# Rookery Bay (RKB) National Estuarine Research Reserve (NERR) Nutrient Metadata (January 2015 – December 2015) Latest Update: May 31, 2016

Note: This is a provisional metadata document; it has not been authenticated as of its download date. Contents of this document are subject to change throughout the QAQC process and it should not be considered a final record of data documentation until that process is complete. Contact the CDMO (cdmosupport@belle.baruch.sc.edu) or Reserve with any additional questions.

### 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 v1.7. 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, chlorophyll *a*, the samples were filtered in the field. Sample bottles were pre-cleaned by the contracted laboratory following their Quality Assurance Management Plan (available by request). 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) 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. 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).

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  $\mu$ m glass microfiber filters and 0.45  $\mu$ m 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, nitrite + nitrate, total Kjelldahl nitrogen (TKN), and total phosphorus (TP) (analyzed for grab samples only) contained sulfuric acid for preservation and therefore were not rinsed before adding the samples. 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 in Tallahassee, FL.

At each site physical/chemical water quality parameters were measured at the same depth as where the nutrient samples were taken. From January through July AYSI 600-OMS sonde and a hand held display (YSI model 650) were used and starting in August an YSI EXO1 sonde and hand held display were used to record the measurements. Recorded parameters included salinity (ppt), specific conductivity (mS/cm), temperature (°C), dissolved oxygen (% and mg/L) and beginning in August pH and turbidity (NTU). Equipment calibration was done according to FDEP SOP 001/01.

#### b) Monthly 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 in the grab sampling methods. 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. The HDPE sample bottles for ammonium and nitrite + nitrate contained sulfuric acid for preservation and therefore were not rinsed before adding the filtrate, capped, and immediately stored in a cooler with ice. For the dissolved phosphorus and nitrite, HDPE sample bottles were filled with 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 were used for each sample. Samples were shipped overnight to the FDEP lab in Tallahassee, FL.

# 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 0.26 m to 2.11 m (average 1.26 m). Salinity at this site ranged from 12.3 to 35.4 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 0.6 to 37.7 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 1.7 meters. Salinity at this site ranged from 0.5 to 37.6 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 0.5 to 37.7 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 1-1.44 meters. The mean tide range is approximately 0.0- 0.4 meters. Salinity at this site ranged from 11.5 to 37.6 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

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)

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 2015, the data collection period was from January to December.

Monthly Grab Sampling			
Station Code	Date Time Stamp (rep 1)	(rep 2)	
rkblhnut	01/07/2015 15:44	01/07/2015 15:47	
rkblhnut	02/04/2015 09:41	02/04/2015 09:46	
rkblhnut	03/04/2015 09:30	03/04/2015 09:35	
rkblhnut	04/07/2015 08:10	04/07/2015 08:14	
rkblhnut	05/06/2015 11:57	05/06/2015 12:00	
rkblhnut	06/09/2015 11:18	06/09/2015 11:23	
rkblhnut	07/07/2015 06:34	07/07/2015 06:38	
rkblhnut	08/04/2015 11:19	08/04/2015 11:25	
rkblhnut	09/09/2015 06:45	09/09/2015 06:50	
rkblhnut	10/07/2015 06:53	10/07/2015 06:58	
rkblhnut	11/04/2015 12:45	11/04/2015 12:50	
rkblhnut	12/02/2015 12:58	12/02/2015 13:02	
rkbmbnut	01/07/2015 14:09	01/07/2015 14:13	
rkbmbnut	02/04/2015 13:14	02/04/2015 13:17	
rkbmbnut	03/04/2015 12:48	03/04/2015 12:51	
rkbmbnut	04/07/2015 12:05	04/07/2015 12:09	
rkbmbnut	05/06/2015 09:55	05/06/2015 09:59	
rkbmbnut	06/09/2015 07:48	06/09/2015 07:52	
rkbmbnut	07/07/2015 08:05	07/07/2015 08:08	
rkbmbnut	08/04/2015 07:20	08/04/2015 07:25	
rkbmbnut	09/09/2015 08:13	09/09/2015 08:17	
rkbmbnut	10/07/2015 08:40	10/07/2015 08:45	
rkbmbnut	11/04/2015 08:39	11/04/2015 08:49	
rkbmbnut	12/02/2015 08:45	12/02/2015 08:51	
rkbfunut	01/07/2015 11:10	01/07/2015 11:14	
rkbfunut	02/04/2015 11:36	02/04/2015 11:41	
rkbfunut	03/04/2015 11:17	03/04/2015 11:23	
rkbfunut	04/07/2015 10:53	04/07/2015 10:56	
rkbfunut	05/06/2015 08:42	05/06/2015 08:45	

rkbfunut	06/09/2015 08:51	06/09/2015 08:55
rkbfunut	07/07/2015 09:03	07/07/2015 09:06
rkbfunut	08/04/2015 08:41	08/04/2015 08:45
rkbfunut	09/09/2015 09:17	09/09/2015 09:20
rkbfunut	10/07/2015 09:53	10/07/2015 09:56
rkbfunut	11/04/2015 09:47	11/04/2015 09:53
rkbfunut	12/02/2015 10:14	12/02/2015 10:18
rkbfbnut	01/07/2015 12:48	01/07/2015 12:52
rkbfbnut	02/04/2015 12:01	02/04/2015 12:05
rkbfbnut	03/04/2015 11:43	03/04/2015 11:47
rkbfbnut	04/07/2015 10:27	04/07/2015 10:33
rkbfbnut	05/06/2015 09:06	05/06/2015 09:11
rkbfbnut	06/09/2015 09:26	06/09/2015 09:29
rkbfbnut	07/07/2015 09:28	07/07/2015 09:31
rkbfbnut	08/04/2015 09:13	08/04/2015 09:17
rkbfbnut	09/09/2015 08:54	09/09/2015 08:58
rkbfbnut	10/07/2015 10:23	10/07/2015 10:27
rkbfbnut	11/04/2015 10:19	11/04/2015 10:24
rkbfbnut	12/02/2015 10:34	12/02/2015 10:38
rkbpbnut	01/07/2015 13:34	01/07/2015 13:38
rkbpbnut	02/04/2015 12:37	02/04/2015 12:40
rkbpbnut	03/04/2015 12:15	03/04/2015 12:19
rkbpbnut	04/07/2015 11:21	04/07/2015 11:26
rkbpbnut	05/06/2015 08:15	05/06/2015 08:20
rkbpbnut	06/09/2015 08:25	06/09/2015 08:29
rkbpbnut	07/07/2015 08:40	07/07/2015 08:44
rkbpbnut	08/04/2015 08:07	08/04/2015 08:12
rkbpbnut	09/09/2015 09:41	09/09/2015 09:44
rkbpbnut	10/07/2015 09:24	10/07/2015 09:28
rkbpbnut	11/04/2015 09:20	11/04/2015 09:26
rkbpbnut	12/02/2015 09:29	12/02/2015 09:34
ткоронис	12/02/2013 09:29	12/02/2015 07:51
Diel Sampling		
Station Code	Date Time Stamp (begin)	(end)
rkblhnut	01/14/2015 03:00	01/15/2015 04:00
rkblhnut	02/17/2015 06:30	02/18/2015 07:30
rkblhnut	03/17/2015 05:00	03/18/2015 06:00
rkblhnut	04/15/2015 05:00	04/16/2015 06:00
rkblhnut	05/18/2015 07:00	05/19/2015 08:00
rkblhnut	06/16/2015 07:00	06/17/2015 08:00
		07/16/2015 07:00
rkblhnut	07/15/2015 06:00	
rkblhnut	08/11/2015 04:00	08/12/2015 05:00
rkblhnut	09/15/2015 09:30	09/16/2015 10:30
rkblhnut	10/14/2015 07:00	10/15/2015 08:00
rkblhnut	11/17/2015 09:30	11/18/2015 10:30
rkblhnut	12/09/2015 05:00	12/10/2015 06:00

# 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 <a href="http://cdmo.baruch.sc.edu">http://cdmo.baruch.sc.edu</a>.

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 June 2013, October 2015 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:

NOAA National Estuarine Research Reserve System (NERRS). 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 <a href="www.nerrsdata.org">www.nerrsdata.org</a>. 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 Julie Brader Drevenkar, Water Quality Program Manager. Upon receiving the results, Julie reviewed the data for errors. Julie 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 6.6. 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 Category

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

Data Category	Parameter	Variable Name	<b>Units of Measure</b>
Phosphorus and Nitrogen:			
	*Orthophosphate, Filtered Total Phosphorus *Ammonium, Filtered *Nitrite, Filtered *Nitrate, Filtered *Nitrate, Filtered Dissolved Inorganic Nitrogen Total Kjelldahl Nitrogen	PO4F TP NH4F NO2F NO3F NO23F DIN TKN	mg/L as P mg/L as P mg/L as N mg/L as N mg/L as N mg/L as N mg/L as N mg/L as N
Plant Pigments:	*61.		Œ
	*Chlorophyll <i>a</i> Phaeophytin	CHLA_N PHEA	μg/L μg/L
Field Parameters (grabs or	ıly):		
	Water Temperature Specific Conductance Salinity Dissolved Oxygen % Dissolved Oxygen Saturatio pH Turbidity	WTEM_N SCON_N SALT_N DO_N ON DO_S_N PH_N TURB_N	°C mS/cm ppt mg/L % pH units NTU/FNU

#### 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 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 lab's acceptance criteria then the MDL was not recommended for change. The MDL for all parameters were determined by Florida Department of Environmental Protection, Bureau of Laboratories.

Parameter	Variable	MDL	Approved
Orthophosphate	PO4F	0.004  mg/L	01/01/15-12/31/15
Ammonium	NH4F	0.002  mg/L	01/01/15-12/31/15
Nitrite	NO2F	0.002  mg/L	01/01/15-12/31/15
Nitrite +Nitrate	NO23F	0.004  mg/L	01/01/15-12/31/15
Chlorophyll a	CHLA	$0.55 \mu g/L$	01/01/15-12/31/15
Phaeophytin	PHEA	$0.4 \mu g/L$	01/01/15-12/31/15
Kjelldahl Nitrogen	TKN	0.08  mg/L	01/01/15-12/31/15
Total Phosphorus	TP	0.002  mg/L	01/01/15-12/31/15

# 13) Laboratory Methods

Chemical and biological analysis was performed by Florida Department of Environmental Protection, Bureau of Laboratories.

#### a. Parameter: PO4F

**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 H<sub>2</sub>SO<sub>4</sub> and stored at 4 °C until analysis.

#### c. Parameter: NH4F

**EPA or other Reference Method**: EPA 350.1 Rev. 2.0 (1993) (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 H<sub>2</sub>SO<sub>4</sub> and stored at 4 °C until analysis.

#### d. Paramter: NO2F

**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 H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> and stored at 4 °C until analysis.

# g. Parameter: CHLA and PHEA

EPA or other Reference Method: SM 10200 H

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

Based on the 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 Variablity** Duplicates (successive grabs at each station) were taken every month at each station
  - ii) **Laboratory variability** 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** 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- 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  $\pm$  15 % for water matrices.
  - ii) **Standard reference material analysis** 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 – The laboratory participates in a number of Performance Testing (PT) studies and interlaboratory comparison studies every year. They include PT studies that are required as part of our lab's NELAC certification and others such as those conducted by the USGS. The results from these studies are posted at <a href="http://depnet/burlabs/ptinfo.htm">http://depnet/burlabs/ptinfo.htm</a>. In addition our nutrients group also participates in two round robins conducted by the Regional Ambient Monitoring Program (RAMP).

### c) Other QAQC methods

Field equipment blanks were taken every sampling event to indicate any potential contamination problems during sampling.

#### 15. OAOC 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 Historical Data: Pre-Auto OAOC
- 5 Corrected Data

#### 16) QAQC code definitions

QAQC codes are used in conjunction with QAQC flags to provide further documentation of the data and are also applied by insertion into the associated flag column. There are three (3) different code categories, general, sensor, and comment. General errors document general problems with the sample or sample collection, sensor errors document common sensor or parameter specific problems, and comment codes are used to further document conditions or a problem with the data. Only one general or sensor error and one comment code can be applied to a particular data point. However, a record flag column (F Record) in the nutrient data allows multiple comment codes to be applied to the entire data record.

General error	'S
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 C	omments
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 com	ments
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	1
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
             0.6 \text{ to} > 1.0 \text{ meters}
   WH3
   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
             from the south
   S
   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
```

> 30 to 40 knots

> 40 knots

#### 17) Other remarks/notes

WS4

WS5

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.

From January 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 all 2015 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.

The March grab samples were delivered late due to icy weather preventing FedEx from shipping. PO4F data and NO2F data were analyzed beyond acceptable hold time. CHLA and PHEA were not analyzed.

For the 20150204 sampling event, rkbmbnut site the field data for salinity were not recorded correctly.

For the 20150304 sampling event, rkbmbnut site the field data for SpCond and salinity were not recorded correctly.

For the grab samples at rkbmbnut on 05/06/2015 09:59 until 12:00, Total-P data were J-qualified: Quality control failure(s) observed. The result was confirmed on 05/18/2015 by the lab.

For the grab samples at rkbpbnut on 06/09/2015 08:29 until 11:23, results were V-qualified due to laboratory blank failure for Phaeophytin-a component only.

For the grab sample at rkbfbnut on 07/07/2015 09:31, CHL was A-qualified where the value reported is the mean of 2 or more determinations.

For the diel sample at rkblhnut on 08/11/2015 21:30, PO4F data was flagged as suspect because it was a significant outlier beyond 4 standard deviations from the mean and it did not fit the data trend.

For the grab sample at rkbfbnut on 09/09/2015 08:54, CHL and PHEA were A-qualified where the value reported is the mean of 2 or more determinations.

For the grab sample at rkbmbnut on 09/09/2015 08:13 until 12:00, TKN data was J-qualified: Quality control failure(s) observed.

For the 20150909 sampling event, rkbfbnut site the field data for DO% and DO mg/L were not recorded correctly.

For the grab sample at rkblhnut on 11/04/2015 12:50, CHL and PHEA were A-qualified where the value reported is the mean of 2 or more determinations.

For the 20151104 sampling event, field data for all sites except LH were not recorded due to the handheld stopped working.

Weather conditions based on Big Cypress Basin (BCB) Hydrologic Summary and Rainfall Reports:

**January:** Rainfall this month continued to disappoint. Significant frontal activity across South Florida did not generate much rainfall, and data reported from 18 stations across the BCB failed to match the historic January amounts. An average of 0.68 inches was collected, 62% less than the normal 1.78 inches.

**February:** In a departure from the dry conditions of January, incoming frontal activity early in February generated much needed rainfall over the BCB. Although most of the month remained uneventful, a subsequent cold front in late February caused significant precipitation, raising the monthly totals well above the normal average. Rainfall recorded by 20 stations across the BCB registered an average of 3.39 inches, 77% more than the historic February total of 1.91 inches.

March: March saw a continuation of typical winter weather patterns throughout the Big Cypress Basin [BCB], with sporadic cold front activity generating much needed rainfall. Levels of precipitation were moderate, but still significant enough to raise monthly totals almost to par with the norm. Surface water and canal levels in the major BCB systems ended the month lower, albeit consistent with typical trends for March. March saw a replay of February conditions with early and late month rainfall events. A late March storm system was particularly significant, helping to raise the month's aggregate rainfall to 1.83 inches, almost up to the historic mean of 2.29 inches. The 20 rainfall stations in the BCB have now registered a cumulative 5.89 inches thus far in 2015, generally matching the 5.94 inches typically received in an average year.

**April:** Starting in early April, the Big Cypress Basin [BCB] saw a noticeable increase in late afternoon thundershowers, a weather pattern normally associated with summer conditions. This phase proved short-lived however, and by month's end the sporadic cold front activity typical of the winter/dry season had reasserted itself. The BCB rainfall situation was considerably improved by a late month event which resulted in totals well above the norm. Rainfall for the first half of April was moderate, however the totals were boosted by a late month event which raised the aggregate precipitation to 3.73 inches, 1.37 inches above the historic mean of 2.36 inches. Thus far this year, the twenty (20) BCB rainfall stations have registered a cumulative 9.63 inches, representing an increase of 1.33 inches above the 8.30 inches typically received.

May: Developing weather patterns turned decidedly wet this month as the Big Cypress Basin [BCB] transitioned out of the dry season. Starting around mid-May, the Basin saw a resurgence of afternoon thunderstorms and early evening showers, fairly typical indicators of the arriving wet season. Rainfall activity this month was significant, in particular the latter half, which saw a fairly consistent increase in afternoon and early evening thunderstorms. Although these occurrences were widely distributed, aggregate totals received by the end of May topped 4.84 inches, well above the historic mean of 3.40 inches. The 20 rainfall stations in the BCB have now registered a cumulative 14.12 inches thus far in 2015, well ahead of the 11.70 inches typically received in an average year.

June: Although rainfall activity early in the month was promising, developing weather conditions in the Big Cypress Basin (BCB) lowered this outlook considerably for the latter half of June. Starting around mid-month, a noticeable lull in the typical pattern of afternoon thunderstorms effectively reduced incident rainfall for the Basin. This is reflected in the monthly totals which fell short of the historic norms for June. Rainfall activity for the Lower West Coast was particularly significant for the first half of June, then somewhat subdued for the rest of the month. Precipitation recorded at twenty (20) rainfall stations in the BCB indicate an average 7.21 inches received for June, lower than the historic mean of 9.33 inches. These sites have now registered a cumulative 21.67 inches thus far in 2015, slightly above the 20.72 inches typically received in an average year July: Weather conditions across the Big Cypress Basin [BCB] turned decidedly wet in July. A persistent regional low pressure system resulted in above average rainfall, raising totals in excess of nine inches, easily the wettest month so far this year. Although the eastern Atlantic has remained rather quiet thus far, tropical activity is ongoing, and to date has resulted in three (3) named Tropical Storms, ending with TS Claudette in July. However these weather systems have all been rather less significant to the Basin, and this past month southwest Florida felt the larger effects attributed to an area of low pressure centered over the Gulf of Mexico, generally to the northwest of the BCB area. Rainfall from this system was distributed Basin-wide, and the average (taken from 20 individual stations) totaled 9.54 inches, or 12% more than the July historic average of 8.54 inches. The accumulated rainfall amounts for the year are now also above par. Aggregated totals indicate that by the end of the month the BCB area had received 30.72 inches, slightly above (+4%) the 29.52 inches normally expected by now.

**August:** Wet season conditions persisted across the Big Cypress Basin [BCB] throughout most of August, normally the wettest month of the season. Tropical cyclone activity in the eastern Atlantic brought us TS Erika, the fifth (5) named storm of the season, which however failed to gain strength and ultimately dissipated

prior to making landfall in south Florida. The normal summer pattern of afternoon and early evening thunderstorms, helped by some frontal activity and remnants of TS Erika, generated an average of 8.86 inches of rain over the BCB in August. However, this tally averaged across the 20 individual stations did not top the historic average of 9.38 inches. The accumulated precipitation for the year is now up to 40.07 inches, a slight increase over the Basin's historic mean of 38.89 inches. The 2015 hurricane season now includes the tenth (10) storm of the season, Hurricane Joaquin, which reached a category 4 status in September, fortunately churning in the Atlantic and never posing a threat to the Florida mainland.

**September:** September is normally the last month of significant rainfall for the year, and the conditions recorded this past few weeks would generally bear this out. Rainfall was in excess of nine inches, continuing a trend previously noted in July and August, the two other important months of the wet season. Groundwater levels remained positive for the month, also consistent with the seasonal cycle. Although tropical disturbances were noted, the normal pattern of late afternoon and early evening thunderstorms generally held sway, sufficient to generate significant rain over the Basin. Rainfall observed at BCB's twenty (20) reporting stations averaged 9.15 inches, edging past the normal average of 8.61 inches. The accumulated precipitation for the year is now up to 49.22 inches, a slight increase over the Basin's historic mean of 47.51 inches.

**October:** Coincident with the closing wet season, weather conditions in the Big Cypress Basin [BCB] turned decidedly dry in October. In an abrupt change from the past three months, Basin-wide rainfall barely topped 2 inches. Coasting into the final month of the Hurricane season, the Atlantic remained generally quiet, free of any significant storms or tropical depressions. In terms of rainfall received, weather conditions this past month were uneventful for the Basin. With the onset of fall, the typical convective pattern of afternoon and early evening thunderstorms quickly abated. Incident rainfall across the BCB, as recorded by 20 stations, averaged 2.10 inches, a striking 41% less than the normal October average of 3.54 inches. However, accumulated totals for the year are now up to 51.32 inches, still ahead of the historic mean (51.04 inches), mostly due to a generous wet season.

**November:** November was unusually wet this year in the Big Cypress Basin [BCB]. Thus far, the typical dry season weather patterns appear to have been replaced by wetter trends, consistent with the long range forecast offered by NOAA earlier in October. The final month of the 2015 Hurricane Season closed out uneventfully, and by the end of November eleven (11) named storms had been noted, including four (4) hurricanes. BCB rainfall was unusually high in November. Basin-wide records from 20 stations noted a total of 3.43 inches, almost twice the normal monthly average of 1.75 inches. The accumulated total for 2015, is now up to 54.75 inches, slightly in excess of the area's historic normal of 52.64 inches, as measured at these BCB monitoring locations.

**December:** Prevailing temperatures across the Big Cypress Basin [BCB] remained uncharacteristically warm in December. Possibly of a related pattern, the normal dry winter conditions failed to materialize, and basin-wide rainfall remained generous for the month, with totals well in excess of the norm. Basin-wide totals from 20 stations topped 2.20 inches, 39% more than the normal monthly average of 1.59 inches. Although unusual, we note that rainfall this month was hardly sufficient to match the 5.8 inches which fell in December 1997, the highest basin-wide total recorded over the BCB in the past twenty years. The year's final tally is slightly above par, with rainfall totals of 56.95 inches, slightly in excess of the Basin's historic normal of 54.39 inches.

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