Rookery Bay (RKB) National Estuarine Research Reserve (NERR) Nutrient Metadata (January 2011 – December 2011)

Latest Update: September 23, 2015

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

Phone: (239) 417-6310 ext 402

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 and diel sampling, data management, data QAQC and final data submission)

Beverly Anderson, Research Biologist (responsible for field collection and diel sampling)

Rookery Bay NERR 300 Tower Road Naples, FL 34113

Phone: (239) 417-6310 ext 403

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 were 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. Duplicate grab samples were taken every month at each of the water quality stations 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 the travel time between sites and the time constraints with the contracted laboratory. Rainfall conditions prior to grab sampling were generally not considered due to constraints with the contracted laboratory.

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 from January 2011 through June 2011. Starting in July 2011 through December 2011, the chlorophyll a samples were filtered, extracted, and analyzed at Rookery Bay NERR. Sample bottles were pre-cleaned by the contracted laboratory following their Quality Assurance Management Plan (available by request). From July 2011 through December 2011, amber bottles for the chlorophyll were pre-cleaned using a Fl Department of Environmental (FDEP) decontamination procedure (FDEP SOP FC1000/DEP-OAA-01/001) which involved: cleaning the with phosphate-free soap, rinsing three times with tap water, soaking from 4 - 24 hours in a 10% hydrochloric acid bath, rinsing three times with deionized water, and drying for 24 hours. 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 or peristaltic pumps), 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 holders were assembled with in-line filters (0.7 um glass microfiber filters and 0.45 um membrane filters).

At each sampling station, grab samples for dissolved nutrients were collected 12 inches below the surface (near surface grab) using either a Van Dorn sampler (January 2011 – June 2011) or a peristaltic pump (July 2011 – December 2011). A disposable 60 cc syringe with an attached filter holder or the peristaltic pump tubing with a filter holder attached were used to filter the dissolved nutrients samples. Nitrile gloves were worn through the entire process of sample collection and filtering. For the chlorophyll a samples, 1000 ml or 500 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, HDPE sample bottles were rinsed three times with the filtered water and then filled with 120 ml (syringe method) or 250 ml (peristaltic pump method) of the filtrate, capped, and immediately stored in a cooler with ice. For the dissolved ammonium and nitrite + nitrate, HDPE sample bottles were filled with 25-30 ml (syringe method) or 125 ml (peristaltic pump method) of the filtrate, capped, and immediately stored in a cooler with ice. The HDPE sample bottles for ammonium and nitrite + nitrate contained sulfuric acid for preservation and therefore were not rinsed before adding the filtrate. To avoid cross contamination, the Van Dorn sampler or the peristaltic pump tubing was rinsed thoroughly 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, filters, and syringes were used at each site. 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), specific conductivity, 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). 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 auto-sampler was set up and programmed. The siphon hose was rinsed with 900 ml 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: Nitrile gloves were worn through the entire sample processing. At Rookery Bay's laboratory, each polyethylene bottle containing 900 ml of sample water was shaken to redistribute sediments on the bottom. From January 2011 – June 2011, a disposable 60 cc syringe with an attached filter holder was used to filter the samples. From July 2011 – December 2011, a peristaltic pump with a filter holder attached to the sampling tube was used to filter the samples. For the dissolved ammonium and nitrite + nitrate, HDPE sample bottles were filled with 25-30 ml (syringe method) or 125 ml (peristaltic pump method) of the filtrate, capped, and immediately stored in a cooler with ice. For the dissolved phosphorus and nitrite, HDPE sample bottles were rinsed three times with the filtered water and then filled with 120 ml (syringe method) or 250 ml (peristaltic pump method) 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 filters and syringes 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 mid-channel 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). Salinity at this site ranged from 8.2 to 37.4 ppt during the year. 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. Salinity at this site ranged from 3.6 to 39.2 ppt during the year. Salinity fluctuates 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. Salinity at this site ranged from 0.5 to 39.8 ppt during the year. Salinity fluctuates 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. Salinity at this site ranged from 7.5 to 41.0 ppt during the year. Salinity fluctuates 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 and 2 for the second sample at each 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 2011, the data collection period was from January to December.

Monthly	Grah	Sami	nling
1410111111	OI ab	Sam	UIIIIE

Station Code	Date Time Stamp (rep 1)	(rep 2)
rkblhnut	01/06/2011 10:01	01/06/2011 10:02
rkblhnut	02/03/2011 10:40	02/03/2011 10:50
	03/03/2011 10:40	03/03/2011 10:30
rkblhnut	04/07/2011 09:38	
rkblhnut		04/07/2011 09:20
rkblhnut	05/05/2011 08:51	05/05/2011 08:56
rkblhnut	06/02/2011 08:51	06/02/2011 08:59
rkblhnut	07/11/2011 11:54	07/11/2011 11:58
rkblhnut	08/03/2011 09:17	08/03/2011 09:23
rkblhnut	09/01/2011 09:05	09/01/2011 09:10
rkblhnut	10/06/2011 08:55	10/06/2011 09:00
rkblhnut	11/03/2011 08:10	11/03/2011 08:15
rkblhnut	12/01/2011 09:13	12/01/2011 09:17
rkbmbnut	01/06/2011 11:15	01/06/2011 11:42
rkbmbnut	02/03/2011 11:50	02/03/2011 11:55
rkbmbnut	03/03/2011 10:51	03/03/2011 10:56
rkbmbnut	04/07/2011 09:15	04/07/2011 09:45
rkbmbnut	05/05/2011 09:32	05/05/2011 09:37
rkbmbnut	06/02/2011 08:38	06/02/2011 08:43
rkbmbnut	07/11/2011 08:20	07/11/2011 08:22
rkbmbnut	08/03/2011 07:48	08/03/2011 07:53
rkbmbnut	09/01/2011 08:00	09/01/2011 08:04
rkbmbnut	10/06/2011 08:21	10/06/2011 08:24
rkbmbnut	11/03/2011 08:10	11/03/2011 08:16
rkbmbnut	12/01/2011 09:07	12/01/2011 09:13
rkomonat	12/01/2011 05:07	12/01/2011 07:13
rkbfunut	01/06/2011 13:15	01/06/2011 13:20
rkbfunut	02/03/2011 13:33	02/03/2011 13:38
rkbfunut	03/03/2011 12:20	03/03/2011 12:25
rkbfunut	04/07/2011 11:18	04/07/2011 11:30
rkbfunut	05/05/2011 11:23	05/05/2011 11:28
rkbfunut	06/02/2011 10:50	06/02/2011 10:55
rkbfunut	07/11/2011 09:08	07/11/2011 09:11
rkbfunut	08/03/2011 08:54	08/03/2011 09:00
rkbfunut	09/01/2011 09:32	09/01/2011 09:37
rkbfunut	10/06/2011 09:46	10/06/2011 09:50
rkbfunut	11/03/2011 09:32	11/03/2011 09:40
rkbfunut	12/01/2011 10:26	12/01/2011 10:31
rkbfbnut	01/06/2011 13:45	01/06/2011 13:50
rkbfbnut	02/03/2011 14:09	02/03/2011 14:16
		03/03/2011 14.10
rkbfbnut	03/03/2011 13:31	
rkbfbnut	04/07/2011 12:10	04/07/2011 12:20
rkbfbnut	05/05/2011 12:02	05/05/2011 12:07
rkbfbnut	06/02/2011 11:36	06/02/2011 11:41
rkbfbnut	07/11/2011 09:35	07/11/2011 09:39
rkbfbnut	08/03/2011 09:25	08/03/2011 09:29
rkbfbnut	09/01/2011 10:13	09/01/2011 10:17
rkbfbnut	10/06/2011 10:21	10/06/2011 10:25
rkbfbnut	11/03/2011 10:11	11/03/2011 10:15

rkbfbnut	12/01/2011 11:02	12/01/2011 11:07
Diel Sampling		
Station Code	Date Time Stamp (start)	(end)
rkblhnut	01/05/2011 07:30	01/06/2011 08:30
rkblhnut	02/02/2011 06:00	02/03/2011 07:00
rkblhnut	03/02/2011 06:30	03/03/2011 07:30
rkblhnut	04/06/2011 07:30	04/07/2011 08:30
rkblhnut	05/04/2011 07:00	05/05/2011 08:00
rkblhnut	06/05/2011 09:00	06/06/2011 10:00
rkblhnut	07/06/2011 05:00	07/07/2011 06:00
rkblhnut	08/02/2011 08:30	08/03/2011 09:30
rkblhnut	08/31/2011 08:00	09/01/2011 09:00
rkblhnut	10/05/2011 07:30	10/06/2011 08:30

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 retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The NERRS retains the right to be fully credited for having collected and process the data. Following academic courtesy standards, the NERR site where the data were collected should be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

Requested citation format:

National Estuarine Research Reserve System (NERRS). 2012. System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2012.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page www.nerrsdata.org. Data are available in comma separated version format.

II. Physical Structure Descriptors

9. Entry Verification -

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. Data entry was validated by one other person. 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 "*".

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus &			
Nitrogen:	*Orthophosphate, Filtered	PO4F	mg/L as P
C .	*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 Nitro	ogen DIN	mg/L as N
Plant Pigments:	*Chlorophyll <i>a</i>	CHLA N	μg/L
	Phaeophytin	PHEA	μg/L
Field Parameters (gra	bs only):		
	Water Temperature	WTEM N	°C
	Specific Conductance	SCON_N	mS/cm
	Salinity	SALT_N	ppt
	Dissolved Oxygen	DO_N	mg/L
	Dissolved Oxygen % Satur	ration DO_S_N	%
	рН	PH_N	standard units

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 N and PHEA

b. Calculated ParametersNO3F: 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. The Collier County Pollution Control and Prevention Department Laboratory determined the chlorophyll and phaeophytin MDL from 1/1/2011-6/31/2011. Starting 7/1/2011 through the end of the year, the MDL was based on the Turner Designs Trilogy manual by Rookery Bay NERR staff.

Parameter	Variable	MDL	Approved
Orthophosphate	PO4F	0.004 mg/L	1/1/2011-12/31/2011
Ammonium	NH4F	0.012 mg/L	1/1/2011-1/31/2011
		0.007 mg/L	2/1/2011-3/30/2011
		0.006 mg/L	4/1/2011-12/31/2011
Nitrite	NO2F	0.002 mg/L	1/1/2011-12/31/2011
Nitrite +Nitrate	NO23F	0.002 mg/L	1/1/2011-12/31/2011
Chlorophyll <i>a</i>	CHLA	3 μg/L	1/1/2011-6/30/2011
		$0.03~\mu g/L$	7/1/2011-12/31/2011
Phaeophytin	PHEA	3 μg/L	1/1/2011-6/30/2011
		$0.03~\mu g/L$	7/1/2011-12/31/2011

13. Laboratory Methods-

Orthophosphate, ammonium, nitrite, nitrite+nitrate 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). From January 2011 through June 2011, Chlorophyll *a* and phaeophytin analysis were performed by Collier County Pollution Control and Prevention Department Laboratory. From July 2011 through December 2011, Chlorophyll *a* and phaeophytin analysis were performed by staff at Rookery Bay NERR.

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 Date: January 2011 – June 2011

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.

Date: July 2011 - December 2011

EPA or other Reference Method: EPA 445.0

Method Reference: Standard Methods for the Examination of Water and Wastewater, 20th Edition **Method Description**: An extractive fluorometric technique was used to determine chlorophyll a concentrations. Samples were filtered (120 ml) immediately at the laboratory. Filters were placed in 10 ml culture tubes and stored at -20 °C in the dark for up to four weeks until extraction. 8 ml of 90% aqueous acetone was used to extract the pigments from each filter. Extracts were sonicated for 25 minutes on ice and then steeped for 24 hours at -20 °C in the dark. Extracts were analyzed using a Turner Designs Trilogy laboratory fluorometer with a Chl a (acid) module for the acidification method.

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 taken every month at each station

- 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.

c) Other QAQC methods

Field equipment blanks were taken every sampling event to indicate any potential contamination problems during sampling. For the chlorophyll *a* analysis performed July 2011 – December 2011, control blank samples were used to indicate any potential contamination problems during the filtration and extraction steps. Additionally, a solid standard was used at the beginning and end of sample analysis to indicate any potential drift with the Turner Trilogy instrument.

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

Re

PDR

drizzle

Record comm	nents
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

```
PLR
            light rain
  PHR
            heavy rain
  PSQ
            squally
  PFQ
            frozen precipitation (sleet/snow/freezing rain)
            mixed rain and snow
  PSR
Tide stage
  TSE
            ebb tide
  TSF
            flood tide
  TSH
            high tide
            low tide
  TSL
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 \text{ to} > 1.0 \text{ meters}
  WH4
            1.0 to 1.3 meters
  WH5
            1.3 or greater meters
Wind direction
  Ν
            from the north
  NNE
            from the north northeast
  NE
            from the northeast
  ENE
            from the east northeast
  Е
            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
  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
```

17. Other remarks/notes –

WS5

> 40 knots

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 all January samples (diel and grabs), NH4 data should be considered suspect. The laboratory Control Sample failed low which validates a low bias to the results. The data is estimated and therefore, use of the data for analysis requires careful consideration. The associated calculated DIN data should also be considered suspect.

rkbmbnut January grab samples were taken approximately 30 minutes apart due to a problem with the sonde used to collect field data.

For rkblhnut diel sample collected on 04/07/2011 06:00, PO4 should be considered suspect because the data was outside 4 standard deviations from the mean and did not fit the data trend.

For rkblhnut diel sample collected on 04/07/2011 08:30, NO23 should be considered suspect because the data did not fit the data trend. The associated calculated NO3 and DIN data should also be considered suspect.

rkbmbnut grab samples were collected approximately 30 minutes apart, there are no field notes indicating what caused the delay.

For rkblhnut diel sample collected on 08/02/2011 11:00, NO2 should be considered suspect because the data did not fit the data trend. The associated calculated NO3 data should also be considered suspect.

All diel data collected from 08/31/2011 08:00 until 09/01/2011 09:00 should be considered suspect because the refrigeration on the ISCO auto-sampler may have failed to keep the samples cool during sampling.

All diel data collected from 10/05/2011 07:30 until 10/06/2011 08:30 should be considered suspect because the refrigeration on the ISCO auto-sampler may have failed to keep the samples cool during sampling.

For the November grab samples, NO23 data should be considered suspect due to possible contamination. The NO23 concentration for the equipment blank (0.408 mg/L) was significantly higher than the MDL (0.002 mg/L) and higher than the sample concentrations. There is a high bias to the data and therefore, use of the data for analysis requires careful consideration. The associated calculated NO3 and DIN data should also be considered suspect.

For November and December 2011, all diel data was missing due to instrument malfunction. The ISCO auto-sampler was evaluated but could not be repaired in a cost effective manner. The auto-sampler was replaced but was not received until January 2012.

El Niño/Southern Oscillation (ENSO) conditions based on the Climate Prediction Center, National Centers for Environmental Prediction, NOAA/National Weather Service

La Niña conditions persisted at a lesser intensity in the Northern Hemisphere through the spring of 2011. Impacts in the United States included below-average precipitation across the southwestern and southeastern states. An increased chance of above-average temperatures was forecasted for much of the southern and central U.S. ENSO-neutral conditions prevailed through the summer and fall. Weak-to-moderate strength La Niña conditions occurred in the Northern Hemisphere starting in the winter of 2011 causing an increased chance of

above-average temperatures across the south-central and southeastern U.S. and increased chance of drier-than-average conditions across the southern tier of the U.S.

Weather conditions based on Big Cypress Basin Hydrologic Summary Reports:

January: No report.

February: Considerably drier than normal hydrologic conditions prevailed in February. High atmospheric ridges prevented major cold fronts in south Florida. This month was the driest month in the last 10 years and tied for the third driest month during the last 80 years. The weighted average rainfall was 0.73 inches.

March: Drought conditions lightened in March. Two cold fronts during the second and fourth weeks of the month brought rain to south Florida. The weighted average rainfall was 2.74 inches, or 107% of normal for March. However, the dry season rainfall up to this point was 71% of historic average.

April: Severe drought conditions continued across south Florida. No low pressure systems or cold fronts reached south Florida. The month was very dry with a weighted average rainfall of 1.92 inches, or 81% of normal for the month. Dry season rainfall up to this point was 69% of historic average.

May: No report

June: Wet season had a very late start and the severe drought conditions continued across south Florida. High atmospheric pressure ridges dominated the weather pattern for the first two-thirds of the month. Summertime convective thunderstorms were very scattered across the region when they appeared the fourth week of the month. The weighted average rainfall was 6 inches, or about 64% of normal for June. Year-to-date rainfall for the region was 25% below normal.

July: Overall hydrologic conditions across the region continued to be drier than average through July. Summertime convective thunderstorms were a regular occurrence for the first week of July. However, they dissipated during the fourth week of the month due to high atmospheric pressure ridges dominating the weather pattern for south Florida. The weighted average rainfall was 7.21 inches, or about 85% of normal for July.

August: The hydrologic conditions across the region were near normal in August. Summertime convective thunderstorms were frequent. Tropical Storm Emily and Hurricane Irene pulled considerable moisture from south Florida, but were not strong enough to adversely affect the overall monthly rainfall. The weighted average rainfall was 9.61 inches, approximately 105% of normal for the month.

September: Hydrologic conditions were near normal across the region in September. Wet season convective thunderstorms were frequent but varied spatially in intensity and duration across the region. The weighted average rainfall was 8.89 inches, approximately 107% of normal for the month.

October: The end of the wet season came with some very wet weather episodes. The hydrologic conditions were significantly wetter than normal for the month. Three multi-day heavy rain events caused such wet hydrologic conditions. The weighted average rainfall was 10.18 inches, or about 294% of normal for the month. Year-to-date rainfall for the region was 2% above normal.

November: Dry season started with favorable hydrologic conditions. Two mild cold fronts during the second and third weeks of the month generated light rainfall across the region. The weighted average rainfall for was 0.68 inches, approximately 33% of normal for the month.

December: Hydrologic conditions were dry throughout the region. There were few cold fronts during the month but two mild fronts during the second and fourth weeks brought some light rainfall across the region. The weighted average rainfall was 0.40 inches, approximately 24% of normal for the month. The average annual rainfall for the region was 53.4 inches, about 3% below normal.

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.



