ortho-phosphate	04/06/2016 (0.0204 and 0.0400 mg/L)

Passed Initial QAQC Checks (Flag <0>)

St. Pierre Creek

Rejected Data (Flag <-3>)

Missing Data (Flag <-2>)

Suspect Data (Flag <1>)

The ammonium values (0.176 and 0.166 mg/L) during the July 13 sampling event were suspect due to the spike in values (approximately two times higher) which was not observed at other ACE sites. The values are flagged as <1> [GQS] (CSM).

The differences in field replicates for the identified parameter during the following sampling events were suspect. The percent difference between field replicates was greater than 50. The values are flagged as <1> [SRD] (CSM).

Chlorophyll-a 09/28/2016 (0.863 and 3.433 ug/L)

Passed Initial QAQC Checks (Flag <0>)

The ortho-phosphate values (0.0614 and 0.0606 mg/L) during the November 16 sampling event were not suspect because values also spiked at the Edisto Island during this sampling event. The values are flagged as <0> (CSM).

Diel Samples: St. Pierre Creek (Monitoring Program 2)

Rejected Data (Flag <-3>)

The ortho-phosphate spike (0.3740 mg/L) at 14:50 on August 16 during the August 16-17 sampling event was rejected. After looking at the five year average, this point is 108% greater than the next highest orthophosphate value. The value is flagged as <-3> [GQD] (CSM).

Missing Data (Flag <-2>)

The ISCO sampler did not collect samples on September 27 at 09:33 and 11:37 during the September 27-28 sampling event. It is not known why the sampler did not collect water samples during these time periods. The values are flagged as <-2> [GDM] (CSM).

The DIN could not be calculated for September 27 at 09:33 and 11:37 during the September 27-28 sampling event because no samples were collected due to instrument failure. It is not known why the sampler did not collect water samples during these time periods. The values are flagged as <-2> [GCM] (CSM).

Suspect Data (Flag <1>)

The nitrate+nitrite and dissolved organic nitrogen values at 15:32 (0.102 mg/L and 0.114 mg/L, respectively) on May 17 during the May 17-18 sampling event was suspect due to the value being over two times higher than any other value during that time period. The value is flagged as <1> [GQS] (CSM).

Passed Initial QAQC Checks (Flag <0>)

The nitrate+nitrite values 04:35 (0.095 mg/L) and 16:59 (0.077 mg/L) on February 9 during the February 9-10 sampling event were not suspect due to a rain event that affected the discharge rate on the Edisto River (see Blanket Statement). The values are flagged as <0> (CSM).

The ammonium values during the following sampling times were not suspect although they are much higher than other values during those deployments. In both cases, the values were recorded around low tide when values are usually the highest. The values are flagged as <0> (CSM).

07/12/2016 @ 07:06 (0.179 mg/L)

12/13/2016 @ 01:14 (0.172 mg/L)