Rookery Bay (RKB) National Estuarine Research Reserve (NERR) Nutrient Metadata (January 2008 – December 2008)

Latest Update: August 13, 2013

I. Data Set and Research Descriptors

1. Principal investigator(s) and contact persons

a. Reserve Contact

Christina Ottman, Research Coordinator
Rookery Bay NERR
300 Tower Road
Naples, FL 34113-8059
Phone: (239) 417-6310
e-mail: Christina.Ottman@dep.state.fl.us

b. Laboratory Contact

Joseph N. Boyer, Ph.D., Associate Director and Scientist
Southeast Environmental Research Center
Florida International University
Miami, FL 33199
Phone: (305) 348-3095
e-mail: boyerj@fiu.edu

c. System Wide Monitoring Program Technicians

Vicki K. McGee, former Water Quality Program Manager (responsible for 2008 sample processing and data management)
Christina Panko Graff, current Water Quality Program Manager (responsible for final 2008 data submission)
Rookery Bay NERR
300 Tower Road
Naples, FL 34113-8059
Phone: (239) 417-6397
e-mail: vicki.mcgee@dep.state.fl.us

2. Research Objectives – The four stations were in estuaries affected by watersheds demonstrating different patterns of land-use. Their placement addresses priority resource management issues that are identified in the Reserve's management plan. Specifically, the data from these stations provide valuable information concerning the effects of land-use activities on the quantity, quality and timing of freshwater inflow into the Reserve. Each bay studied demonstrates a different pattern of altered freshwater inflow.

a. Monthly grab- The principal objective of the monthly grab sampling was to determine spatial and temporal differences in water quality between sites representing different land-use patterns.

b. Diel Sampling Program – The principal objective of the diel sampling was to quantify temporal variability over a tidal cycle and determine the impact of tidal water exchange within Henderson Creek (the main source of freshwater into Rookery Bay).

3. Research Methods- From January to September 2008, grab samples were collected in coordination with the Southeastern Environmental Research Center (SERC) Water Quality Monitoring Program at Florida International University (FIU). All methods of bottle and equipment cleaning, collection, preservation, and chemical analysis were based on the SERC Quality Assurance (QA) Plan (revision 12/18/07) or SERC Field QA Plan (effective 11/20/07) and associated Standard Operating Procedures (SOPs). Diel samples were collected and processed by Rookery Bay staff, Vicki McGee. From October –December 2008, both grab and

diel samples were collected and processed by Rookery Bay staff, Vicki McGee, and sent to the SERC lab but they were no longer collected as part of SERC's Water Quality Monitoring Program.

a. Monthly Grab Sampling Program –

From January-September 2008:

Monthly grab samples were collected within 50 meters of all four System Wide Monitoring Program (SWMP) water quality stations (Henderson Creek, Middle Blackwater River, Faka Union Bay and Fakahatchee Bay). Each month duplicate grab samples were taken at Henderson Creek, Middle Blackwater, and Fakahatchee Bay water quality stations. Only one grab sample was collected at Faka Union Bay. This is a deviation from the National Estuarine Research Reserve System Nutrient and Chlorophyll Monitoring Program and Database Design SOP v 1.3 which requires duplicate grabs at all four of the water quality stations or triplicate grabs at one randomly chosen station every other month. Slack low tide was generally not considered for the grab sampling events. Rainfall conditions prior to grab sampling were not considered. Typically three types of water samples were taken: 1) filtered soluble nutrient samples; 2) chlorophyll *a* samples; and 3) unfiltered total nutrient samples. All sample bottles and associated sampling equipment were cleaned as per section 6.2 of SERC Field QA Plan. Grab samples for dissolved nutrient analysis were collected 10 cm below the surface using pre-washed and sample-rinsed (x 3) 150 ml syringes. The water samples were filtered in the field using 25 mm (0.7 µm) glass microfiber filters. Pre-washed and sample-rinsed 60 ml HDPE bottles were filled to the neck with the filtrate, capped, and immediately stored in a cooler with ice. The wet filters (25 mm / 0.7 µm GF/F filters), used for chlorophyll *a* analysis, were placed in 2 ml plastic micro-centrifuge tubes to which 1.5 ml of 90% acetone was added. They were then capped and put into a dark amber bottle on ice for transport. For the unfiltered total nutrient samples, pre-washed and sample-rinsed 125 ml HDPE bottles were inverted 10 cm below the surface and filled to the neck. The unfiltered samples were kept at ambient temperature in the dark.

Field water quality parameters were measured with a YSI 600-xl multi-parameter data logger and a hand held display (YSI model 650). Salinity (ppt) and temperature (°C) were measured using a combination salinity-conductivity-temperature probe (YSI model 6560); dissolved oxygen (DO, mg/L) was measured using a Rapid Pulse-Clarke Type probe (YSI model 6562), and pH was measured using a (YSI model 6561) as per method SM4500HB SERC Quality Manual. Equipment calibration and field verification were done according to FDEP SOP 001/01. From January – June 2008, field parameter data reported were from bottom readings. From July – September 2008, it is unclear whether the field data reported were from surface or bottom readings. It is unclear for the entire year whether pH data were from surface or bottom readings. No field data were reported for the remainder of the year.

From October-December 2008:

Monthly grab samples were collected at the exact location of the SWMP water quality stations. However, a duplicate grab sample was taken at only one randomly chosen station each month. This is a deviation from the National Estuarine Research Reserve System Nutrient and Chlorophyll Monitoring Program and Database Design SOP v 1.3 as stated above. Three types of water samples were taken: 1) filtered soluble nutrients; 2) chlorophyll *a*; and 3) unfiltered total nutrients. All the sample bottles and associated sampling equipment were cleaned with phosphate-free soap, rinsed with tap water, soaked in 10% HCL for at least 3 hours, rinsed with deionized water, and then air dried. The 25 mm / 0.7 µm GF/F filters were pre-soaked in deionized water for up to 24 hours before being loaded into the filter assemblies. All other field collection methods were the same as above. Surface physical/chemical water quality parameters were not measured.

b. Diel Sampling Program - Monthly diel samples (10) were collected at the depth of the water quality datasonde (6 inches above the bottom) every 2.5 hours over a lunar day (24hr:48 min) using an ISCO model 3700FR refrigerated auto-sampler. The sampler was stationed at the end of the Rookery Bay dock, approximately 100 meters from the water quality station. For each sampling event, collection began at 8 am and ended at 6:30 am the following day over the course of a tidal cycle. Prior to sampling, the polyethylene bottles were washed using (Liqui-Nox® soap), soaked in an acid bath (10% HCL) for at

least 3 hours, rinsed 3-6 times with tap water and distilled-deionized water, and then air dried. The siphon hose was rinsed 3 times with ambient water prior to setting up and running the auto-sampler.
Sample filtration: In the lab, each polyethylene sample bottle was shaken to redistribute sediments on the bottom. The 25 mm / 0.7µm glass microfiber filters (Whatman GF/F) were pre-soaked in deionized water for up to 24 hours before loading into the filter assembly. Using a 60 ml syringe, 30 ml of sample water was filtered into a 30 ml Nalgene/HDPE sample bottle and labeled. This was done for all 10 water samples.
Chlorophyll a: A total of 120 ml of the water sample was passed through the filter (unless noted on Chain-of- Custody sheets). Air was forced through the filter three times to aid in drying the filter. Using forceps, the filter was carefully folded and transferred to a 2 ml micro-centrifuge tube and the tube was filled with 90% acetone (approx. 1.5 ml). The tube was labeled and placed in an amber Nalgene HDPE bottle. This procedure was repeated for all 10 water samples collected from the ISCO sampler. The samples were then transported in a cooler on ice to the analytical laboratory.

4. Site location and character-

Lower Henderson Creek (rkblhnut)– This site is located at the mouth of Henderson Creek. While this station receives most of its freshwater from a canal system that drains a watershed area approximately 50% development versus natural landscape, a weir controls most of the freshwater flow. This structure has been upgraded to mimic more natural conditions. The water quality data logger is located within the creek channel at the "manatee caution" marker. The diel samples were taken off the Rookery Bay Dock located within Henderson Creek approximately 100 meters from the water quality station.

The creek bottom is comprised mostly of fine sand and mud. The dominant vegetation near the sampling site is red mangrove. Watershed activities that potentially impact the site include non-point source pollution from road runoff, drift of mosquito control pesticides, and runoff from upstream agricultural areas as well as leachate from nearby residential septic systems.

Salinity Range: 0 – 40 ppt
Tidal Range: 0 – 2.7 meters
Average depth (mid-channel at MHW): 2.0 meters
Position: Latitude: 26.0257 N
Longitude: 81.7332 W

Middle Blackwater River (rkbmbnut) - This site is located mid-way down the river at navigational marker #17 within the channel. The "Middle" Blackwater labeling is to distinguish it from other historical sites. The substrate within the channel is a mixture of silt, sand, and oyster shell. Red mangroves are the dominant vegetation at the site. Upstream influences consist of the Collier-Seminole State Park's boat basin, SR 41 canal, and some agricultural influences. Additionally to the northeast of Middle Blackwater's watershed, canals and roads were built during the 1960's for a subdivision (Southern Golden Gate Estates) that fell through. This failed subdivision has altered overland sheet-flow reducing the amounts of freshwater flowing to this estuary. Restoration work (Picayune Strand Restoration Project) is currently underway to restore a near- natural water flow regime to the watershed and the receiving estuaries.

Salinity Range: 0 – 42 ppt
Tidal Range: 0.2 – 1.8 meters
Average Depth at MHW: 2.0 meters
Position: Latitude: 25.9343 N
Longitude: 81.5946 W

Faka Union Bay (rkbfunut) – This site is located at the mouth of the Faka Union Canal at the "Manatee Caution" marker within the main channel. The substrate within the channel is a mixture of sand and silt. Red mangrove forest and spoil islands dominate the area around the canal. Upstream influences consist of Port-of-the Islands development and marina. The upstream flow consists of an elaborated canal system (formerly

Southern Golden Gate Estates Drainage basin, now Picayune Strand- a restoration project). This system has altered natural freshwater flow into Faka Union Bay.

Salinity Range: 0 – 42 ppt
Tidal Range: 0.2 – 1.6 meters
Average Depth at MHW: 2.0 meters
Position: Latitude: 25.9005 N
Longitude: 81.5159 W

Fakahatchee Bay (rkbfbnut)– This site is located between the mouths' of the Fakahatchee River and the East River. The substrate within the channel is a mixture of sand, shell and silt. Red mangrove forests are the dominant vegetation. Upstream there are minimal influences from the Picayune Strand State Forest with non-point source pollutants possible from the culverts under I-75 and US 41. Fakahatchee Strand State Preserve and Big Cypress National Park manage the headwaters of Fakahatchee Bay.

Salinity Range: 0.7 – 43 ppt
Tidal Range: 0.2 – 1.8 meters
Average Depth at MHW: 2.0 meters
Position: Latitude: 25.8922 N
Longitude: 81.4770 W

5. Code variable definitions-

rkblhnut **=** Rookery Bay Lower Henderson Creek nutrients (monthly grabs and diel sampling)
rkbmbnut = Rookery Bay Middle Blackwater River nutrients (monthly grabs)
rkbfunut = Rookery Bay Faka Union Bay nutrients (monthly grabs)
rkbfbnut = Rookery Bay Fakahatchee Bay nutrients (monthly grabs)

Monitoring Codes:

Monitoring codes were established for the table to indicate which type of sampling procedure was used:
1 = Grab Samples
2 = Diel Samples
Replicate grab samples were denoted as 1 for the first sample and 2 for the second sample. Since 1 diel sample was collected every 2.5 hrs, the replicate number was always denoted as 1.

6. Data Collection Period- The System Wide Monitoring Program nutrient sampling began in January 2002.

Monthly Grab Sampling

rkbfunut		
rkbfunut	01/15/2008 14:52	01/15/2008 14:53
rkbfunut	02/20/2008 10:28	02/20/2008 10:29
rkbfunut	03/12/2008 11:17	03/12/2008 11:18
rkbfunut	04/26/2008 15:00	04/26/2008 15:01
rkbfunut	05/19/2008 11:48	05/19/2008 11:49
rkbfunut	06/17/2008 12:36	06/17/2008 12:37
rkbfunut	07/22/2008 11:09	07/22/2008 11:10
rkbfunut	08/26/2008 11:09	08/26/2008 11:10
rkbfunut	09/23/2008 10:19	09/23/2008 10:20
rkbfunut	10/30/2008 11:19	10/30/2008 11:20
rkbfunut	11/25/2008 11:15	11/25/2008 11:16
rkbfunut	12/18/2008 11:12	12/18/2008 11:13

rkbmbnut

rkbmbnut	01/15/2008 14:03	01/15/2008 14:04
rkbmbnut	02/20/2008 09:08	02/20/2008 09:09
rkbmbnut	03/12/2008 10:07	03/12/2008 10:08
rkbmbnut	04/26/2008 14:20	04/26/2008 14:21
rkbmbnut	05/19/2008 10:40	05/19/2008 10:41
rkbmbnut	06/17/2008 10:05	06/17/2008 10:06
rkbmbnut	07/22/2008 09:54	07/22/2008 09:55
rkbmbnut	08/26/2008 10:05	08/26/2008 10:06
rkbmbnut	09/23/2008 09:44	09/23/2008 09:45
rkbmbnut	10/30/2008 10:45	10/30/2008 10:46
rkbmbnut	11/25/2008 10:30	11/25/2008 10:31
rkbmbnut	12/18/2008 10:25	12/18/2008 10:30

rkbfbnut

rkbfbnut	01/15/2008 15:09	01/15/2008 15:10
rkbfbnut	02/20/2008 10:49	02/20/2008 10:50
rkbfbnut	03/12/2008 11:36	03/12/2008 11:37
rkbfbnut	04/26/2008 15:14	04/26/2008 15:15
rkbfbnut	05/19/2008 12:06	05/19/2008 12:07
rkbfbnut	06/17/2008 12:47	06/17/2008 12:48
rkbfbnut	07/22/2008 11:20	07/22/2008 11:21
rkbfbnut	08/26/2008 11:26	08/26/2008 11:27
rkbfbnut	09/23/2008 10:31	09/23/2008 10:32
rkbfbnut	10/30/2008 11:30	10/30/2008 11:31
rkbfbnut	11/25/2008 11:25	11/25/2008 11:26
rkbfbnut	12/18/2008 11:38	12/18/2008 11:39

rkblhnut

rkblhnut	01/16/2008 13:40	01/16/2008 13:41
rkblhnut	02/12/2008 15:05	02/12/2008 15:06
rkblhnut	03/12/2008 14:25	03/12/2008 14:26
rkblhnut	04/23/2008 09:47	04/23/2008 09:48
rkblhnut	05/20/2008 16:20	05/20/2008 16:21
rkblhnut	06/16/2008 14:42	06/16/2008 14:43
rkblhnut	07/21/2008 16:30	07/21/2008 16:31
rkblhnut	08/25/2008 17:05	08/25/2008 17:06
rkblhnut	09/22/2008 09:37	09/22/2008 09:38
rkblhnut	10/30/2008 10:35	10/30/2008 10:36
rkblhnut	11/25/2008 10:15	11/25/2008 10:16
rkblhnut	12/18/2008 14:00	12/18/2008 14:01

Diel Sampling

Station Code	Begin Date Time Stamp	End Date Time Stamp
rkblhnut	01/03/2008 08:00	01/04/2008 06:30
rkblhnut	02/10/2008 08:00	02/11/2008 06:30
rkblhnut	03/09/2008 08:00	03/10/2008 06:30
rkblhnut	04/21/2008 08:00	04/22/2008 06:30
rkblhnut	05/19/2008 08:00	05/20/2008 06:30
rkblhnut	06/17/2008 08:00	06/18/2008 06:30
rkblhnut	07/21/2008 08:00	07/22/2008 06:30
rkblhnut	08/18/2008 08:00	08/19/2008 06:30
rkblhnut	09/22/2008 08:00	09/23/2008 06:30
rkblhnut	10/27/2008 08:00	10/28/2008 06:30

rkblhnut	11/24/2008 08:00	11/25/2008 06:30
rkblhnut	12/15/2008 08:00	12/16/2008 06:30

7. Associated Researchers and Projects- RKB SWMP nutrient data collection and analysis was part of the Southeastern Environmental Research Center (SERC) Water Quality Monitoring Program. This program was established to address regional water quality concerns outside the boundaries of individual agencies. This "network" collects some 479 sites within the South Florida Region (for more information visit the following website: http://serc.fiu.edu).

Rookery Bay participates in the NERR SWMP for water quality and meteorological data collection. The principal objective of these programs is to record long-term data within Rookery Bay in order to observe any changes or trends over time. The four water quality sites were also selected to represent various degrees of watershed hydrologic alteration. Both water quality and meteorological data are available from the Research Coordinator or online at http://cdmo.baruch.sc.edu.

Both water quality and nutrient data generated by Rookery Bay are being used to analyze restoration targets established for the Picayune Strand Restoration Project (PSRP; formerly known as Southern Golden Gate Estates) which is a portion of the Comprehensive Everglades Restoration Plan (CERP). Additional datasets used in this analysis include a long-term fisheries survey (July 1998 to the present), a shark demographics survey (May 2000 to the present), and an oyster reef/benthic crab survey (1999 to 2008). These data are available from the Research Coordinator.

8. Distribution- NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature, including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal Resource Management, National Ocean Services, 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 Recipients or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

NERR nutrient/water quality data and metadata can be obtained from the Research Coordinator at Rookery Bay NERR site (please see Section 1. Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under general information link on the CDMO home page) and online at the CDMO home page http://cdmo.baruch.sc.edu/. Data are available in text tab-delimited format.

II. Physical Structure Descriptors

9. Entry Verification – Nutrient data collection and analysis for Rookery Bay NERR was part of a partnership with Florida International University/ Southeast Environmental Research Center's Estuarine Water Quality Monitoring Network. Water quality data was collected monthly during the annual period of record (POR) from 8 stations in the Ten Thousand Islands, and 16 stations in Cape Romano-Rookery Bay. The analytical results (electronic report-Excel files) and a quarterly report (which includes Rookery Bay's SWMP sites) were submitted to Christina Ottman, Research Coordinator at RKBNERR and Vicki McGee, former Water Quality Program Manager at RKBNERR as deliverables as per their annual purchase order agreement. For details on FIU/SERC laboratory QA/QC procedures please contact Dr. Joseph Boyer, Associate Director of SERC: boyerj@fiu.edu. Upon receiving the quarterly reports Vicki McGee reviewed the data for errors. Due to staff changes, Christina Panko Graff (current Water Quality Program Manager) was responsible for compilation and QA/QC of the final data set according to chapter 10 of the Centralized Data Management Office (CDMO) NERR SWMP Data Management Manual v 6.2. The data reported from the lab were in the required units making it unnecessary to convert the data prior to entering it into Microsoft Excel.

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.

10. Parameter Titles and Variable Names by Data Category

Required NOAA/NERRS System-wide Monitoring Program water quality parameters are denoted by and asterisks "*".

Grabs:

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus & Nitrogen:	*Orthophosphate, Filtered	PO4F	mg/L as P
	Total Phosphorus	TP	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Total Nitrogen	TN	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L
	Total Organic Nitrogen	TON	mg/L as N
Carbon:	Total Organic Carbon	TOC	mg/L
Plant Pigments:	*Chlorophyll *a*	CHLA_N	µg/L
Field Parameters:	Water Temperature	WTEM_N	°C
	Dissolved Oxygen	DO_N	mg/L
	Salinity	SALT_N	ppt
	pH	PH_N	standard units

Diel:

Phosphorus & Nitrogen:	*Orthophosphate, Filtered	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L
Plant Pigments:	*Chlorophyll *a*	CHLA_N	µg/L

Notes:

1. Time is coded based on a 2400 hour clock and is referenced to Eastern Standard Time (EST).
2. Reserves have the option of measuring either NO2 and NO3 or they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3.

11. Measured and Calculated Laboratory Parameters –

a. Parameters Measured Directly-

Phosphorous species: PO4F, TP
Nitrogen species: NH4F, NO2F, NO23F, TN
Carbon: TOC
Plant Pigments: CHLA

b. Calculated Parameters-

NO3: NO23F –NO2F
DIN: NO23F +NH4F
TON: TN-NH4F-NO23F

12. Limits of Detection- Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, were established by the Florida International University/ Southeastern Environmental Research Center Analytical Laboratory. These values are reviewed and revised periodically.

Parameter	Variable	MDL	Approved
Orthophosphate	PO4	0.0016 mg/L	01/07/08
Total Phosphorous	TP	0.0019 mg/L	01/07/08
Ammonium	NH4	0.0049 mg/L	01/07/08
Nitrite	NO2	0.0006 mg/L	01/07/08
Nitrate + Nitrite	NO23	0.0039 mg/L	01/07/08
Total Nitrogen	TN	0.05 mg/L	01/07/08
Total Organic Carbon	TOC	0.16 mg/L	01/07/08
Chlorophyll a	CHLA	0.1 µg/L	01/07/08

13. Laboratory Methods– All laboratory analysis was performed by Southeast Environmental Research Center Florida International University, Miami, Florida (see Table 5.0 QA Plan Objectives Laboratory Measurements on page 17 of the SERC QA Plan)

a. Parameter: Orthophosphate: PO4

EPA or other Reference Method: EPA 365.1(d); SERC SOP #002-98
Method Reference: Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983
Method Description: Analysis for inorganic filtered nutrients (ammonium, nitrite, nitrate and soluble reactive phosphorus) was run simultaneously by flow injection analysis using a four-channel Alpken RFA-300 (Rapid Flow Analyzer). Soluble reactive phosphate was determined by reacting phosphate with molybdenum (IV) and antimony (III) in an acid medium to form a phosphoantimonyl-molybdenum complex; this complex was reduced with ascorbic acid to form a colored dye. The color's absorbance is directly proportional to analyte concentration and is measured as peak height units.
Preservation Method: Samples were filtered in the field and stored at 4 ºC for up to 24 hours.

b. Parameter: TP

EPA or other Reference Method: EPA 365.1(e); SERC #001-98
Reference Method: Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983
Method Description: Total Phosphorous is determined by oxidizing and hydrolyzing all the phosphorus-containing compounds in a sample to soluble reactive phosphate. Soluble reactive phosphate then is determined by reacting phosphate with molybdenum (VI) and antimony (III) in an acid medium to form phosphoantimonyl-molybdenum complex; this complex is reduced with ascorbic acid to form a colored dye. The concentration is determined on an ALPKEM 305 Rapid Flow Analyzer.
Preservation Method: Samples were stored at 4 ºC for up to 24 hours.

c. Parameter: NH4
EPA or other Reference Method: EPA 350.1(d); SERC SOP #002-98
Method Reference: Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983
Method Description: Analysis for inorganic filtered nutrients (ammonium, nitrite, nitrate and soluble reactive phosphorus) was run simultaneously by flow injection analysis using a four-channel Alpken RFA-300 (Rapid Flow Analyzer). The indophenol blue method for ammonium was used. Ammonium reacts with alkaline phenol and hypochlorite to form indophenol. Sodium nitroferricyanide intensifies the blue color. The color's absorbance is directly proportional to analyte concentration and is measured as peak height units.
Preservation Method: Samples were filtered in the field and stored at 4 ºC up to 24 hours.

d. Paramter: NO2
EPA or other Reference Method: EPA 353.2(d); SERC SOP #002-98
Method Reference: Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983
Method Description: Analysis for inorganic filtered nutrients (ammonium, nitrite, nitrate and soluble reactive phosphorus) was run simultaneously by flow injection analysis using a four-channel Alpken RFA-300 (Rapid Flow Analyzer). Nitrite was determined as an azo dye formed by the reaction of nitrite with sulfanilamide and subsequent coupling with N-1-naphthylethylenediamine (NEDA). The color's absorbance is directly proportional to analyte concentration and is measured as peak height units.
Preservation Method: Samples were filtered in the field and stored at 4 ºC up to 24 hours.

e. Parameter: NO23
EPA or other Reference Method: EPA 353.2(d)
Reference Method: Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983
Method Description: Analysis for inorganic filtered nutrients (ammonium, nitrite, nitrate and soluble reactive phosphorus) was run simultaneously by flow injection analysis using a four-channel Alpken RFA-300 (Rapid Flow Analyzer).
Preservation Method: Samples were filtered in the field and stored at 4 ºC for up to 24 hours.

f. Parameter: TN
EPA or other Reference Method: ASTM 5176-D; SERC SOP TN in Natural Waters
Reference Method: Annual Book of ASTM Standards, Vol. 11.01
Method Description: The procedure is a modification of the classical Dumas (1831) method of determining nitrogen by combustion technique with the addition of chemiluminescence. The method involves converting all forms of nitrogen into nitric oxide (NO) upon combustion of a sample with oxygen at a temperature in excess of 1000 ºC. The NO is reacted with ozone (O3) to form a meta-stable form of nitrogen dioxide (NO2-). As the meta-stable form of nitrogen dioxide decays, a quantum of light is emitted in an amount directly proportional to the amount of nitrogen in the sample. The chemiluminescent emission is detected by a photomultiplier tube at a specific wavelength. An ANTEK Instrument, Inc, Model 7000N Nitrogen Analyzer was used to determine total nitrogen of a 5µl injection of a preserved water sample.
Preservation Method: Samples were stored at 4 ºC for up to 24 hours.

g. Parameter: TOC
EPA or other Reference Method: EPA 415.1(h); SERC # 001-04
Reference Method: Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983
Method Description: Samples are analyzed by hot-platinum catalyst combustion of the non-purgeable organic carbon in the sample to CO2 on a Shimadzu 5000 Total Organic Carbon Analyzer with auto-sampler.

Preservation Method: Samples were stored at 4 ºC for up to 24 hours. Samples should be processed within 28 days of collection.

h. Parameter: CHLA
EPA or other Reference Method: SM 10200H(i); SERC SOP #009-98
Method Reference: Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1989
Method Description: An extractive fluorometric technique was used to determine chlorophyll *a* concentrations. Filters were allowed to extract for a minimum of 2 days at 4 °C before analysis. Extracts were analyzed using a Gilford Fluoro IV Spectrofluorometer (excitation = 435 nm, emission = 667 nm) and compared to a standard curve of pure chlorophyll *a* (Sigma). The amount of fluorescence was directly proportional to chlorophyll *a* concentration as determined by the standard curve of pure chlorophyll *a*.
Preservation Method: Filters were stored in 90% acetone and placed in the dark and stored at 4 ºC for a minimum of 48 hours.

i. Parameter: Field Measurements
EPA or other Reference Method: EPA 170.1 (temp), EPA 120.1 (conductivity), EPA 360.1 (DO), EPA 150.1(pH)
Reference Method: Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Revised March 1983 (SERC SOP #005-98)
Method Description: This procedure applies to the measurements of temperature, dissolved oxygen, salinity/conductivity, and pH at the surface and bottom of the water column at each sampling station.

14. Field and Laboratory QAQC programs- (Please reference pages 55-57 in the SERC Laboratory QA Plan)

a) Precision: is defined as the agreement or closeness of two or more results.

i) **Field Variablity –** Typically SERC collects all field samples in duplicate. In addition, SERC typically analyzes all samples in replicate, thereby, producing four data points for one sample location. This QA protocol allows for easy identification of unusual sample results, and provides a constant check of analytical precision and accuracy. Two successive grab samples were collected at Henderson Creek, Middle Blackwater River, and Fakahatchee Bay for each monthly sampling event from January to September 2008. From October to December 2008, two successive grab samples were collected at one randomly chosen site for each sampling event. Please see section 3.a. of this document for more details.

ii) **Laboratory variability –** Standard laboratory QC checks include: blanks, replicates, and QC standards and QC check samples. Typically, SERC determines the mean (X) and standard deviation (SD) of the four data points (as described above) and estimates precision in terms of percent relative standard deviation (% RSD). The control limits for precision are set at +/- two standard deviations of the mean. The Relative Percent Difference (RPD) is another parameter used to monitor the precision of analytical results and it is calculated for Matrix Spike duplicates and/or sample duplicates. The acceptance criteria is usually RPD <= 20 %.

iii) **Inter-organizational splits –** Quality control samples are prepared in-house or from a NIST certified source. These samples are submitted blind to the analyst every 6 months to check instrument and user performance. The QC samples are run with each proficiency testing to ensure precision and accuracy.

b) Accuracy: is defined as the agreement between the analytical results and the known concentration.

i) **Sample spikes and standard reference material analysis-** Accuracy is determined by running matrix spikes (MS) and/or standard reference materials and is determined as % recovery. MS samples are prepared by splitting a sample from the survey or using an S2 (not a blank, in the absence of enough sample or of high concentration that will go over the calibration curve) into two duplicates and spiking one of the duplicates with a known concentration. The concentration from the un-spiked one of the duplicates is subtracted from the spiked results and the percent recovery by comparing the remainder to the known spike concentration. MS % recovery should be between 90 – 110%. The control limits for QC % recovery are +/- three standard deviations of the historical percent recovery average, with warning limits set at +/- two standard deviations.

ii) **Cross calibration exercised –** N/A

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

Cloud cover

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

Precipitation

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

Tide stage

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

Wave height

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

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest

WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest

Wind speed

WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17. Other remarks/notes –

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.

For the 10/30/2008 grab sampling, the lab analysis report indicated that the field blank was contaminated for nitrogen and phosphorous species. The field blank sample showed higher concentrations of these species than the actual grab samples. Therefore for all four sites, all data except chlorophyll and total organic carbon should be considered suspect.

<u>Weather Conditions</u>:

January: Severe drought conditions persisted through the month. A lack of cold fronts lead to warmer than normal weather and dry conditions. Only 35% of normal rainfall for this month.

February: The drought conditions got a bit of relief from two strong cold fronts that produced wide-spread rain.

March: Two moderate cold fronts on the 6th and 22nd generated sporadic, but much needed rain in the region – these did not bring much relief.

April: Continued drought conditions prevailed with one front bringing rain the first week of April, with some areas receiving as much as 4 inches of rain.

May: Except for some summer-time convective thunderstorm activity during the last week in May, there was no measurable rainfall the entire month.

June: Wet season finally began with regular afternoon thunderstorms beginning the last two weeks of this month. About 80% of normal rainfall for this month.

July: Typical summer time weather patterns started with most of the stronger storms occurring inland. Some areas received as much as 11 inches of rain.

August: Tropical storm Fay impacted south Florida with week-long rains (8/19/08). This along with the usual summer time storms created wetter than normal conditions.

September: September was typical rainy season conditions, with indirect impacts from Hurricane Ike (9/10/08) generating moderate rainfall early in the month.
October: Normal hydrologic conditions with continued occurrence of scattered thunderstorms. Average rainfall of 3.99 inches.
November: Start of the dry season with considerably drier than normal hydrologic conditions. No major rainfall event occurred however, there were two moderate cold fronts during the month.
December: Drier than normal hydrologic conditions for this month. Moderately high pressure systems dominated during this event. However, one front brought widespread rainfall the second week of the month.