

**Rookery Bay (RKB) National Estuarine Research Reserve (NERR) Nutrient Metadata
(January 2012 – December 2012)
Latest Update: February 16, 2016**

I. Data Set and Research Descriptors

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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 (a 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. Beginning in October 2012, grab samples were also collected at Pumpkin Bay (a Secondary SWMP station). 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, extracted, and analyzed at Rookery Bay NERR from January 2012 through September 2012. Starting in October 2012 through December 2012, the chlorophyll *a* samples were filtered and analyzed by the contracted laboratory. Sample bottles were pre-cleaned by the contracted laboratory following their Quality Assurance Management Plan (available by request). From January 2012 through September 2012, amber bottles for chlorophyll were pre-cleaned using a FI Department of Environmental (FDEP) decontamination procedure (FDEP SOP FC1000/DEP-QAA-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.

The bottle kits for each 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 device (peristaltic pump) tubing, carboys (for deionized water), and filter holders were pre-cleaned using a FDEP decontamination procedure (FDEP SOP FC1000/DEP-QAA-01/001) as described above. One to two days prior to field sampling, the filter holders were assembled 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 peristaltic pump. The peristaltic pump tubing with a filter holder attached were used to filter for dissolved nutrients. Nitrile gloves were worn through the entire process of sample collection and filtering. For the chlorophyll *a* samples, HDPE amber sample bottles were rinsed three times with the sample water and then filled to the shoulder, 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 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. For total Kjeldahl nitrogen (TKN) and total phosphorus (TP) (analyzed for grab samples only), HDPE sample bottles were rinsed three times with the sample water and then filled to the shoulder, capped, and put on ice. To avoid cross contamination, 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 and filters 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. Samples were shipped overnight to the FDEP lab beginning in October 2012, prior to that they were analyzed by the Collier County lab.

At each site physical/chemical water quality parameters were measured at the same depth as where the nutrient samples were taken. AYSI 600-OMS sonde and a hand held display (YSI model 650) were used to record the measurements. Recorded parameters included salinity (ppt), specific conductivity (mS/cm),

temperature (°C), and dissolved oxygen (% and mg/L). Equipment calibration was 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 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 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 programming 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). Bottle kits for each 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 during sample processing. At Rookery Bay's laboratory, each polyethylene bottle containing 1000 ml of sample water was shaken to homogenize the sample. A peristaltic pump with a filter holder attached to the sampling tube was used to filter for dissolved nutrients. For the dissolved ammonium and nitrite + nitrate, HDPE sample bottles were filled with the filtrate, capped, and immediately stored in a cooler with ice. For the dissolved phosphorus and nitrite, HDPE sample bottles were filled the filtrate, capped, and immediately stored in a cooler with ice. For the chlorophyll *a* samples, HDPE amber sample bottles were filled with at least 500 ml of unfiltered sample, capped, and immediately stored in a cooler with ice. New filters and syringes were used for each sample. Samples were shipped overnight to the FDEP lab beginning in October 2012, prior to that they were analyzed by the Collier County lab.

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 13.9 to 38.1 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 (rkmbnut):

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 2.3 to 38.6 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 0.7 to 38.9 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 4.1 to 38.4 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.

Pumpkin Bay (rkbpbnut):

Lat/Long (Decimal Degrees): 25.9141 N, 81.5404 W

This Secondary SWMP site is located at the mouth of the Pumpkin River and does not have an associated water quality data logger. Mean high water is approximately 1 – 2 meters. The mean tide range is approximately 0.40 meters. Salinity at this site ranged from 16.6 to 40.1 ppt during the year. The bottom habitat is predominantly fine sand and there is no bottom vegetation. Mature red mangrove forests dominate the Pumpkin River and the bay. Upland land use is minimal with the main influence US 41 and the Picayune Strand State Forest canal system, which diverts freshwater from Pumpkin Bay and its tributary. Due to the altered freshwater inflow, generally this site can be freshwater limited.

5. Code variable definitions-

rkbhnut = Rookery Bay Lower Henderson Creek nutrients (monthly grabs and diel sampling)
 rkmbnut = Rookery Bay Middle Blackwater River nutrients (monthly grabs)
 rkbfnut = Rookery Bay Faka Union Bay nutrients (monthly grabs)
 rkbfbnut = Rookery Bay Fakahatchee Bay nutrients (monthly grabs)
 rkbpbnut = Rookery Bay Pumpkin Bay nutrients (monthly grabs, Secondary SWMP station)

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 SWMP sampling stations. Sampling began in October 2012 at the non-SWMP station, rkbpbwq. For 2012, the data collection period was from January to December.

Monthly Grab Sampling

Station Code	Date Time Stamp (rep 1)	(rep 2)
rkbhnut	01/05/2012 09:00	01/05/2012 09:02
rkbhnut	02/02/2012 14:06	02/02/2012 14:08
rkbhnut	03/01/2012 13:44	03/01/2012 13:46
rkbhnut	04/05/2012 15:10	04/05/2012 15:12
rkbhnut	05/03/2012 13:25	05/03/2012 13:26
rkbhnut	06/07/2012 13:27	06/07/2012 13:30
rkbhnut	07/05/2012 12:58	07/05/2012 13:00
rkbhnut	08/01/2012 13:05	08/01/2012 13:07
rkbhnut	09/06/2012 13:40	09/06/2012 13:42
rkbhnut	10/04/2012 12:58	10/04/2012 13:02
rkbhnut	11/08/2012 13:55	11/08/2012 13:57
rkbhnut	12/06/2012 14:20	12/06/2012 14:23
rkmbnut	01/05/2012 11:00	01/05/2012 11:02
rkmbnut	02/02/2012 09:49	02/02/2012 09:52
rkmbnut	03/01/2012 09:35	03/01/2012 09:37
rkmbnut	04/05/2012 09:05	04/05/2012 09:07
rkmbnut	05/03/2012 08:59	05/03/2012 09:01
rkmbnut	06/07/2012 09:18	06/07/2012 09:21
rkmbnut	07/05/2012 09:07	07/05/2012 09:09
rkmbnut	08/01/2012 09:03	08/01/2012 09:06
rkmbnut	09/06/2012 08:49	09/06/2012 08:51
rkmbnut	10/04/2012 10:53	10/04/2012 10:56
rkmbnut	11/08/2012 09:44	11/08/2012 09:46
rkmbnut	12/06/2012 09:49	12/06/2012 09:52

rkbfunut	01/05/2012 12:14	01/05/2012 12:16
rkbfunut	02/02/2012 11:05	02/02/2012 11:07
rkbfunut	03/01/2012 10:42	03/01/2012 10:44
rkbfunut	04/05/2012 11:34	04/05/2012 11:35
rkbfunut	05/03/2012 10:14	05/03/2012 10:16
rkbfunut	06/07/2012 10:32	06/07/2012 10:35
rkbfunut	07/05/2012 10:15	07/05/2012 10:17
rkbfunut	08/01/2012 10:05	08/01/2012 10:07
rkbfunut	09/06/2012 10:15	09/06/2012 10:17
rkbfunut	10/04/2012 10:01	10/04/2012 10:04
rkbfunut	11/08/2012 11:05	11/08/2012 11:07
rkbfunut	12/06/2012 11:20	12/06/2012 11:23
rkbfbnut	01/05/2012 12:45	01/05/2012 12:47
rkbfbnut	02/02/2012 11:36	02/02/2012 11:38
rkbfbnut	03/01/2012 11:19	03/01/2012 11:21
rkbfbnut	04/05/2012 12:50	04/05/2012 12:52
rkbfbnut	05/03/2012 10:44	05/03/2012 10:47
rkbfbnut	06/07/2012 11:05	06/07/2012 11:07
rkbfbnut	07/05/2012 10:45	07/05/2012 10:47
rkbfbnut	08/01/2012 10:35	08/01/2012 10:37
rkbfbnut	09/06/2012 10:55	09/06/2012 10:57
rkbfbnut	10/04/2012 09:31	10/04/2012 09:34
rkbfbnut	11/08/2012 11:36	11/08/2012 11:38
rkbfbnut	12/06/2012 11:50	12/06/2012 11:53
rkbpbnut	10/04/2012 08:51	10/04/2012 08:54
rkbpbnut	11/08/2012 10:33	11/08/2012 10:36
rkbpbnut	12/06/2012 10:42	12/06/2012 10:45

Diel Sampling

Station Code	Date Time Stamp (begin)	(end)
rkbllhnut	01/31/2012 07:30	02/01/2012 08:30
rkbllhnut	02/28/2012 09:00	02/29/2012 10:00
rkbllhnut	04/03/2012 05:00	04/04/2012 06:00
rkbllhnut	05/01/2012 05:30	05/02/2012 06:30
rkbllhnut	06/05/2012 07:00	06/06/2012 08:00
rkbllhnut	07/02/2012 05:00	07/03/2012 06:00
rkbllhnut	07/30/2012 05:00	07/31/2012 06:00
rkbllhnut	09/03/2012 09:00	09/04/2012 10:00
rkbllhnut	10/02/2012 08:30	10/03/2012 09:30
rkbllhnut	11/06/2012 13:00	11/07/2012 14:00
rkbllhnut	12/11/2012 05:45	12/12/2012 06:45

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. Florida DEP used the nutrient data to develop numeric nutrient criteria for the southwest region of Florida, which were approved by the Environmental Protection Agency.

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 files) were provided monthly from the contracted laboratory to Christina Panko Graff, Water Quality 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 6.5. 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 an asterisks “*”.

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
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Total Kjeldahl Nitrogen	TKN	mg/L as N
	Total Nitrogen	TN	mg/L as N
	Total Organic Nitrogen	TON	mg/L as N
Plant Pigments:	*Chlorophyll <i>a</i>	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
Field Parameters (grabs only):			
	Water Temperature	WTEM_N	°C
	Specific Conductance	SCON_N	mS/cm
	Salinity	SALT_N	ppt
	Dissolved Oxygen	DO_N	mg/L
	% Dissolved Oxygen Saturation	DO_S_N	%

Notes:

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

11. Measured or Calculated Laboratory Parameters –

a. Parameters Measured Directly-

Phosphorus species: PO4F, TP

Nitrogen species: NH4F, NO2F, NO23F, TKN

Plant Pigments: CHLA_N and PHEA

b. Calculated Parameters-

NO3F: NO23F –NO2F

DIN: NO23F +NH4F

TN: TKN + NO23F

TON: TKN – 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 or Florida Department of Environmental Protection, Bureau of Laboratories. 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 labs employed verification checks on all MDLs. If the verification checks met the labs' acceptance criteria then the MDL was not recommended for change. From 7/1/2011 through 09/30/2012, the MDL for chlorophyll and phaeophytin were based on the Turner Designs Trilogy manual by Rookery Bay NERR staff. From 10/1/2012 through the end of the year, the MDL for all parameters was determined by Florida Department of Environmental Protection Bureau of Laboratories ,

Parameter	Variable	MDL	Approved
Orthophosphate	PO4F	0.004 mg/L	01/01/12-12/31/12
Ammonium	NH4F	0.006 mg/L	01/01/12-09/30/12
		0.010 mg/L	10/01/12-12/31/12
Nitrite	NO2F	0.002 mg/L	01/01/12-12/31/12
Nitrite +Nitrate	NO23F	0.002 mg/L	01/01/12-09/30/12
		0.004 mg/L	10/01/12-12/31/12
Chlorophyll <i>a</i>	CHLA	0.03 µg/L	01/01/12-09/30/12
		0.55 µg/L	10/01/12-12/31/12
Phaeophytin	PHEA	0.03 µg/L	01/01/12-09/30/12
		0.40 µg/L	10/01/12-12/31/12
Kjeldahl Nitrogen	TKN	0.059 mg/L	01/01/12-09/30/12
		0.080 mg/L	10/01/12-12/31/12
Total Phosphorus	TP	0.004 mg/L	01/01/12-09/30/12
		0.002 mg/L	10/01/12-12/31/12

13. Laboratory Methods–

From January 2012 through September 2012, chemical 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 2012 through September 2012, Chlorophyll *a* and phaeophytin analysis were performed by staff at Rookery Bay NERR. From October 2012 through December 2012, chemical and biological analysis was performed by Florida Department of Environmental Protection, Bureau of Laboratories.

a. Parameter: PO4F

Date: January 2012 – September 2012

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.

Date: October 2012 - December 2012

EPA or other Reference Method: EPA 365.1

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

Method Description: Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phosphomolybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration and is measured with a rapid flow autoanalyzer.

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

b. Parameter: TP

EPA or other Reference Method: EPA 365.1

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

Method Description: Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phosphomolybdate complex. All of the phosphorus present in the sample regardless of forms is measured by the persulfate digestion procedure.

Preservation Method: Samples were preserved with H₂SO₄ and stored at 4 °C until analysis.

c. 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 with a rapid flow autoanalyzer.

Preservation Method: Samples were preserved with H₂SO₄ and stored at 4 °C until analysis.

NOTE: This method measures total ammonia, NH₃ is considered negligible

d. Parameter: NO₂F

Date: January 2012 – September 2012

EPA or other Reference Method: SM 4500-NO₂ B and EPA 353.2

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.

Date: October 2012 - December 2012

EPA or other Reference Method: EPA 353.2

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 a rapid flow autoanalyzer

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

e. 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 a rapid flow autoanalyzer

Preservation Method: Samples were preserved with H₂SO₄ and stored at 4 °C until analysis.

f. Parameter: TKN

EPA or other Reference Method: EPA 351.2

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 a rapid flow autoanalyzer

Preservation Method: Samples were preserved with H₂SO₄ and stored at 4 °C until analysis.

g. Parameter: CHLA and PHEA

Date: January 2012 – September 2012

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.

Date: October 2012 – December 2012

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 UV/VIS Spectrophotometer.

Preservation Method: Stored at 4 °C and filtered at the lab upon arrival.

14. Field and Laboratory QAQC programs-

Based on Collier County Pollution Control and Prevention Department (CCPCP) Laboratory's Quality Assurance Management Plan version 04-02-08 (available by request) and FDEP SOP 5361 QAQC manual and FDEP Quality Manual (available by request).

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

i) **Field Variability** – Duplicates (successive grabs at each station) were taken every month at each station

ii) **Laboratory variability – CCPCP:** 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. **FDEP:** The RPD for matrix duplicates was measured either by the instrument or the analyst. When the average value of the concentration was above the PQL then the RPD must be no more than 20 % in order to be acceptable.

iii) **Inter-organizational splits – CCPCP and FDEP:** The laboratories participate 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 known concentration.

i) **Sample spikes- CCPCP:** 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 nitrate-nitrite and ammonium and 85-115 % for nitrite and orthophosphate. **FDEP:** A representative sample was spiked with known quantities (preferably approximately 2 to 10 times the practical quantitation limit (PQL)) of the analyte before processing. Percent recoveries were calculated for the added analyte. Matrix spike recoveries were indicators of sample matrix interference and contamination. The confidence range was set at ± 15 % for water matrices.

ii) **Standard reference material analysis- CCPCP:** 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 % recovery was 90-110 % for nitrate-nitrite and ammonium and 85-115 % nitrite and orthophosphate. **FDEP:** Standard curves were checked against certified or other independently prepared standards during each analytical run. Control standards were

analyzed at least every 20 samples. The correlation coefficient for a standard curve should be 0.995 or greater and the recovery for each calibrant above the PQL should be $\pm 10\%$.

iii) **Cross calibration exercised – CCPCP:** 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 January 2012 – September 2012, 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
GSM	See metadata

Sensor errors

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

Parameter Comments

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

Record comments

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

Cloud cover

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

Precipitation

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

Tide stage

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

Wave height

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

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest

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 February grab samples, the NO₂3F data should be considered suspect at all stations due to possible contamination. The NO₂3 concentration for the equipment blank (0.062 mg/L) was significantly higher than the MDL (0.002 mg/L) and higher than most sample concentrations. There is a high bias to the data and therefore, use of the data for analysis requires careful consideration. The associated NO₃F and DIN data should also be considered suspect since they are calculated from NO₂3F.

For July through December 2012 grab samples, NH₄F and NO₂3F samples were not filtered due to a mix up with the lab. As a result, analyses may have been skewed by the presence of microbes or particulates that may have interfered with sample analysis or introduced additional nutrients. Measured values are likely higher than they would have been from filtered samples. This also impacted calculated parameters NO₃, DIN, TN, and TON. All grab samples for these parameters have been marked 1 CSM or GSM beginning July 2012 through January 2016.

For the August grab samples, the CHLA and PHEA replicate samples were taken using different field methods. Replicate 1 was taken by dipping the bottle just below the surface for the grab. Replicate 2 was taken by using the peristaltic pump. This was done to test for a difference between the field methods. The Relative Percent Difference for CHLA was greater than the limit of 25% for rkbmbnut 08/01/2012 09:03 and 09:06 and rkbfunut 08/01/2012 10:05 and 10:07 so they were flagged as suspect.

From October through December for all sites and for both diel and grab programs, the NH₄ data reported is actually total ammonia. The analysis was performed by a different laboratory during this period. Their explanation of the method is that through acidification of field samples, any available NH₃ (un-ionized ammonia) is converted to NH₄ (ammonium) and total ammonia is measured analytically. The ammonium present following acid preservation represents the total ammonia in the original sample.

For the diel sample at rkbhnut on 10/02/2012 13:30, PO₄F data was flagged as suspect because it was a significant outlier beyond 3 standard deviations from the mean and it did not fit the data trend.

For the diel sample at rkbhnut on 10/03/2012 09:30, NO₂F data was flagged as suspect because it was a significant outlier beyond 4 standard deviations from the mean. The corresponding NO₃F data was flagged as suspect as well since it is calculated from NO₂F.

For the diel sample at rkbhnut on 12/12/2012 06:45, NO₂3F data was flagged as suspect because it was a significant outlier beyond 3 standard deviations from the mean and did not fit the data trend. The corresponding NO₃F and DIN data were flagged as suspect as well since they are calculated from NO₂3F.

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

A majority of models predicted a weak or moderate strength La Niña in early Northern Hemisphere spring season before dissipating during the March to May period. During January - March, there was an increased chance of above-average temperatures across the south-central and southeastern U.S. and drier-than-average conditions were more likely across the southern tier of the U.S. La Niña weakened during March and a transition from La Niña to ENSO-neutral conditions occurred in April. ENSO-neutral conditions continued

through September. Borderline ENSO-neutral/ weak El Niño conditions developed in October but dissipated and ENSO-neutral conditions were favored for the rest of the year.

Noteworthy weather events:

Tropical Storm Debby peripherally impacted the area from 6/23/2012-6/27/2012.

Tropical Storm Isaac peripherally impacted the area from 8/26/2012-8/27/2012.

Weather conditions based on Big Cypress Basin Hydrologic Summary Reports:

January: The hydrologic conditions in southwest Florida were abnormally dry. There were only two mild cold fronts, which brought very little rainfall across the region. The weighted average rainfall was 0.25 inches, which was 12% of the long-term average for this month. Surface and groundwater levels retreated on the dry season cycle.

February: The hydrologic conditions in the region were dry. There were very infrequent cold fronts, which did not bring very much rainfall to the region. The weighted average rainfall was 1.70 inches, which was 85% of the long-term average for this month. Surface and groundwater levels continued to retreat on the dry season cycle.

March: No report

April: Drought-like hydrologic conditions in the region received some relief from two low atmospheric systems in the eastern Gulf of Mexico. The weighted average rainfall was 2.42 inches, which was 102% of the long-term average for this month. Surface and groundwater levels continued to retreat on the dry season cycle.

May: Hydrologic conditions in the region continued to be drier than the long-term average. Only scattered rainfall across the region with a weighted average of 3.45 inches, which was 93% of the long-term average for this month. Surface and groundwater levels continued the downward trend of the dry season cycle.

June: The annual wet season cycle was later than usual in the region. Typical wet season convective thunderstorms did not begin until late June. Tropical Storm Debby in the fourth week of the month brought only some peripheral rain. The weighted average rainfall was 6.12 inches, which was 65% of the long-term average for this month. Surface and groundwater levels continued a downward trend to lower than normal for the season.

July: Typical wet season convective thunderstorms were sporadic causing the hydrologic conditions in the region to be drier than the long-term records for the month. The weighted average rainfall was 5.48 inches, which was 65% of the long-term average for this month. Year-to-date the rainfall was 30% below the long-term average. Surface and groundwater levels began the upward trend of the annual wet season cycle but were still lower than normal.

August: Typical wet season convective thunderstorms were sporadic causing the hydrologic conditions in the region to be drier than the long-term records for the month. Tropical Storm Isaac only brought an average of 2.5 inches of rain to the region. The weighted average rainfall was 10.9 inches, which was 19% above the long-term average for this month. Year-to-date the rainfall was 20% below the long-term average. Surface and groundwater levels continued the upward trend of the annual wet season cycle but were still lower than normal.

September: Peak wet season conditions prevailed in the region, however conditions were still drier than average. Heavy rainfall during the first week of the month produced the bulk of the month's rainfall. The weighted average rainfall was 7.43 inches, which was 88% of the long-term average for this month. Year-to-date the rainfall was about 18% below the long-term average. Surface and groundwater levels continued the upward trend of the annual wet season cycle.

October: Hydrologic conditions in the region were wetter than the long-term average. The weighted average rainfall was 6.00 inches, which was 163% of the long-term average for this month. Year-to-date the rainfall was about 14% below the long-term average.

November: The annual transition from wet season to dry season was one of the driest on record in the region since 1932. There was an abrupt end to the typical raining season convective thunderstorms and no cold fronts to bring rainfall to the region. The weighted average rainfall was 0.36 inches, which was 18% below the long-term average for this month. Year-to-date the rainfall was about 18% below the long-term average. Surface and groundwater levels began the downward trend of the annual cycle and residual effects of a wet October kept water levels near normal for the month.

December: Hydrologic conditions were wetter than average across the region. Cold fronts during the second and third weeks helped generate rainfall events. The weighted average rainfall was 2.82 inches, which was 171% above the long-term average for this month. The total rainfall for the year was 47.17 inches, about 14% below the long-term average. Surface and groundwater levels continued the downward trend of the annual cycle but stayed near average levels.

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