Rookery Bay (RKB) National Estuarine Research Reserve (NERR) Nutrient Metadata (January 2010 – December 2010)

Latest Update: August 13, 2013

I. Data Set and Research Descriptors

1. Principal investigator(s) and contact persons

a. Reserve Contact

Victoria Vazquez, Research Coordinator

Rookery Bay NERR 300 Tower Road Naples, FL 34113-8059

Phone: (239) 417-6310

e-mail: victoria.vazquez@dep.state.fl.us

b. Laboratory Contact

Elizabeth Woods, Laboratory Supervisor

Collier County Pollution Control and Prevention Department 3301 East Tamiami Trail

Naples, Florida 34112 Phone: (239) 252-2502

e-mail: ElizabethWoods@colliergov.net

c. System Wide Monitoring Program Technicians

Christina Panko Graff, System-Wide Monitoring Program Manager (responsible for coordinating the program, field collection at three stations, data management, data QA/QC and final data submission) **Beverly Anderson, Research Biologist** (responsible for field collection and diel sampling at one station)

Rookery Bay NERR

300 Tower Road

Naples, FL 34113-8059 Phone: (239) 417-6397

e-mail: christina.pankograff@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 exhibits a different pattern of altered freshwater inflow.
 - a. Monthly Grab Sampling Program- 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 lunar tidal cycle and to determine the impact of tidal water exchange within Henderson Creek (the main source of freshwater into the Rookery Bay waterbody).

3. Research Methods-

a. Monthly Grab Sampling Program

Monthly grab samples were collected at all four System-Wide Monitoring Program (SWMP) water quality stations: Henderson Creek, Middle Blackwater River, Faka Union Bay and Fakahatchee Bay. Triplicate grab samples were taken every other month at one randomly chosen water quality station following the National Estuarine Research Reserve System Nutrient and Chlorophyll Monitoring Program and Database Design SOP v 1.3. Slack low tide was generally not considered for the grab sampling events due to time constraints with the contracted laboratory. Rainfall conditions prior to grab sampling were not considered. For analysis of dissolved inorganic nutrients the samples were filtered in the field. For chlorophyll a analysis the samples were filtered at the contracted laboratory. Sample bottles were precleaned by the contracted laboratory following their Quality Assurance Management Plan (available by request). Three different bottles per station were labeled with a unique sample identification and chain of custody sheets were completed for tracking the samples during laboratory analysis and in the laboratory database. Water sampling devices (Van Dorn), carboys (for deionized water), and filter assemblies were pre-cleaned using a Fl Department of Environmental (FDEP) decontamination procedure (FDEP SOP FC1000/DEP-QAA-01/001) which involved cleaning the equipment with phosphate-free soap, rinsing three times with tap water, rinsing with a 10% solution of hydrochloric acid, rinsing three times with deionized water, and drying for 24 hours. One to two days prior to field sampling, the filter assemblies were preassembled with in-line filters (0.7 µm glass microfiber filters and 0.45 µm membrane filters). At each sampling station, grab samples for dissolved nutrients were collected 12 inches below the surface (near surface grab) using a Van Dorn sampler. Nitrile gloves were worn through the entire process of sample collection and filtering. For the chlorophyll a samples, 1000 ml HDPE amber sample bottles were rinsed three times with the sample water and then filled to the neck, capped, and immediately stored in a cooler with ice. For the dissolved phosphorus and nitrite, 250 ml HDPE sample bottles were rinsed three times with the filtered water (using a disposable 60 cc syringe with an attached filter assembly) and then filled with 120 ml of the filtrate, capped, and immediately stored in a cooler with ice. For the dissolved ammonium and nitrite + nitrate, 125 ml HDPE sample bottles were filled with 25-30 ml of the filtrate (using a disposable 60 cc syringe with an attached filter assembly), capped, and immediately stored in a cooler with ice. For the December sampling, the 125 ml HDPE sample bottle was filled with 120 ml of filtrate at the request of the contracted laboratory. The 125 ml HDPE sample bottles contained sulfuric acid for preservation and therefore were not rinsed before adding the filtrate. To avoid cross contamination, the Van Dorn sampler was rinsed three times with deionized water after each sampling at each station and then rinsed three times with sample water before sampling at each new station. New gloves, syringes, and filter assemblies were used for each sample. Additionally, an equipment blank was performed at the end of each sampling event by following all the same procedures but with deionized water as the sample.

At each site physical/chemical water quality parameters were measured at the same depth as where the nutrient samples were taken. AYSI 600-xl multi-parameter data logger and a hand held display (YSI model 650) were used to record the measurements. 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). pH data were not collected at the LH site. Equipment calibration and field verification were done according to FDEP SOP 001/01.

b. Diel Sampling Program - Monthly diel samples (11) 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 refrigerated auto-sampler (model 3700FR). The sampler was stationed at the end of the Rookery Bay dock, approximately 100 meters from the water quality station. Prior to sampling, the polyethylene bottles used in the ISCO were washed following the same FDEP decontamination procedure as described above. A day or two before the sampling was to begin, the ISCO autosampler was set up and programmed. The siphon hose was rinsed three times with ambient water prior to setting up and running the auto-sampler. Sample bottles for the laboratory analysis were pre-cleaned by the contracted laboratory following their Quality Assurance Management Plan (available by request). Three different bottles per sample interval (11) were labeled with a unique sample identification and chain of custody sheets were completed for tracking the samples during laboratory analysis and in the laboratory database.

Sample filtration: At Rookery Bay's laboratory, each polyethylene bottle containing 900 ml of sample water was shaken to redistribute sediments on the bottom. For the dissolved ammonium and nitrite + nitrate, 125 ml HDPE sample bottles were filled with 25-30 ml of the filtrate (using a disposable 60 cc syringe with an attached filter assembly), capped, and immediately stored in a cooler with ice. For the dissolved phosphorus and nitrite, 250 ml HDPE sample bottles were rinsed three times with the filtered water (using a disposable 60 cc syringe with an attached filter assembly) and then filled with 120 ml of the filtrate, capped, and immediately stored in a cooler with ice. For the chlorophyll *a* samples, 1000 ml HDPE

amber sample bottles were rinsed three times with the sample water and then filled with the remaining amount of unfiltered sample, capped, and immediately stored in a cooler with ice. New gloves, syringes, and filter assemblies were used for each sample.

4. Site location and character-

Lower Henderson Creek (rkblhnut)-

Lat/Long (Decimal Degrees): 26.0257 N, 81.7332 W

The Lower Henderson Creek water quality station is located at the mouth of Henderson Creek. The monitoring site is approximately 5 km downstream of a four-lane highway (SR 951) that crosses Henderson Creek. 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 is 5.8 km long (mainstream linear dimension), has an average midchannel depth of approximately 2 meters at MHW, and an average width of 239 meters. At the sampling site, the depth is 2 meters at MHW and the width is 600 meters. Tides at Lower Henderson Creek are mixed and range from 0 m to 2.76 m (average 1.06 m). Salinities at this site range from 0 to 40 ppt. Creek bottom habitats are predominantly fine sand and there is no bottom vegetation. The dominant marsh vegetation near the sampling site is red mangrove. The dominant natural vegetation of the watershed is hydric pine and cypress.

Upland land use near the sampling site includes residential areas with septic systems. Watershed activities that potentially impact the site include non-point source pollution from road runoff, drift of mosquito control pesticides, runoff from upstream agricultural areas and leachate from nearby residential septic systems and a weir structure located at SR 41. The amount of water released from this weir can sometimes mask natural tidal salinity patterns. The historic Henderson Creek watershed was approximately 50% under State ownership and much of this protected area had intact cypress sloughs and other wetland vegetation. Canals and water use for agriculture and human consumption have altered the hydroperiod of this watershed. Consequently, the Henderson creek watershed may receive non-point source pollution runoff from a variety of sources.

Middle Blackwater River (rkbmbnut) -

Lat/Long (Decimal Degrees): 25.9343 N, 81.5946 W

The Middle Blackwater River water quality station is located at the mouth of the river at navigational marker #17 within the channel. The "Middle" Blackwater labeling is to distinguish it from other historical sites. The water quality data logger is affixed to marker #17. The average depth at this marker is approximately 2 meters at MHW. The tidal range for Middle Blackwater River varies between 0.2 and 1.8 meters. Blackwater salinities range from 0 to 42.1 ppt and fluctuate with the tides and watershed rainfall. The substrate within the channel is a mixture of sand and silt with oyster shell and some organic matter mixed in. Mature red mangrove forests dominate the banks of the river.

Upstream influences consist of the Collier-Seminole State Park boat basin and upstream agricultural fields adjacent to Blackwater River's main feeder canal (SR 41 canal). Nonpoint source pollution from agricultural operations and golf courses may affect this site. In addition, canals and roads built during the 1960's (Picayune Strand, formerly Southern Golden Gate Estates) have caused significant disruptions to overland sheet-flow reducing the amounts of freshwater flowing to this estuary. Despite these alterations, the salinity fluctuations of this site suggest that seasonal fluctuations in salinity are more closely correlated to watershed rainfall patterns than salinities of estuaries with water control structures, such as Henderson Creek.

Faka Union Bay (rkbfunut) -

Lat/Long (Decimal Degrees): 25.9005 N, 81.5159 W

The Faka Union Bay water quality station is located at the mouth of the Faka Union Canal. The water quality data logger is affixed to a manatee speed zone sign within the main channel. The average depth at this site is approximately 2 meters at MHW. The tidal range for Faka Union Bay varies between 0.2 and 1.6 meters. Salinities range from 0 to 42.3 ppt and fluctuate daily with tides, seasonal rainfall, and water management use of upstream water control structures. The substrate within the channel is a mixture of sand and silt with some organic matter. Mature red mangrove forests and spoil islands dominate the banks of the canal.

Upstream influences consist of the Port of the Islands development and marina. The watershed consists of an elaborate canal system (Picayune Strand, formerly Southern Golden Gate Estates) which has altered natural water drainage patterns into Faka Union Bay.

Fakahatchee Bay (rkbfbnut)-

Lat/Long (Decimal Degrees): 25.8922 N, 81.4770 W

The Fakahatchee Bay water quality station is located between the mouths' of the Fakahatchee River and the East River. The water quality data logger is placed in a 4" PVC housing secured to a 6" PVC pipe at this location. The average depth at MHW is approximately 2 meters. The tide range for Fakahatchee varies between 0.2 and 1.8 meters. Salinities range from 0.7 – 42.6 ppt and fluctuate daily with the tides and seasonal rainfall. The substrate within the channel is a mixture of sand, silt and some organic matter. Mature red mangrove forests dominate the banks of the rivers.

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. Fakahatchee Bay's watershed is considered the least altered.

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:

1 = monthly grab sample program

2 = monthly diel sample program

Replicate grab samples were denoted as 1 for the first sample, 2 for the second sample, and 3 for the third sample at one station. 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 at all of the sampling stations. For 2010, the data collection period was from January to December.

Monthly Grab Sampling

01/07/2010 10:41
02/04/2010 10:37
03/03/2010 10:15
04/01/2010 11:36
05/13/2010 08:23
06/10/2010 09:51
07/08/2010 09:23
08/05/2010 08:00
09/02/2010 07:50

rkblhnut 10/07/2010 08:22 rkblhnut 11/04/2010 08:48

rkblhnut 12/02/2010 10:11 – 10:30

rkbmbnut

rkbmbnut 01/07/2010 11:50

rkbmbnut 02/04/2010 12:04 – 12:31

rkbmbnut 03/08/2010 09:42 rkbmbnut 04/01/2010 11:40 rkbmbnut 05/13/2010 11:56 rkbmbnut 06/10/2010 09:45 rkbmbnut 07/08/2010 09:15

rkbmbnut $08/05/2010\ 09:25-09:50$

rkbmbnut 09/02/2010 08:55 rkbmbnut 10/07/2010 12:00 rkbmbnut 11/04/2010 09:15 rkbmbnut 12/02/2010 10:20

rkbfunut

rkbfunut 01/07/2010 11:05 rkbfunut 02/04/2010 11:13 rkbfunut 03/08/2010 10:46 rkbfunut 04/01/2010 10:50 rkbfunut 05/13/2010 10:02

rkbfunut $06/10/2010\ 10:45-11:10$

rkbfunut 07/08/2010 10:35 rkbfunut 08/05/2010 11:20 rkbfunut 09/02/2010 10:00

rkbfunut 10/07/2010 10:42 – 11:00

rkbfunut 11/04/2010 10:48 rkbfunut 12/02/2010 12:15

rkbfbnut

rkbfbnut 01/07/2010 10:35 rkbfbnut 02/04/2010 10:40 rkbfbnut 03/08/2010 11:17

rkbfbnut $04/01/2010\ 09:45 - 10:09$

rkbfbnut 05/13/2010 10:51 rkbfbnut 06/10/2010 11:45 rkbfbnut 07/08/2010 11:00 rkbfbnut 08/05/2010 12:00 rkbfbnut 09/02/2010 10:50 rkbfbnut 10/07/2010 10:00 rkbfbnut 11/04/2010 12:46 rkbfbnut 12/02/2010 12:45

Diel Sampling

Station Code Begin Date Time Stamp rkblhnut 01/06/2010 07:30

End Date Time Stamp 01/07/2010 09:30

rkblhnut	02/03/2010 07:30	02/04/2010 09:30
rkblhnut	03/02/2010 07:30	03/03/2010 09:30
rkblhnut	03/31/2010 07:30	04/01/2010 09:30
rkblhnut	05/12/2010 06:00	05/13/2010 07:00
rkblhnut	06/09/2010 05:00	06/10/2010 06:00
rkblhnut	07/07/2010 07:00	07/08/2010 08:00
rkblhnut	08/04/2010 08:00	08/05/2010 09:00
rkblhnut	09/01/2010 05:30	09/02/2010 06:30
rkblhnut	10/06/2010 06:30	10/07/2010 07:30
rkblhnut	11/03/2010 05:30	11/04/2010 06:30
rkblhnut	12/01/2010 03:30	12/02/2010 04:30

7. Associated Researchers and Projects-

Rookery Bay NERR participates in the NERR SWMP for water quality and meteorological data collection. The principal objective of these programs is to record long-term environmental data within Rookery Bay NERR 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 Service, National Oceanic and Atmospheric Administration. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

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

II. Physical Structure Descriptors

9. Entry Verification – The analytical results (electronic Excel files) were provided monthly from the contracted laboratory to Christina Panko Graff, System-Wide Monitoring Program Manager. Upon receiving the results Christina reviewed the data for errors. Christina 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 6.3. 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 were copied and pasted into a Microsoft Excel worksheet and data transfer was checked once. Data were 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 "*".

Parameter V	Variable Name	Units of Measure
*Orthophosphate, Filtered *Ammonium, Filtered *Nitrite, Filtered *Nitrate, Filtered *Nitrite + Nitrate, Filtered Dissolved Inorganic Nitrog	PO4F NH4F NO2F NO3F NO23F gen DIN	mg/L as P mg/L as N mg/L as N mg/L as N mg/L as N mg/L
*Chlorophyll <i>a</i> Phaeophytin	CHLA_N PHEA	μg/L μg/L
Water Temperature Specific Conductance Salinity Dissolved Oxygen % Dissolved Oxygen Saturation		°C mS/cm ppt mg/L % standard units
	*Orthophosphate, Filtered *Ammonium, Filtered *Nitrite, Filtered *Nitrate, Filtered *Nitrite + Nitrate, Filtered Dissolved Inorganic Nitrog *Chlorophyll a Phaeophytin rabs only): Water Temperature Specific Conductance Salinity Dissolved Oxygen	*Orthophosphate, Filtered *Ammonium, Filtered NH4F *Nitrite, Filtered NO2F *Nitrate, Filtered NO3F *Nitrite + Nitrate, Filtered Dissolved Inorganic Nitrogen *Chlorophyll a Phaeophytin *Chlorophyll a Phaeophytin *WTEM_N Specific Conductance Scon_N Salinity Dissolved Oxygen % Dissolved Oxygen Solved Oxygen

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 or Calculated Laboratory Parameters -

a. Parameters Measured Directly-

Phosphorus species: PO4F

Nitrogen species: NH4F, NO2F, NO23F Plant Pigments: CHLA and PHEA

b. Calculated Parameters-

NO3: NO23F –NO2F DIN: NO23F +NH4F

12. Limits of Detection- Method Detection Limits (MDL), the minimum concentration of a parameter that an analytical procedure can reliably detect, were established by the Collier County Pollution Control and Prevention Department Laboratory. MDLs were determined using the U.S. Environmental Protection Agency MDL procedure found in Title 40 Code of Federal Regulations Part 136 (40 CFR 136, Appendix B, revision

1.11). Once the MDL was established using this method, verification was done prior to use. Verification included analyzing a known standard at 2-3 times the calculated MDL. Additionally, various checks and balances were used to ensure suitability of the MDL. Every year the lab employed verification checks on all MDLs. If the verification checks met the lab's acceptance criteria then the MDL was not recommended for change.

Parameter	Variable	MDL	Approved
Orthophosphate	PO4F	0.004 mg/L	1/1/2010
Ammonium	NH4F	0.012 mg/L	1/1/2010
Nitrite	NO2F	0.002 mg/L	1/1/2010
Nitrite +Nitrate	NO23F	$0.002~\mathrm{mg/L}$	1/1/2010
Chlorophyll a	CHLA	3 μg/L	1/1/2010
Phaeophytin	PHEA	$3 \mu g/L$	1/1/2010

13. Laboratory Methods— All laboratory analysis was performed by Collier County Pollution Control and Prevention Department Laboratory according to their Quality Assurance Management Plan version 04-02-08 (available by request).

a. Parameter: PO4F

EPA or other Reference Method: SM 4500-P E (ascorbic acid method)

Method Reference: Standard Methods for Examination of Water and Wastewater, 20th ed.

Method Description: Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid—phosphomolybdic acid—that is reduced to intensely colored molybdenum blue by ascorbic acid. The color's absorbance is directly proportional to analyte concentration and is measured as peak height units with an Astoria Pacific Rapid Flow Analyzer.

Preservation Method: Samples were filtered in the field and stored at 4 °C until analysis.

b. Parameter: NH4F

EPA or other Reference Method: EPA 350.1 (no distillation)

Method Reference: Methods for Chemical Analysis of Water and Wastes

Method Description: Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside. The color's absorbance is directly proportional to analyte concentration and is measured as peak height units with an Astoria Pacific Rapid Flow Analyzer.

Preservation Method: Samples were filtered in the field and stored with sulfuric acid at 4 °C until analysis.

c. Paramter: NO2F

EPA or other Reference Method: SM 4500-NO2 B

Method Reference: Standard Methods for Examination of Water and Wastewater, 20th ed. **Method Description**: 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 with an Astoria Pacific Rapid Flow Analyzer.

Preservation Method: Samples were filtered in the field and stored at 4 °C until analysis.

d. Parameter: NO23F

EPA or other Reference Method: EPA 353.2

Reference Method: Methods for Chemical Analysis of Water and Wastes

Method Description: A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that was originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically with an Astoria Pacific Rapid Flow Analyzer .

Preservation Method: Samples were filtered in the field and stored with sulfuric acid at 4 °C until analysis.

e. Parameter: CHLA and PHEA

EPA or other Reference Method: SM 10200 H

Method Reference: Standard Methods for the Examination of Water and Wastewater, 20th Edition **Method Description**: An extractive spectrophotometric technique was used to determine chlorophyll *a* concentrations. Samples were filtered immediately at the laboratory. Filters were placed in a tissue grinder with 2-3 ml of 90% aqueous acetone. Extracts steeped for at least 2 hours at 4 °C in the dark. Extracts were analyzed using a GBC UV/VIS Spectrophotometer.

Preservation Method: Stored at 4 °C and filtered at the lab on the same day as collection.

- **14. Field and Laboratory QAQC programs-** based on Collier County Pollution Control and Prevention Department Laboratory's Quality Assurance Management Plan version 04-02-08 (available by request).
 - a) Precision: is defined as the agreement or closeness of two or more results.
 - i) **Field Variablity** Duplicates (successive grabs at each station) were not taken every month; instead triplicate grabs were taken at one randomly chosen station every other month.
 - ii) **Laboratory variability** –Matrix duplicates (replicate aliquots of the same sample taken through the entire analytical procedure) were conducted for each analyte with a frequency of one per analytical batch (10 or 20 samples per analytical batch). Low level precision was defined as a concentration less than 20 times the MDL and the high level precision was defined as a concentration greater than 20 times the MDL. The low level precision and high level precision for all analytes was 25 % RPD and 10 % RPD respectively.
 - iii) **Inter-organizational splits** The laboratory participates in external audit programs including split sample analysis with both public and private laboratories.
 - **b)** Accuracy: is defined as the agreement between the analytical results and the know concentration.
 - i) **Sample spikes-** Matrix spikes were conducted for each analyte with a frequency of one per analytical batch (10 or 20 samples per analytical batch). The % recovery was 90-110 % for nitratenitrite and ammonium and 85-115 % for nitrite and orthophosphate.
 - ii) **Standard reference material analysis-** Laboratory control samples were evaluated for each analyte with a frequency of beginning and end of each analytical batch (10 or 20 of samples per analytical batch). The % recover was 90-110 % for nitrate-nitrite and ammonium and 85-115 % nitrite and orthophosphate.
 - iii) **Cross calibration exercised** The laboratory participates in external audit programs including split sample analysis with both public and private laboratories. The laboratory also participates in several inter-laboratory comparisons annually. The laboratory supervisor evaluates the results of these comparisons and if necessary, operational changes are implemented and documented.

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 OAOC
- 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	b]	loom

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
CAD	Aigai	UIUUIII

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
                cloud (no percentage)
      CCC
Precipitation
      PNP
                none
      PDR
                drizzle
      PLR
                light rain
                heavy rain
      PHR
      PSO
                squally
      PFQ
                frozen precipitation (sleet/snow/freezing rain)
      PSR
                mixed rain and snow
Tide stage
                ebb tide
      TSE
      TSF
                flood tide
                high tide
      TSH
      TSL
                low tide
Wave height
      WH0
                0 \text{ to } < 0.1 \text{ meters}
      WH1
                0.1 to 0.3 meters
      WH2
                0.3 to 0.6 meters
                0.6 \text{ to} > 1.0 \text{ meters}
      WH3
      WH4
                1.0 to 1.3 meters
      WH5
                1.3 or greater meters
Wind direction
                from the north
      N
      NNE
                from the north northeast
      NE
                from the northeast
                from the east northeast
      ENE
      Ε
                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
                from the west southwest
      WSW
                from the west
      W
      WNW
                from the west northwest
      NW
                from the northwest
                from the north northwest
      NNW
Wind speed
      WS0
                0 to 1 knot
      WS1
                > 1 to 10 knots
      WS2
                > 10 to 20 knots
                > 20 to 30 knots
      WS3
      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.

On 11/04/2010 06:30 at station code rkblhnut, all data were missing because the eleventh bottle of the diel samples was dropped and the bottle broke. There was not enough sample for chlorophyll *a* analysis or to filter for dissolved nutrients.

For the October sampling, NH4 and DIN data were considered suspect for the following samples. The equipment blank had a NH4 concentration (0.74 mg/L) that was higher than the MDL (0.012 mg/L) and the blank was higher than most samples taken. Therefore, the NH4 data and the DIN data were considered suspect. The diel samples were also considered suspect even though they were separate from the grabs but the concentrations appeared to be higher than normal as well.

rkblhnut 10/06/2010 06:30 rkblhnut 10/06/2010 09:00 rkblhnut 10/06/2010 11:30 rkblhnut 10/06/2010 14:00 rkblhnut 10/06/2010 16:30 rkblhnut 10/06/2010 19:00 rkblhnut 10/06/2010 21:30 rkblhnut 10/07/2010 00:00 rkblhnut 10/07/2010 02:30 rkblhnut 10/07/2010 05:00 rkblhnut 10/07/2010 07:30 rkblhnut 10/07/2010 08:22 rkbmbnut 10/07/2010 12:00 rkbfunut 10/07/2010 10:42 rkbfunut 10/07/2010 10:52 rkbfunut 10/07/2010 11:00 rkbfbnut 10/07/2010 10:00

For the November sampling, NO23, NO3, and DIN were considered suspect for the following samples. The equipment blank had a NO23 concentration (0.03 mg/L) that was higher than the MDL (0.002 mg/L). Although the concentration was lower than most of the samples, the NO23, NO3, and DIN concentrations appeared to be unusually high. The diel samples were also considered suspect even though they were separate from the grabs but the concentrations appeared to be higher than normal as well.

rkblhnut 11/03/2010 05:30 rkblhnut 11/03/2010 08:00 rkblhnut 11/03/2010 10:30 rkblhnut 11/03/2010 13:00 rkblhnut 11/03/2010 15:30 rkblhnut 11/03/2010 18:00 rkblhnut 11/03/2010 20:30 rkblhnut 11/03/2010 23:00 rkblhnut 11/04/2010 01:30

rkblhnut 11/04/2010 04:00 rkblhnut 11/04/2010 08:48 rkbmbnut 11/04/2010 09:15 rkbfunut 11/04/2010 10:48 rkbfbnut 11/04/2010 12:46.

El Niño conditions based on the Climate Prediction Center, National Centers for Environmental Prediction, NOAA/National Weather Service

El Niño strengthened during December 2009, with above-average sea surface temperatures (SST) encompassing the central and eastern equatorial Pacific Ocean. Expected El Niño impacts during January-March 2010 for the contiguous United States include, above-average precipitation for the southern tier of the country, with below-average precipitation in the Pacific Northwest and in the Ohio and Tennessee Valleys. Below-average snowfall and above-average temperatures are most likely across the northern tier of states (excluding New England), while below-average temperatures are favored for the south-central and southeastern states. Expected impacts during March-May 2010 for the contiguous United States include, above-average precipitation for the Southwest, the south-central states, and Florida, and below-average precipitation in the Pacific Northwest and Great Lakes region. Above-average temperatures are most likely across the northern tier of states (excluding New England and the Northern Plains), while below-average temperatures are favored for the south-central and southeastern states.

Weather conditions based on Big Cypress Basin Hydrologic Summary Reports:

January: Near average dry season hydrologic conditions prevailed in January with significantly colder temperatures. Weekly systems of strong cold fronts penetrated into south Florida bringing record cold temperatures to the region as well as several small rainfall events. The weighted average rainfall for January was 2.86 inches, approximately 40% above average rainfall for the month.

February: Wetter than average dry season hydrological conditions with significantly colder temperatures continued in February. Three systems of strong cold fronts penetrated into south Florida bringing continued cold temperatures to the region as well as several rainfall events. The weighted average rainfall for February was 2.74 inches, approximately 38% above average rainfall for the month.

March: March was the wettest dry month season in over 12 years in south Florida. Much cooler temperatures continued in the region through the month. There were moderate cold front systems that penetrated into south Florida generating several rainfall events across the region. The weighted average rainfall for March was 6.49 inches, approximately 167% above average rainfall for the month.

April: Wetter than average hydrologic conditions continued through April. Moderately strong cold front systems penetrated south Florida through the month generating widespread rainfall events. Most of the south Florida region received rainfall ranging from four inches to seven inches during the month. The weighted average rainfall for April was 6 inches, approximately 168% above average rainfall for the month.

May: Hydrologic conditions across the region became much drier in May. May was a relatively dry month with an end in rainfall activity associated with cold fronts. A sea breeze induced convective system generated rain the last week of May. The weighted average rainfall for May was 2.65 inches, approximately 30% below average rainfall for the month.

June: Hydrologic conditions across the region were drier than average in June. Wet season clouds were slow to arrive in June and rainfall events were few and far between across the region. The weighted average rainfall for June was 7.13 inches, approximately 25% below average rainfall for the month.

July: Hydrologic conditions across the region continued to be drier than average through July. The sea breeze induced convective rainfall events were active during the first week of July. However, high atmospheric pressure ridges prevented the typical summer thunderstorm activity for the rest of the month. Rainfall from Tropical Storm Bonnie on July 23rd was not enough to make up the rainfall deficit for the month. The weighted average rainfall for July was 6.72 inches, approximately 24% below average rainfall for the month.

August: The hydrologic conditions across the region were slightly wetter than average in August. High atmospheric pressure ridges across the south central U.S. sea breeze induced convection generated rainfall events across the region. The weighted average rainfall for August was 11.22 inches, approximately 24% above average rainfall for the month.

September: Hydrologic conditions were drier than average across the region in September. Wet season convective thunderstorm activity continued through the first two weeks of the month but decreased the last two weeks of the month. The weighted average rainfall for September was 5.87 inches, approximately 29% below average rainfall for the month.

October: Hydrologic conditions were dry in October. There was very little rainfall activity with only one major rainfall event at the end of the month.

November: Slightly drier than average hydrologic conditions prevailed across the region during November. November begins the downward trend into the dry season cycle. A few early-season cold fronts and sea breeze thunderstorms generated the rainfall events during the month. Rainfall activities were sporadic. The weighted average rainfall for November was 1.39 inches, approximately 69% below average rainfall for the month. **December:** Drier than average hydrologic conditions prevailed across the region with unusually cold temperatures and many rainless days. There were unusually frigid temperatures during the month associated with cold fronts. In spite of the several major cold fronts, moisture conditions were not favorable for producing

temperatures and many rainless days. There were unusually frigid temperatures during the month associated with cold fronts. In spite of the several major cold fronts, moisture conditions were not favorable for producing rainfall activity during the month. Two events during the end of the third and fourth weeks generated measureable rain. The weighted average rainfall for December was 1.25 inches, approximately 73% below average rainfall for the month. Due to a wet spring, the total rainfall for the region was 55.40 inches, which is about average for the year.

Acknowledgement: The data included with this document were collected by the staff of the Florida Department of Environmental Protection at the Rookery Bay National Estuarine Research Reserve with funding through NOAA's Estuarine Research Division. Any products derived from these data should clearly acknowledge this source (please use the attached logos). This recognition is important for ensuring that this long-term monitoring program continues to receive the necessary political and financial support.



