ACE Basin (ACE) NERR Nutrient Metadata
January-December 2007
Latest Update: November 15, 2011

I. Data Set & Research Descriptors

1. Principal investigator & contact persons:

Address: SCDNR/Marine Resources Division
217 Fort Johnson Road
Charleston, SC 29422
(843) 953-9820 [phone]

ACE Basin NERR Research station
15717 Bennett's Point Road
Green Pond, SC 29441
(843) 844-8822 [phone & fax]

a) Reserve Contact:

Dr. Elizabeth Wenner, Research Coordinator
E-mail: wennere@dnr.sc.gov , Phone: (843) 953-9226
Saundra Upchurch, Reserve Biologist
E-mail: upchurchs@dnr.sc.gov , Phone: (843) 953-9223
Patrick Williams, Reserve Technician
E-mail: williamsp@dnr.sc.gov, Phone: (843) 953-9225
Justin L. Hart, Water Quality Technician
E-mail: hartj@dnr.sc.gov, Phone: (843) 953-9225

b) Laboratory Contact:

Kenneth C. Hayes, Environmental Health Specialist
Aquatic Biology Section - Bureau of Water
217 Ft Johnson Road - PO Box 12559
Charleston, SC 29422
Phone: (843) 953-9075
E-mail: khayes@belle.baruch.sc.edu

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 nutrient diel 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 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*).

In-situ measurements of dissolved oxygen (mg/L), salinity (ppt), pH, and air and water temperatures (degree 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 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 and the Atlantic Ocean. The NERR consists of approximately 180,000 acres of diverse estuarine and freshwater wetlands and uplands, which provide habitats for fish and wildlife.

Two sampling sites are in tributaries of the South Edisto River. One site is in a tributary of the North Edisto River and one is in a tributary of both the South Edisto and Ashepoo rivers, contributing to freshwater input to each site. The average annual tidal range at all sites is approximately 2.0 m (6.5 feet), with a maximum of 2.36 m (7.8 feet) and a minimum of 1.39 m (4.6 feet). The bottom habitat at each of the four sites consists of mud intermixed with dead shell hash. A more detailed description of each site is provided below.

Station A (Big Bay Creek [BB]) - GPS coordinates: 32.4941N and -80.3241W

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 2007, the mean depth at the station was 3.4 m (11.15 ft), and the mean salinity was 31.78 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.

Station B (St. Pierre Creek [SP]) - GPS coordinates: 32.5233N and -80.3568W
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 2007, the mean depth at the station was 3.19 m (10.47 ft), and the mean salinity was 30.73 parts per thousand (ppt).

Station C (Fishing Creek [FC]) – GPS coordinates: 32.6358 N and -80.3655W
This site is in a tidal creek, which is a tributary of Fishing Creek. Located within the boundaries of Jehossee Island, a protected Wildlife Management Area, this site is surrounded by extensive big cordgrass (*Spartina cynosuroides*) marsh and vast mud flats. The upland area of the island is dominated by slash pine (*Pinus taeda*) and live oak (*Quercus virginiana*). The tidal wetlands on the island were rice fields during the Antebellum Era, and they are now managed as waterfowl habitat by the U.S. Fish and Wildlife Service. These managed wetlands, or impoundments, are not subject to pesticides and herbicides. With relatively light boat traffic and sparse development, this station is designated as a "control" site. In 2007, the mean depth at the station was 3.24 m (10.63 ft), and the mean salinity was 12.97 parts per thousand (ppt).

Station D (Mosquito Creek [MC]) – GPS coordinates: 32.5558 N and -80.4380W
This site is in Mosquito Creek, which is a tributary of both the South Edisto and Ashepoo rivers. Surrounded by agricultural lands and low-density residential housing, this station is designated as a “treatment” site. Sources of nonpoint source pollution along the creek include managed wetlands (impoundments); private docks that are constructed of creosote, concrete and Wolmanized pilings; public boat ramp and dock; and a commercial seafood and fueling area with three commercial shrimp boats. Several impoundment trunks drain into the creek, thus increasing the nutrient load and possibly introducing herbicides and pesticides to the water. The salt marsh at the site is dominated by smooth cordgrass (*Spartina alterniflora*) and black needlerush (*Juncus roemerianus*). Upland fringe areas consist of cabbage palmetto (*Sabal palmetto*), live oak (*Quercus virginiana*) and slash pine (*Pinus taeda*). In 2007, the

mean depth at the station was 4.22 m (13.87 ft), and the mean salinity was 22.69 parts per thousand (ppt).

5. Coded variable definitions:

Each individual sample is given a 3 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	01/17/2007	1033	01/17/2007	1034
BB	02/14/2007	0937	02/14/2007	0938
BB	03/15/2007	0848	03/15/2007	0849
BB	04/12/2007	0822	04/12/2007	0823
BB	05/15/2007	0940	05/15/2007	0941
BB	06/14/2007	1015	06/14/2007	1016
BB	07/11/2007	0758	07/11/2007	0759
BB	08/09/2007	0921	08/09/2007	0922
BB	09/06/2007	0808	09/06/2007	0809
BB	10/09/2007	1043	10/09/2007	1045
BB	11/06/2007	1100	11/06/2007	1101
BB	12/06/2007	0931	12/06/2007	0932

Site	Start Date	Rep 1 Time	Start Date	Rep 2 Time
SP	01/17/2007	1102	01/17/2007	1103
SP	02/14/2007	1007	02/14/2007	1008
SP	03/15/2007	0918	03/15/2007	0919
SP	04/12/2007	0858	04/12/2007	0859
SP	05/15/2007	1017	05/15/2007	1018
SP	06/14/2007	1044	06/14/2007	1045
SP	07/11/2007	0833	07/11/2007	0834
SP	08/09/2007	0959	08/09/2007	1000

SP	09/06/2007	0831	09/06/2007	0832
SP	10/09/2007	1117	10/09/2007	1119
SP	11/06/2007	1130	11/06/2007	1131
SP	12/06/2007	1010	12/06/2007	1011

Site	Start Date	Rep 1 Time	Start Date	Rep 2 Time
FC	01/17/2007	1245	01/17/2007	1246
FC	02/14/2007	1147	02/14/2007	1148
FC	03/15/2007	1033	03/15/2007	1034
FC	04/12/2007	1016	04/12/2007	1017
FC	05/15/2007	1138	05/15/2007	1139
FC	06/14/2007	1230	06/14/2007	1231
FC	07/11/2007	1053	07/11/2007	1054
FC	08/09/2007	1045	08/09/2007	1046
FC	09/06/2007	0915	09/06/2007	0916
FC	10/09/2007	1204	10/09/2007	1206
FC	11/06/2007	1235	11/06/2007	1236
FC	12/06/2007	1135	12/06/2007	1136

Site	Start Date	Rep 1 Time	Start Date	Rep 2 Time
MC	01/17/2007	1159	01/17/2007	1200
MC	02/14/2007	1216	02/14/2007	1218
MC	03/15/2007	1127	03/15/2007	1128
MC	04/12/2007	1040	04/12/2007	1042
MC	05/15/2007	1221	05/15/2007	1223
MC	06/14/2007	1223	06/14/2007	1224
MC	07/11/2007	1129	07/11/2007	1130
MC	08/09/2007	1017	08/09/2007	1019
MC	09/06/2007	0954	09/06/2007	0957
MC	10/09/2007	1135	10/09/2007	1136
MC	11/06/2007	1010	11/06/2007	1011
MC	12/06/2007	1304	12/06/2007	1305

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	01/10/2007	0622	01/11/2007	0710
SP	02/07/2007	0500	02/08/2007	0548
SP	03/07/2007	0355	03/08/2007	0343
SP	04/19/2007	0330	04/20/2007	0418
SP	05/02/2007	0153	05/03/2007	0241

SP	06/06/2007	0538	06/07/2007	0426
SP	07/17/2007	0359	07/17/2007	0447
SP	08/15/2007	0316	08/16/2007	0404
SP	09/12/2007	0205	09/13/2007	0253
SP	10/17/2007	0505	10/18/2007	0553
SP	11/14/2007	0430	11/15/2007	0518
SP	12/12/2007	0302	12/12/2007	0350

7. Associated researchers and projects:

The ACE Basin NERR received initial funding from the U.S. Environmental Protection Agency to establish a National Atmospheric Deposition Program site in the Reserve. Sampling efforts began on January 1, 2002 and ended on December 25 2007. Weekly precipitation samples were collected and analyzed for atmospheric pollutants. The precipitation collector is located on Bear Island, a Wildlife Management Area inside the NERR.

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.

On September 19, 2006 the Algal Ecology Lab began screening water samples from the ACE BASIN. Algal assemblages are being identified at these sites to monitor these areas and identify any harmful algal blooms. If a bloom is present, the fixed sample will be counted to determine algal density. These water samples are also being processed for HPLC (High Performance Liquid Chromatography), which will identify the pigments that are present in the water at that time, and can be later analyzed for estimates of algal community biomass.

In February 2006, the ACE Basin NERR installed a RASSL – Remote Access Satellite Sensor Link – transmitter unit to the deployment structure at the Mosquito Creek water quality sampling station, and in August 2006 installed an additional transmitter unit at the Big Bay station. North Star Science and Technology, funded by a CITCEET grant, designed a compact and field rugged satellite communicator. The transmitter unit, compatible with YSI 6 series data sondes, communicates directly to the sonde and asks the sonde to take an additional reading once an hour. This additional reading is not stored by the data sonde and does not interfere with the scheduled SWMP data collection. The additional hourly reading is then transmitted via a satellite link. The provisional data is posted to a secure website provided and maintained by North Star Science and Technology. December 2007 marked the last month of the RASSLs operating due to funding restrictions. The transmitters have not been removed in hopes that they will be utilized in the near future.

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 data is gathered 24/7 and is transmitted to the Centralized Data Management Office (CDMO). Historic water quality, nutrient, and weather data can be obtained at http://cdmo.baruch.sc.edu/QueryPages/viewstations.cfm?Site_ID=ace.

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:

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 the 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 water quality and nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (See Section 1 *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, Microsoft Excel spreadsheet format and comma-delimited 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; 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 automatically flags and codes values below MDL; calculates parameters chosen by the user and automatically flags for component values below MDL and negative values; allows the user to apply QAQC flags and codes to the data;

graphs selected parameters for review; append files; and export the resulting data files to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

The laboratory data sheets are checked against the laboratory analysis reports for transcription errors and edited as needed. 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/coded 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 unpreserved samples. Justin Hart is 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-1 based on atomic weights 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	ug/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 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. ACE NERR staff and the Analytical Laboratory staff determined that separate NO_2 and NO_3 data were not necessary. The concentration of NO_2 is negligible when compared to the concentration of NO_3.

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 current MDL values; 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	1/1/07	12/31/07	0.0010
NH4F	1/1/07	12/31/07	0.0006
NO23F	1/1/07	12/31/07	0.0002

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

Parameter	Start Date	End Date	MDL in ug/L
CHL-A	1/1/07	12/31/07	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 25mm pore size]; 7) 25 mum 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. 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 4^{o}C. 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.

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 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, and stored at 4°C up to 14 days. Prior to analysis, the filtrate (25 mm) is passed through a 0.7 μm 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 4°C up to 14 days. Prior to analysis, the filtrate (25 mm) is passed through a 0.7 μm 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 880nm to determine the value.

Preservation Method: Water is initially filtered through 25-mm glass filter and stored at 4°C up to 14 days. Prior to analysis, the filtrate (25 mm) is passed through a 0.7 μm 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 4°C for 18-24 hours.

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

*The -4 Outside Low Sensor Range flag was added to the 2007 dataset in August of 2011. See the Other Remarks section for more details.

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 Value calculated with a value that is below the MDL
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

1) Missing 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 with -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.

*The 2007 dataset was updated on August of 2011 to include the -4 Outside Low Sensor Range flag. The 2007 data published prior to that time used the -3 Rejected data flag with the SBL and SCB QAQC codes to indicate that data were below the minimum detection limit. These flag code

b) During the February 2007 St. Pierre nutrient diel samplings, the ISCO malfunctioned and sample numbers one (02/07/2007 05:00), six (02/07/2007 15:20), seven (02/07/2007 17:24), eight (02/07/2007 19:28), 12 (02/08/2007 03:44), and thirteen (02/08/2007 05:48) were not taken. These missing samples have been marked as missing <-2>.

c) During the April 2007 St. Pierre nutrient diel samplings, the ISCO malfunctioned and sample numbers 11 (04/20/2007 00:10) and 12 (04/20/2007 02:14) were not taken. These missing samples have been marked as missing <-2>.

d) During the May 2007 St. Pierre nutrient diel samplings, the ISCO malfunctioned and sample numbers six (06/06/2007 14:58), and seven (06/06/2007 17:02) were not taken. These missing samples have been marked as missing <-2>.

e) All November St. Pierre nutrient diel samples were held beyond their holding time before being analyzed. They have been marked as suspect <1>.

2) 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 at all the weather stations in the Reserve.