# Rookery Bay (RKB) National Estuarine Research Reserve (NERR) Nutrient Metadata (January 2013 – December 2013) Latest Update: May 6, 2014

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# I. Data Set and Research Descriptors

Reserve with any additional questions.

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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 non-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, 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).

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 was 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 Kjelldahl nitrogen (TKN) and total phosphorus (TP), 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.

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 samples 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.

# 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 6.5 to 37.6 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 2.0 to 37.4 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 0.4 to 37.1 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 3.3 to 37.6 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

The site is located at the mouth of the Pumpkin River. Mean high water is approximately 1-2 meters. Salinity at this site ranged from 11.4 to 37.5 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 has diverted freshwater. Typically this site does not receive enough freshwater inflow.

# 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)

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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)
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# **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 2013, the data collection period was from January to December.

# Monthly Grab Sampling Station Code Date Time Sta

Station Code	Date Time Stamp
rkbfunut	01/03/2013 11:50
rkbfunut	01/03/2013 11:53
rkbfbnut	01/03/2013 11:17
rkbfbnut	01/03/2013 11:20
rkbmbnut	01/03/2013 12:53
rkbmbnut	01/03/2013 12:56
rkbpbnut	01/03/2013 10:30
rkbpbnut	01/03/2013 10:33
rkblhnut	01/03/2013 14:43
rkblhnut	01/03/2013 14:46
rkblhnut	02/07/2013 09:00
rkblhnut	02/07/2013 09:03
rkbmbnut	02/07/2013 10:50
rkbmbnut	02/07/2013 10:53
rkbpbnut	02/07/2013 11:44
rkbpbnut	02/07/2013 11:47
rkbfunut	02/07/2013 12:22
rkbfunut	02/07/2013 12:25
rkbfbnut	02/07/2013 13:00
rkbfbnut	02/07/2013 13:03
rkblhnut	02/19/2013 03:15
rkblhnut	02/19/2013 05:45
rkblhnut	02/19/2013 08:15
rkblhnut	02/19/2013 10:45
rkblhnut	02/19/2013 13:15
rkblhnut	02/19/2013 15:45
rkblhnut	02/19/2013 18:15
rkblhnut	02/19/2013 20:45
rkblhnut	02/19/2013 23:15
rkblhnut	02/20/2013 01:45
rkblhnut	02/20/2013 04:15
rkbmbnut	03/07/2013 11:14
rkbmbnut	03/07/2013 11:17
rkbpbnut	03/07/2013 11:55
rkbpbnut	03/07/2013 11:58

rkbfunut	03/07/2013 12:35
rkbfunut	03/07/2013 12:38
rkbfbnut	03/07/2013 13:10
rkbfbnut	03/07/2013 13:13
rkblhnut	03/07/2013 09:22
rkblhnut	03/07/2013 09:25
rkblhnut	03/19/2013 10:30
rkblhnut	03/19/2013 13:00
rkblhnut	03/19/2013 15:30
rkblhnut	03/19/2013 18:00
rkblhnut	03/19/2013 20:30
rkblhnut	03/19/2013 23:00
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rkblhnut	03/20/2013 06:30
rkblhnut	03/20/2013 09:00
rkblhnut	03/20/2013 11:30
rkbmbnut	04/04/2013 08:34
rkbmbnut	04/04/2013 08:37
rkbpbnut	04/04/2013 09:24
rkbpbnut	04/04/2013 09:27
rkbfunut	04/04/2013 10:12
rkbfunut	04/04/2013 10:15
rkbfbnut	04/04/2013 10:46
rkbfbnut	04/04/2013 10:49
rkblhnut	04/04/2013 13:05
rkblhnut	04/04/2013 13:09
rkblhnut	04/09/2013 06:45
rkblhnut	04/09/2013 09:15
rkblhnut	04/09/2013 11:45
rkblhnut	04/09/2013 14:45
rkblhnut	04/09/2013 16:45
rkblhnut	04/09/2013 19:15
rkblhnut	04/09/2013 21:45
rkblhnut	04/10/2013 00:15
rkblhnut	04/10/2013 02:45
rkblhnut	04/10/2013 05:15
rkblhnut	04/10/2013 07:45
rkbmbnut	05/02/2013 08:30
rkbmbnut	05/02/2013 08:33
rkbpbnut	05/02/2013 10:23
rkbpbnut	05/02/2013 10:26
rkbfunut	05/02/2013 09:48
rkbfunut	05/02/2013 09:51
rkbfbnut	05/02/2013 09:23
rkbfbnut	05/02/2013 09:26
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rkblhnut	05/14/2013 20:30
rkblhnut	05/15/2013 01:30
rkblhnut	05/15/2013 01:30
rkblhnut	05/15/2013 04:00
INCIIIIUt	05/15/2015 00.50

rkblhnut	05/15/2013 09:00
rkblhnut	05/15/2013 11:30
rkblhnut	05/15/2013 14:00
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rkbmbnut	06/05/2013 08:57
rkbpbnut	06/05/2013 09:51
rkbpbnut	06/05/2013 09:54
rkbfunut	06/05/2013 10:31
rkbfunut	06/05/2013 10:35
rkbfbnut	06/05/2013 11:03
rkbfbnut	06/05/2013 11:07
rkblhnut	06/05/2013 11:07
rkblhnut	06/05/2013 13:05
rkbmbnut	07/02/2013 08:29
rkbmbnut	07/02/2013 08:32
rkbpbnut	07/02/2013 10:16
rkbpbnut	07/02/2013 10:19
rkbfunut	07/02/2013 09:11
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rkbfbnut	07/02/2013 09:45
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rkbmbnut	08/01/2013 08:26
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rkbfbnut	10/3/2013 10:49
rkblhnut	10/3/2013 13:24
rkblhnut	10/3/2013 13:27
rkbmbnut	12/12/2013 9:48
rkbmbnut	12/12/2013 10:00
rkbpbnut	12/12/2013 10:47

rkbpbnut	12/12/2013 10:55
rkbfunut	12/12/2013 11:28
rkbfunut	12/12/2013 11:35
rkbfbnut	12/12/2013 12:07
rkbfbnut	12/12/2013 12:17
rkblhnut	12/12/2013 14:24
rkblhnut	12/12/2013 14:30

Diel Sampling	
Station Code	Date Time Stamp
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rkblhnut	01/08/2013 07:00
rkblhnut	01/08/2013 09:30
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rkblhnut	10/7/2013 11:30
rkblhnut	10/7/2013 14:00
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rkblhnut	10/8/2013 7:30
rkblhnut	10/8/2013 10:00

# 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), 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/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature, including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal Resource Management, National Ocean Service, National Oceanic, and Atmospheric Administration. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

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

# **II. Physical Structure Descriptors**

# 9) Entry Verification

The analytical results (electronic files) were provided monthly from the contracted laboratory to Christina Panko Graff (01/2013-10/2013)/ Julie Brader Drevenkar (11/2013-12/2013), Water Quality Program Manager. Upon receiving the results, Christina/Julie reviewed the data for errors. Christina/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 6.5. 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 were copied and pasted into a Microsoft Excel worksheet and data transfer was checked once by one other person. Data were processed using the NutrientQAQC Excel macro. The NutrientQAQC macro sets up the data worksheet, metadata worksheets, and MDL worksheet; adds chosen parameters and facilitates data entry; allows the user to set the number of significant figures to be reported for each parameter and rounds using banker's rounding rules; allows the user to input MDL values and then automatically flags/codes measured values below MDL and inserts the MDL; calculates parameters chosen by the user and automatically flags/codes for component values below MDL, negative calculated values, and missing data; allows the user to apply QAQC flags and codes to the data; produces summary statistics; graphs selected parameters for review; and exports the resulting data file to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

# 10) Parameter Titles and Variable Names by Data Category

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

Data Category	Parameter	Variable Name	<b>Units of Measure</b>
Phosphorus and			
Nitrogen:	*Orthophosphate, Filtered	PO4F	mg/L as P
G	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	n DIN	mg/L as N
	Total Kjelldahl Nitrogen	TKN	mg/L as N
Plant Pigments:	*Chlorophyll <i>a</i>	CHLA N	μg/L
	Phaeophytin	PHEA	μg/L
Field Parameters (gr	abs only):		
(8	Water Temperature	WTEM N	°C
	Specific Conductance	SCON N	mS/cm
	Salinity	SALT N	ppt
	Dissolved Oxygen	DO N	mg/L
	% Dissolved Oxygen Saturati	ion DO S N	%
lotos			

### 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 and PHEA

# b. Calculated Parameters-

NO3: NO23F -NO2F DIN: NO23F +NH4F TN: TKN + NO2FTON: 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. Tthe MDL for all parameters was determined by Florida Department of Environmental Protection, Bureau of Laboratories,

Parameter	Variable	MDL	Approved
Orthophosphate	PO4F	$0.004~\mathrm{mg/L}$	01/01/13-12/31/13
Ammonium	NH4F	$0.004~\mathrm{mg/L}$	01/01/13-03/01/13
		0.002  mg/L	03/01/13-12/31/13
Nitrite	NO2F	0.002  mg/L	01/01/13-12/31/13
Nitrite +Nitrate	NO23F	$0.004~\mathrm{mg/L}$	01/01/13-12/31/13
Chlorophyll <i>a</i>	CHLA	$0.55 \mu g/L$	01/01/13-12/31/13
Phaeophytin	PHEA	$0.4 \mu g/L$	01/01/13-12/31/13
Kjelldahl Nitrogen	TKN	0.08  mg/L	01/01/13-12/31/13
Total Phosphorus	TP	$0.002~\mathrm{mg/L}$	01/01/13-12/31/13

# 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 (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 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) 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
- O 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.

lata record.	
General errors	
GCM	Calculated value could not be determined due to missing data
GCR	Calculated value could not be determined due to rejected data
GDM	Data missing or sample never collected
GQD	Data rejected due to QA/QC checks
GQS	Data suspect due to QA/QC checks
Sensor errors	
SBL	Value below minimum limit of method detection
SCB	Calculated value could not be determined due to a below MDL component
SCC	Calculation with this component resulted in a negative value
SNV	Calculated value is negative
SRD	Replicate values differ substantially
SUL	Value above upper limit of method detection
Parameter Com	nments
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 comme	nts
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
17577	

PSQ

squally

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PFO
             frozen precipitation (sleet/snow/freezing rain)
   PSR
             mixed rain and snow
Tide stage
             ebb tide
   TSE
   TSF
             flood tide
   TSH
             high tide
             low tide
   TSL
Wave height
   WH0
             0 to < 0.1 meters
   WH1
             0.1 to 0.3 meters
   WH2
             0.3 to 0.6 meters
             0.6 \text{ to} > 1.0 \text{ meters}
   WH3
   WH4
             1.0 to 1.3 meters
   WH5
             1.3 or greater meters
Wind direction
             from the north
   N
   NNE
             from the north northeast
   NE
             from the northeast
   ENE
             from the east northeast
   Ε
             from the east
   ESE
             from the east southeast
   SE
             from the southeast
               from the south southeast
   SSE
             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
   WS4
   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.

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 the January diel samples, samples 6-11 were not shipped to the lab or analyzed due to a faulty cooler that FedEx would not ship.

For the February grab and diel samples, there was a batch recovery failure of matrix spikes for ammonium.

For the May grab sample, rkblhnut was not collected due to bad weather.

For the September grab sample, rkbfbnut was not collected due to bad weather.

For the diel samples at rkblhnut on 10/07/2013 16:30 through 10/8/2014 00:00, PO4F data and NO2F data were analyzed beyond acceptable hold time.

For the diel samples at rkblhnut on 10/07/2013 16:30 through 21:30, Chlorophyll a data was not analyzed.

The November grab and diel samples were not collected due to a period of water quality technician transition at the reserve.

The December diel samples were not collected due to a period of water quality technician transition at the reserve.

# **Noteworthy weather events:**

Tropical Storm Andrea peripherally impacted the area from 6/05/2013-6/06/2013.

# Weather conditions based on Big Cypress Basin Hydrologic Summary Reports:

**January:** Significantly dry hydrologic conditions prevailed across southwest Florida in January. Surface and groundwater levels continued the downward trend of the annual dry season cycle, but stayed at near normal levels. For the twelfth time in the last 14 years, January produced below average rainfall. Cold front intrusion was few and resulted in warmer temperatures and little rainfall. The weighted average rainfall was 0.22 inches, or 11% of normal for January. Surface and groundwater levels continued to retreat from their annual peaks reached previously in October.

**February:** The hydrologic conditions in the region were slightly above normal. There was a strong cold front the second week of February, which generated an average of 2 inches of rain across the region. The weighted average rainfall was 2.54 inches, which was 29% above normal for this month. Surface and groundwater levels continued to retreat on the dry season cycle.

**March:** Hydrologic conditions in the region were significantly below normal with continued decline of surface water. Two mild cold fronts during the second and fourth week of March generated a weighted average of 0.97 inches, which was 61% below normal for this month. Year-to-date rainfall is approximately 45% below normal. Surface and groundwater levels continued the downward trend of the dry season cycle.

**April:** Wetter than normal hydrologic conditions prevailed due to a series of cold fronts throughout April producing the second wettest spring since 1997. The weighted average rainfall was 4.04 inches, or 72% above normal for this month. Surface and groundwater levels continued to retreat on the dry season cycle.

**May:** Dry hydrologic conditions in the region received some relief from several rain events all across the region. Surface and groundwater levels were at near normal and showing an upward retreat from the annual dry season lows. The rain events produced the second wettest May since 1996. The weighted average rainfall was 4.87 inches, or 32% above normal for this month. Surface and groundwater levels were somewhat halted by the rain events to near normal levels.

**June:** The classic onset of the wet season occurred throughout the region with the return of surface and groundwater levels to above normal after several years. Tropical Storm Andrea in the first week of the month

marked the beginning of the wet season with normal patterns of afternoon thunderstorms occurring thereafter. The weighted average rainfall was 12.52 inches, which was 39% above normal for this month. Year-to-date rainfall is approximately 16% above normal. Surface and groundwater levels continued an upward trend of the annual wet season cycle.

**July:** Significantly wetter than normal conditions continued to occur in the region. Remnants of Tropical Storm Chantal and Dorian brought wide-spread rain and ensuring that July 2013 was the wettest month since 2001. Records show that it has been the wettest start to the wet season since 1968, and the wettest April-July since at least 1930. The weighted average rainfall was 12.59 inches, or 53% above normal for this month. Year-to-date the rainfall was 26% above normal. Surface and groundwater levels continued the upward trend of the annual wet season cycle.

**August:** Continued wetter than normal hydrologic conditions for the fourth month in a row in the region with typical regular thunderstorms. The weighted average rainfall was 8.88 inches, which was 17% above the average for this month. Year-to-date the rainfall was 48.21 inches or 17% above normal. Surface and groundwater levels continued the upward trend of the annual wet season cycle.

**September:** Continued wetter than normal hydrologic conditions for the fifth month in a row prevailed in the region. Heavy rainfall during the first week of the month produced the bulk of the month's rainfall. The weighted average rainfall was 10.16 inches, which was 22% above average for this month. Year-to-date the rainfall was about 22% above the long-term average. Surface and groundwater levels were significantly above normal September levels.

**October:** The wet season came to an abrut end in early October. The surface and groundwater hydrologic conditions in the region were above the normal seasonal levels at the end of the wet season. The weighted average rainfall was 1.50 inches, which was 60% below average for this month. Year-to-date the rainfall was 58.80 inches or about 17% above normal.

**November:** Surface and groundwater hydrologic conditions across the Basin remain slightly above normal seasonal levels. Two moderate rain events occurred during the second and fourth week of the month. The weighted average rainfall was 1.22 inches, which was about 29% below normal for this month. Year-to-date the rainfall was 60.37 or about 15% above normal. Surface and groundwater levels began the downward trend of the annual cycle, but remained slightly above normal November levels.

**December:** Surface and groundwater hydrologic conditions across the Basin remain slightly above normal seasonal levels in spite of the low rainfall. Two mild cold fronts during the second and fourth weeks produced some rain across the region. The weighted average rainfall was 0.76 inches, which was about 55% below normal for this month. The total rainfall for the year was 60.66 inches, about 12% above the normal. Surface and groundwater levels continued the downward trend of the annual dry season cycle but stayed above normal December levels.

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