Apalachicola (APA) NERR Nutrient Metadata January – December 2011 Latest Update: May 11, 2012

I. Data Set and Research Descriptors

1) Principal investigators and contact persons

a) Reserve Contact

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2) Research objectives

Previous studies have shown the importance of river flow and flushing rates on nutrients and primary productivity in the bay. Similar studies have determined nitrogen and phosphorus budgets for Apalachicola Bay as well as nutrient limitations related to seasonality and riverflow. There has been an ongoing controversy between the States of Florida, Georgia, and Alabama over the upstream diversion of water for 21 years. Approximately 88% of the drainage basin for the Apalachicola River and Bay is located in Georgia and Alabama and historical flows are being threatened by upstream development. A tri-state compact, between the states and approved by the US Congress, required negotiations between the states to develop a water allocation formula. The states were unable to come to an agreement, the compact has expired, and legal proceedings, which could end up in the US Supreme Court, are underway. This study is one of many looking at short-term variability, long-term change, and the relationship of other environmental factors to the productivity of the Apalachicola Bay system as well as trying to separate natural from man-made variability.

a) Monthly Grab

Monthly grab samples are collected at 11 sites located across Apalachicola Bay to monitor spatial and temporal fluctuations in nutrient/chlorophyll *a* concentrations occurring in diverse sections of the bay. The stations have been chosen to help determine the influence of the river, local rainfall, adjacent habitats and man's impact on these parameters. Sampling sites are located in the lower Apalachicola River, in the coastal area, offshore of the barrier islands, at the SWMP datalogger locations, and throughout the bay. Seasonal, climatic, and anthropogenic factors all impact riverflow, which in turn affects nutrient/chlorophyll *a* concentrations in the bay. Nutrient/chlorophyll *a* concentrations are also influenced by tidal action, wind direction and speed, and the hydrodynamics of the system.

b) Diel Sampling Program

Diel sampling is performed once a month in conjunction with grab sampling for nutrients/ chlorophyll a. The East Bay Surface water quality datalogger site (apaesnut) is utilized each month for placement of the sampler so that temporal water quality data may be compared with the spatial nutrient/ chlorophyll a data collected at this site. Studies by the Reserve and others have shown the influence of tidal action and runoff on other physical parameters in the bay.

3) Research methods

a) Monthly Grab Sampling Program

Monthly grab samples are collected at eleven stations (see Table 1) within and adjacent to Apalachicola Bay. All grab samples are collected on the same day. Due to the distance between the stations it is not always possible to collect all the samples several hours prior to low tide. Tidal condition, wind direction, speed, and cloud cover are recorded for each station at the time of sampling but are not included in this dataset and are available upon request. Climatic data from the ANERR weather station is available online at http://cdmo.baruch.sc.edu/QueryPages/googlemap.cfm. Sampling after heavy rains is avoided if at all possible. Water temperature, salinity, and dissolved oxygen are measured at surface and bottom for each station with a YSI 85 handheld meter. Surface measurements only are included in this dataset for temperature, salinity and dissolved oxygen. Bottom measurements for temperature, salinity, and dissolved oxygen are available on request. pH is also measured and is available on request. Turbidity samples are collected at each site and are tested in the ANERR lab with a DRT-15CE Turbidimeter.

i) Grab sample collection:

A horizontal Van Dorn-style sampler is used to collect 2.2 liters of water from a depth of 0.5 meters at all stations not associated with a SWMP datalogger site. At the Cat Point and Dry Bar SWMP datalogger stations, water samples are collected at a depth of approximately 2 and 1.5 meters (one-half meter from the bottom) respectively, a depth equivalent to the probes of the data loggers deployed at these sites. At the East Bay datalogger station water samples are collected from surface (0.5 meters) and bottom (1.5 meters) depths, equivalent to the depths of the two dataloggers deployed at this site. Triplicate samples are collected each month at one station, rotating through all station locations. The triplicate samples are collected with subsequent dips of the horizontal sampler.

ii) Grab sample filtration and handling:

Water from the Van Dorn sampler is delivered into a polyethylene graduated cylinder. A preliminary discard rinse is performed to flush the sampler spigot and also to rinse the graduated cylinder. The water sample is then filtered through a GFF filter. The GFF filter for chlorophyll *a* analysis is wrapped in aluminum foil and frozen in the dark until delivered to the UF laboratory. The filtrate is split between two acid washed and rinsed polyethylene bottles, provided by the UF laboratory. One bottle contains unpreserved filtrate, the other bottle contains 5N H2SO4 as preservative. Both bottles are placed on ice in the dark until delivery to the UF laboratory. All filtration funnels and containers are rinsed with DI water at least 3 times in between samples. A field blank is also run each month, using DI water for sample blank.

The field blank is filtered as described above. All grab samples are delivered to the UF laboratory on the same day as collection.

b) Diel Sampling Program

Diel sampling is performed with an ISCO 3700 Portable Automated Sampler at the East Bay surface (apaesnut) station. Whenever possible, the ISCO is deployed the day before the bay-wide grab samples are collected and retrieved during the grab sample collection run. The sampler is programmed to collect one 1000 ml water sample every 2.5 hours, over a 25-hour period at the same depth as the East Bay surface datalogger probes (1.7 m above the bottom sediment). This captures a complete 24 hr: 48min lunar-tidal cycle. The ISCO sampler is programmed to purge the suction line before and after each sample collection. The center of the ISCO sampler is filled with ice to aid in sample preservation. All samples are placed in coolers of ice upon retrieval of the ISCO sampler at the end of the sampling period. When conditions permit diel samples are filtered in the field following the same procedure as described above for grab samples. Otherwise all diel samples are stored on ice in the dark and are filtered at ANERR laboratory within 3 hours of retrieval from the ISCO sampler. GFF filters are stored frozen in the dark. Filtrate samples are held on ice in the dark. All diel samples are delivered to the UF laboratory on the same day as collection.

c) Equipment QAQC and maintenance – Grab and Diel Sampling Program:

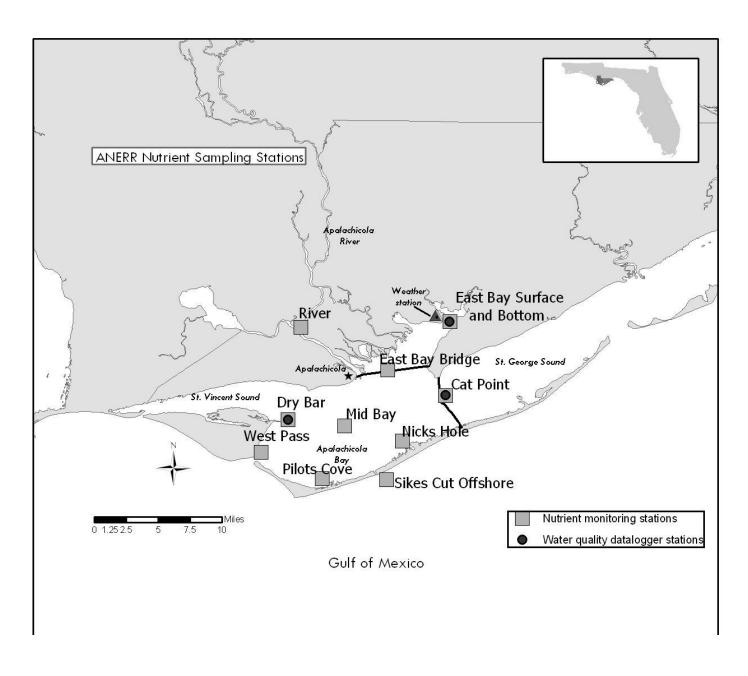
The horizontal Varn Dorn sampler is thoroughly rinsed with tap water after each sampling trip. Spare parts for the sampler are kept on hand and replaced as needed. Filtration funnels, receivers, and graduated cylinders are acid washed with 10% HCl and rinsed at least 3 times with DI water after each sampling trip. Diel sample collection bottles used in the ISCO automated sampler are acid washed and rinsed at least 3 times with DI water after each sampling trip. The ISCO automated sampler tubing is acid washed and rinsed at least 3 times with DI water after each monthly sampling event. The overall condition of the pump and tubing is checked each month prior to deployment, tubing is replaced as needed. Bottles used to hold sample filtrate, both preserved and unpreserved, are supplied and cleaned by UF laboratory. The YSI 85, pH meter, and Turbidimeter are calibrated each day of use.

Table 1. Nutrient and chlorophyll a sampling sites for the Apalachicola NERR SWMP.

Station code	Station name	Latitude	Longitude	Tidal range average (meters)	Salinity range	Water depth average (meters)		Datalogger station name	Sample depth (meters)
apawpnut	West Pass	29 38.279	85 5.341	0.7	euryhaline	5.0	sand		0.5
apadbnut	Dry Bar	29 40.482	85 3.502	0.7	euryhaline	1.7	oyster bar	apadb	1.5
apapcnut	Pilot's Cove	29 36.473	85 1.173	0.7	euryhaline	1.8	patchy seagrass		0.5
apambnut	Mid Bay	29 40.061	84 59.641	0.7	euryhaline	2.2	sandy silt		0.5
apaegnut	East Bay Bridge	29 43.848	84 56.711	0.7	euryhaline	1.6	silty clay		0.5
apaesnut	East Bay Surface	29 47.147	84 52.512	0.7	euryhaline	1.7	clayey sand	apaes	0.5
apaebnut	East Bay Bottom	29 47.147	84 52.512	0.7	euryhaline	1.7	clayey sand	apaeb	1.5
apascnut	Sikes Cut Offshore	29 36.401	84 56.799	0.7	marine	>5.0	sand		0.5
apanhnut	Nick's Hole	29 39.022	84 55.732	0.7	euryhaline	1.0	patchy seagrass		0.5
apacpnut	Cat Point	29 42.128	84 52.811	0.7	euryhaline	1.8	oyster bar	apacp	2.0
aparvnut	River	29 46.743	85 2.606	0.7	oligohaline	e3-4	sandy silt		0.5

Note: Diel samples are collected 2.5 hours apart at the East Bay Surface datalogger site, APAESNUT, with the ISCO automated water sampler. No duplicate diel samples are taken, however there is some overlap with monthly grabs collected at the East Bay Surface station at deployment of the ISCO sampler.

Figure 1. Station locations.



4) Site location and character

The Apalachicola Drainage Basin encompasses over 19,600 square miles and includes parts of three states (Alabama, Georgia, and Florida). The Apalachicola River is the largest in Florida in terms of flow. The amount of river discharge has been shown to be highly significant to the ecology of the estuary, which acts as a buffer between the Gulf of Mexico and fresh water input from upland areas. The nutrient rich plume of "green water" moving out of Apalachicola Bay is also important to the productivity of the northeastern Gulf of Mexico. The Apalachicola National Estuarine Research Reserve is located in the northwestern part of Florida, generally called the panhandle. It is located adjacent to the City of Apalachicola, and encompasses most of the Apalachicola Bay system, including 52 miles of the lower Apalachicola River. Passes, both natural and manmade, connect Apalachicola Bay to the northeastern Gulf of Mexico.

a) East Bay datalogger and nutrient station

East Bay is separated from Apalachicola Bay by two bridges and a causeway and is located to the north of the bay proper. The bay is 8.2 km long, has an average depth of approximately 1.0 m MHW, and an average width of 1.8 km. The tides in East Bay are mixed and range from 0.3 m to 1.0 m (average 0.5 m). The datalogger and nutrient sampling site is located in the upper reaches of East Bay. The piling location for the two East Bay dataloggers (ES and EB) is latitude 29°47.15' N and longitude 84°52.52' W. At the sampling site, the depth is 2.2 m MHW and the width of the bay is 1 km. The tides in the system are mixed, meaning the number of tides can range from one to five tides during a 24 hour period and are not evenly distributed throughout the day. At the East Bay bottom site the meter probes are 0.3 m above the bottom sediment. Salinity ranges from 0 to 30 ppt and the longterm average salinity is approximately 8 ppt. At the East Bay surface site the meter probes are 1.7 m above the bottom sediment and salinity ranges from 0 ppt to 30 ppt with a long term average salinity of 6.3 ppt. The freshwater input is very tannic and usually dark colored. Flows vary with local rainfall and are not quantified due to the diverse sources of the runoff. The bottom habitat at this bay site is soft sediment, primarily silt and clay, with no vegetation present. The dominant marsh vegetation near the sampling site (approximately 300 meters away) is Juncus roemerianus and Cladium jamaicense. The dominant upland vegetation is primarily pineland forests which includes slash pine, saw palmetto, and sand pine. Upland land use near the sampling site includes conservation and silviculture uses with some single family residential in the lower East Bay area. The sampling site is influenced by local runoff from Tate's Hell Swamp, the East Bay marshes, and distributary flow, some of which comes from the Apalachicola River via the East River. Tate's Hell Swamp was ditched, diked, and altered in the late 1960's and early 1970's by timber companies. These changes shortened the drainage period and allowed increased runoff with a concomitant decrease in pH and increase in color, which had a drastic affect on the biological communities in East Bay. Restoration of Tate's Hell Swamp began in 1995 to reduce non-point source runoff and restore historic sheet flow in the area.

b) Cat Point datalogger and nutrient station

The Cat Point datalogger and nutrient sampling site is located in St. George Sound, approximately 400 meters east of the St. George Island Bridge. The piling location is latitude 29°42.12′ N and longitude 84°52.81′ W. The tides at Cat Point are mixed and range from 0.3m to 1.0m (average 0.5m). At the sampling site, the depth is 2.5 m MHW. (The site was moved approximately 600 meters south in October 1997) and the width of the bay is 4 miles. At the Cat Point site the meter probes are 0.3 meters above the bottom sediment. This is also the depth where nutrients are collected monthly. Salinity ranges from 0 to 32 ppt with an average salinity of 20.9 ppt.. Flows vary with local rainfall and are not quantified due to the diverse sources of the runoff. The bottom type is oyster bar with no vegetation present except algae growing on the oysters in the summer. The dominant upland vegetation is primarily pineland forests, which include slash pine, saw palmetto, and sand pine. Upland land use near the sampling site, includes single family residential and commercial use in the Eastpoint area. The sampling site is influenced by local runoff from Tate's Hell Swamp and flow from the Apalachicola River. High salinity water comes mainly from the east, through East Pass at the eastern end of St. George Island.

c) Dry Bar datalogger and nutrient station

The Dry Bar datalogger and nutrient sampling site is located near St. Vincent Sound, in the western part of the Apalachicola Bay system, approximately one-half mile east of St. Vincent Island. The piling location is latitude 29°40.48′ N and longitude 85°03.50′ W. At the sampling site, the depth is 2 meters and the width of the bay is 7 miles. At the Dry Bar site the datalogger probes are located 0.3 meters above the bottom sediment. This is also the depth where nutrients are collected monthly. The tides are mixed and range from 0.3 to 1.0 meters. Salinity ranges from 0 to 34 ppt with an average salinity of 20.2 ppt. The bottom type is oyster bar with no vegetation present, except algae that grows on the oysters during the summer months. The dominant upland vegetation includes slash pine flatwoods with various combinations of gallberry, smooth cordgrass, fetterbush, cabbage palm, saw palmetto, magnolia, and grasses. Upland use near the sampling site includes state owned and managed Cape St. George Island, St. Vincent National Wildlife Refuge, as well as, single family residential and commercial use in the Apalachicola area. The sampling site is influenced by the flow of the Apalachicola River and high salinity water coming through West Pass and Sikes Cut.

d) Additional Apalachicola Bay nutrient stations

Information for an additional 7 nutrient stations, not associated with the required sampling at the datalogger sites, as well as the datalogger sites, is included in Table 1. Monthly grab samples are collected at all nutrient monitoring stations. A map of station locations is given in Figure 1.

5) Code variable definitions

Station code names:

apacpnut = Apalachicola Reserve nutrient data for Cat Point

apadbnut = Apalachicola Reserve nutrient data for Dry Bar

apaebnut = Apalachicola Reserve nutrient data for East Bay Bottom

apaegnut = Apalachicola Reserve nutrient data for East Bay Bridge

apaesnut = Apalachicola Reserve nutrient data for East Bay Surface

apambnut = Apalachicola Reserve nutrient data for Mid Bay

apanhnut = Apalachicola Reserve nutrient data for Nicks Hole

apapcnut = Apalachicola Reserve nutrient data for Pilots Cove

aparvnut = Apalachicola Reserve nutrient data for River

apascnut = Apalachicola Reserve nutrient data for Sikes Cut

apawpnut = Apalachicola Reserve nutrient data for West Pass

Monitoring Programs:

Monthly grab samples = 1

Diel grab sampling = 2

6) Data collection period

Nutrient monitoring began in April 2002 at all stations listed. Sampling has been performed monthly at all stations, unless otherwise noted. This table lists collection times for all nutrient and chlorophyll *a* samples in 2011. The below Start and End time reflect the times that the first and last diel samples were collected for each monthly diel sampling event. Grab sample end time is not recorded in the field. Generally grab sample collection, filtering, and icing are completed within 10 minutes or less depending upon field conditions at the time of sampling. Time is coded based on a 2400 hour clock and is referenced to Eastern Standard Time (EST), without Daylight Savings Time adjustments.

a) Start Date and Time for Monitoring Program 1 (Grab Samples)

Site	Start Date/Time	Site	Start Date/Time	Site	Start Date/Time
apacpnut	01/11/2011 11:28	apadbnut	01/11/2011 13:11	apaebnut	01/11/2011 10:03
apacpnut	02/09/2011 12:51	apadbnut	02/09/2011 10:41	apaebnut	02/09/2011 13:40
apacpnut	02/09/2011 12:55	apadbnut	03/02/2011 14:03	apaebnut	03/02/2011 12:06
apacpnut	02/09/2011 13:03	apadbnut	04/06/2011 09:37	apaebnut	04/06/2011 12:00
apacpnut	03/02/2011 10:36	apadbnut	05/11/2011 08:01	apaebnut	05/11/2011 11:32
apacpnut	04/06/2011 11:29	apadbnut	06/07/2011 08:55	apaebnut	06/07/2011 10:21
apacpnut	05/11/2011 10:38	apadbnut	07/13/2011 08:36	apaebnut	06/07/2011 10:23
apacpnut	06/07/2011 09:54	apadbnut	08/03/2011 08:35	apaebnut	06/07/2011 10:25
apacpnut	07/13/2011 09:43	apadbnut	08/03/2011 08:37	apaebnut	07/13/2011 10:09
apacpnut	08/03/2011 09:30	apadbnut	08/03/2011 08:39	apaebnut	08/03/2011 09:57
apacpnut	09/07/2011 10:12	apadbnut	09/07/2011 08:34	apaebnut	09/07/2011 10:42
apacpnut	10/05/2011 11:05	apadbnut	10/05/2011 11:45	apaebnut	10/05/2011 09:58
apacpnut	11/02/2011 09:34	apadbnut	11/02/2011 08:31	apaebnut	11/02/2011 10:29
apacpnut	12/13/2011 11:15	apadbnut	12/13/2011 09:25	apaebnut	12/13/2011 11:56
Site	Start Date/Time	Site	Start Date/Time	Site	Start Date/Time
apaegnut	01/11/2011 11:12	apaesnut	01/11/2011 10:00	apambnut	01/11/2011 13:24
apaegnut	02/09/2011 13:30	apaesnut	02/09/2011 13:35	apambnut	02/09/2011 09:58
apaegnut	03/02/2011 10:58	apaesnut	03/02/2011 12:04	apambnut	03/02/2011 09:58
apaegnut	04/06/2011 12:28	apaesnut	04/06/2011 11:59	apambnut	04/06/2011 08:58
apaegnut	05/11/2011 12:49	apaesnut	05/11/2011 11:32	apambnut	05/11/2011 07:39
apaegnut	06/07/2011 10:50	apaesnut	06/07/2011 10:19	apambnut	06/07/2011 08:41
apaegnut	08/03/2011 10:23	apaesnut	07/13/2011 10:07	apambnut	07/13/2011 08:57
apaegnut	09/07/2011 11:22	apaesnut	08/03/2011 09:55	apambnut	08/03/2011 07:17
apaegnut	10/05/2011 09:36	apaesnut	09/07/2011 10:41	apambnut	09/07/2011 08:12
apaegnut	11/02/2011 10:02	apaesnut	09/07/2011 10:43	apambnut	10/05/2011 11:30
apaegnut	11/02/2011 10:05	apaesnut	09/07/2011 10:45	apambnut	11/02/2011 08:13
apaegnut	11/02/2011 10:07	apaesnut	10/05/2011 09:57	apambnut	12/13/2011 09:08
apaegnut	12/13/2011 11:35	apaesnut	11/02/2011 10:29		
apaegnut	12/13/2011 11:37	apaesnut	12/13/2011 11:54		
apaegnut	12/13/2011 11:40				
Site	Start Date/Time	Site	Start Date/Time	Site	Start Date/Time
apanhnut	01/11/2011 11:46	apapenut	01/11/2011 12:35	apawpnut	01/11/2011 12:52
apanhnut	02/09/2011 12:20	apapenut	02/09/2011 11:27	apawpnut	02/09/2011 11:03
apanhnut	05/11/2011 10:10	apapenut	04/06/2011 10:36	apawpnut	03/02/2011 14:24
apanhnut	08/03/2011 09:05	apapenut	05/11/2011 09:19	apawpnut	04/06/2011 10:06
apanhnut	09/07/2011 09:54	apapenut	08/03/2011 07:55	apawpnut	05/11/2011 08:47
apanhnut	12/13/2011 10:46	apapenut	09/07/2011 09:09	apawpnut	05/11/2011 08:49
		apapenut	12/13/2011 10:01	apawpnut	05/11/2011 08:55
				apawpnut	08/03/2011 08:11
				apawpnut	09/07/2011 08:50
				apawpnut	12/13/2011 09:41

Site	Start Date/Time	Site	Start Date/Time
aparvnut	01/11/2011 13:48	apascnut	01/11/2011 12:12
aparvnut	01/11/2011 13:50	apascnut	02/09/2011 11:56
aparvnut	01/11/2011 13:51	apascnut	05/11/2011 09:45
aparvnut	02/09/2011 09:22	apascnut	06/07/2011 09:31
aparvnut	03/02/2011 09:08	apasenut	07/13/2011 09:15
aparvnut	03/02/2011 09:12	apasenut	08/03/2011 07:37
aparvnut	03/02/2011 09:16	apasenut	09/07/2011 09:32
aparvnut	04/06/2011 13:18	apasenut	12/13/2011 10:23
aparvnut	04/06/2011 13:21		
aparvnut	04/06/2011 13:25		
aparvnut	05/11/2011 13:27		
aparvnut	06/07/2011 07:42		
aparvnut	07/13/2011 07:18		
aparvnut	07/13/2011 07:20		
aparvnut	07/13/2011 07:23		
aparvnut	08/03/2011 06:45		
aparvnut	09/07/2011 07:46		
aparvnut	10/05/2011 08:57		
aparvnut	10/05/2011 08:59		
aparvnut	10/05/2011 09:02		
aparvnut	11/02/2011 11:22		
aparvnut	12/13/2011 12:53		

b) Start and End Date/Time for Monitoring Program 2 (Diel Sampling)

Site	Start Date/Time	End Date/Time
apaesnut	02/08/2011 14:30	02/09/2011 15:30
apaesnut	03/01/2011 14:00	03/02/2011 15:00
apaesnut	05/10/2011 09:15	05/11/2011 10:15
apaesnut	06/06/2011 08:45	06/07/2011 09:45
apaesnut	07/12/2011 12:00	07/13/2011 13:00
apaesnut	08/02/2011 07:30	08/03/2011 08:30
apaesnut	09/06/2011 09:00	09/07/2011 10:00
apaesnut	10/04/2011 09:30	10/05/2011 10:30
apaesnut	11/01/2011 09:30	11/02/2011 10:30

7) Associated researchers and projects

The Reserve conducts long-term water quality monitoring and maintains a weather station as part of the NERRS SWMP. Other ongoing projects or data that relate to the nutrient monitoring project includes:

Apalachicola River Discharge U.S. Geological Survey http://waterdata.usgs.gov/nwis/

Hagen, S., DeLorme, D., Walters, L., Wang, D., Weishampel, J., Yeh, G., Huang, W., Slinn, D., Morris, J. Ecological Effects of Sea Level Rise

Paula Viveros

NOAA Graduate Research Fellowship

Phytoplankton composition and abundance in relation to salinity, nutrient and light gradients in the Apalachicola National Estuarine Research Reserve (ANERR)

Richard Peterson

Florida State University

NOAA Graduate Research Fellowship

Origin and Fate of Suspended Particulates in the Apalachicola River: Impact on Apalachicola Bay

Thomas Gihring

Florida State University

NOAA Graduate Research Fellowship

The Role of Oligohaline Marshes as a Source or Sink of Nitrogen to the Apalachicola Bay

Chris Anderson

Auburn University

School of Forestry and Wildlife Sciences

Response of coastal riverine wetlands to water allocations in an urbanizing watershed

Jane Caffrey

University of West Florida

Effect of Diurnal and Weekly Water Column Hypoxic Events on Nitrification and Nitrogen

Transformations in Estuarine Sediments

Laura Petes

Florida State University Coastal and Marine Lab

Anthropogenic alterations to freshwater input, and its effect on downstream estuarine oyster reef communities.

Stacy Smith, Jane Caffrey, Jennifer Cherrier

Florida A&M University post-doctoral research associate, ECSC/Environmental Sciences Institute

Drought, Reduced River Flow and Sea Level Rise: Exploring Climate

Impacts on Carbon and Nitrogen Cycling in the Apalachicola Bay System

Putland, J./ Florida State University Department of Oceanography. NOAA Graduate Research Fellowship.

Planktonic food web variations related to salinity and nutrient patterns in Apalachicola Bay.

Wang, H., W. Huang, M. Harwell, L. Edmiston, E. Johnson, P. Hsieh, K. Milla, J. Christensen,

J. Stewart, X. Liu. 2008. Modeling oyster growth rate by coupling oyster population and hydrodynamic models for Apalachicola Bay, Florida, USA. Ecological Modeling 211:77-89.

Wanat, J., Garwood, J., Levi, L., Lamb, M., Jones, C.,

Apalachicola National Estuarine Research Reserve.

Distribution and density of fishes and benthic invertebrates in Apalachicola Bay.

Jones, C., Lamb, M., Wanat, J., Levi, L., Garwood, J.

Apalachicola National Estuarine Research Reserve

System Wide Monitoring Program

Long-Term Water Quality Monitoring

Wanat, J., Levi, L., Garwood, J. Apalachicola National Estuarine Research Reserve System Wide Monitoring Program Long-Term Meteorological Monitoring

"Gauging the effects of the BP Oil Spill on diatoms, calcareous nanoplankton, and related protists at or near the base of the food chain in the NE Gulf of Mexico", funded to principal Investigators, Drs Sherwood W. Wise, Jr. and Akshitnhala K. S. K. Prasad.

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

A hardcopy of the original ANERR Field Sample Collection logsheet accompanies the samples from ANERR to the UF laboratory. Results data are entered into an Excel spreadsheet by UF laboratory staff, reviewed and signed off by the laboratory supervisor (Dr. Ed Phlips). The Excel data file is then electronically transmitted to ANERR. Lauren Levi, ANERR staff, reviews the data file for completeness and processes the data using the NutrientQAQC Excel macro. Missing data are verified by review of field logs and are denoted by a blank space in the database. 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 automatically flags/codes values below 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. Flag and code definitions are listed in sections 15 and 16 of this document.

10) Parameter Titles and Variable Names by Data Category

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

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus:			
1	*Orthophosphate, filtered	PO4F	mg/L as P
	Total Dissolved Phosphorus	TDP	mg/L as P
Nitrogen:			
	*Nitrite + Nitrate, filtered	NO23F	mg/L as N
	*Ammonium, filtered	NH4F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Total Dissolved Nitrogen	TDN	mg/L as N
Plant Pigments:			
Tium Tigments.	*Chlorophyll <i>a</i>	CHLA N	μg/ L
	Uncorrected Chlorophyll <i>a</i>	UncCHLA N	μg/L
	Phaeophytin	PHEA	μg/ L
Field Parameters:			
	Water temperature	WTEM N	^{0}C
	Salinity	SALT N	ppt
	Dissolved oxygen	DO N	mg/L
	%Saturated dissolved oxygen	DO_S_N	%
	Turbidity	TURB_N	NTU

Notes:

- 1. Time is coded based on a 2400 hour 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. ANERR has shown NO2 to be a minor component of NO23.

11) Measured and Calculated Laboratory Parameters

a) Parameters Measured Directly

Nitrogen species: NO23F, NH4F, TDN

Phosphorus species: PO4F, TDP

Other: UncCHLA_N, CHLA_N, PHEA, WTEMP_N, SALT_N, DO_N,

DO S N, TURB N

b) Calculated Parameters

DIN: NO23F+NH4F

12) Limits of Detection – UF Laboratory

The information in Table 3 is provided by UF laboratory. Method detection Limits (MDL) are derived from the replicate samples method in APHA (American Public Health Association). 1998. Standard Methods for the Examination of Water and Wastewater, 20th edition. United Book Press, Inc. Baltimore, Maryland. MDL will change with the background levels of samples; therefore, there is no constant MDL.

Table 3. Method Detection Limits for UF laboratory

Parameter	Start Date	End Date	MDL
NH4F	1/1/11	12/31/11	0.0153
CHLA_N	1/1/11	12/31/11	0.2
NO23F	1/1/11	12/31/11	0.0025
PO4F	1/1/11	12/31/11	0.003
TDN	1/1/11	12/31/11	0.0313
TDP	1/1/11	12/31/11	0.003

13) Laboratory Methods

UF Laboratory methods

a) Parameter: PO4

- Method Reference: APHA (American Public Health Association). 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. Method SM 4500-P-E (Ascorbic acid method). United Book Press, Inc., Baltimore, Maryland.
- 2) Method Description: Ammonium molybdate and potassium antimony in acid medium react with orthophosphate to form an acid that is reduced to a bright blue by ascorbic acid. Concentrations are measured on a dual-beam scanning spectrophotometer at 882 nm. The curve is read within 30 minutes.
- 3) Preservation Method: Samples are filtered through 0.7 µm pore size glass-fiber filters and stored at 4°C and run within 48 hours.

b) Parameter: TDP

- Method Reference: APHA (American Public Health Association). 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. Method SM 4500-P-E+B5 (Ascorbic acid method with persulfate digestion). United Book Press, Inc., Baltimore, Maryland.
- 2) Method Description: Potassium persulfate in DI H₂O is added to sample which is then autoclaved for 30 minutes at 15 psi and cooled to room temperature. Ammonium molybdate and potassium antimony in acid medium are added to sample which reacts with orthophosphate to form an acid that is reduced to a bright blue by ascorbic acid.

- Concentrations are measured on a dual-beam scanning spectrophotometer at 882 nm. The curve is read within 30 minutes.
- 3) Preservation Method: Samples are filtered through 0.7 μm pore size glass-fiber filters, acidified with 1ml of 5N H₂SO₄ per 125ml sample and stored at 4°C, and run within 28 days.

c) Parameter: NH4

- Method Reference: Strickland & Parsons. 1972. A Practical Handbook of Seawater Analysis: Determination of Ammonia (Oxidation Method). Fisheries Research Board of Canada. APHA (American Public Health Association). 1998. Standard Methods for the Examination of Water and Wastewater, (SM 4500-N I). 20th Edition. Baltimore, Maryland: United Book Press, Inc.
- 2) Method Description: Photometric determination of ammonia in seawater based on the oxidation reaction with hypochlorite in an alkaline medium. Results are read on a Bran-Luebbe autoanalyzer without the cadmium column. Final ammonium concentrations are corrected for the original nitrite concentrations in the sample.
- 3) Preservation Method: Samples are filtered through 0.7 μm pore size glass-fiber filters in the field, acidified with 1ml of 5N H₂SO₄ per 125ml sample, stored at 4°C, and run within 28 days.

d) Parameter: NO23

- 1) Method Reference: APHA (American Public Health Association). 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. Method SM4500-NO3-F. United Book Press, Inc. Baltimore, Maryland. Bran + Luebbe Autoanalyzer Applications. Method No. US-158-71 D.
- 2) Method Description: A water sample is passed though a cadmium column where the nitrate is reduced to nitrite, which is then diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine to form a colored azo dye that is measured colorometrically on a Bran-Luebbe autoanalyzer. The procedure is the same for nitrite analysis less the cadmium column.
- 3) Preservation Method: Samples for nitrite + nitrate analysis are filtered through 0.7 μm pore size glass-fiber filters in the field. Analysis is performed on non-acidified samples to avoid potential interferences associated with acidification, as described in Standard Methods.

e) Parameter: TDN

- 1) Method Reference: APHA (American Public Health Association). 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. Method SM4500-N C. United Book Press, Inc.,Baltimore, Maryland. Bran + Luebbe Autoanalyzer Applications. Method No. G-172-96 Rev. 10.
- 2) Method Description: Potassium persulfate in DI H₂O is added to sample which is then autoclaved for 30 minutes at 15 psi and cooled to room temperature. The digested sample is passed though a cadmium column where the nitrate is reduced to nitrite which is then diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine to form a colored azo dye that is measured colorometrically on a Bran-Luebbe autoanalyzer.
- 3) Preservation Method: Samples are filtered through 0.7 µm pore size glass-fiber filters in the field. Analysis is performed on non-acidified samples to avoid potential interferences associated with acidification, as described in Standard Methods.

f) Parameter: CHLA N and UncCHLA N and PHEA

- 1) Method Reference: APHA (American Public Health Association). 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. Method SM 10200 H.2. United Book Press, Inc., Baltimore, Maryland. Extraction method for chlorophyll from Sartory, D. P. & Grobbelaar, J. U. 1984. *Hydrobiologia* **114**, 177-187.
- 2) Method Description: Filters are thawed, placed in test tubes with 90% ethanol and heated in a water bath at 78°C for 5 minutes. They are subsequently placed in the dark for 24 hours followed by centrifugation to remove particulate material. Absorbances are read on a dual-beam scanning spectrophotometer according to Standard Methods. After the initial reading, 0.2N HCl is added to the sample and re-run for pheophytin <u>a</u> determination. Chlorophyll <u>a</u> (CHLA_N) was determined by correcting chlorophyll for pheophytin content using the method described in Standard Methods. Chlorophyll <u>a</u> (UncCHLA_N) represents the chlorophyll <u>a</u> concentration, without correction for pheophytin, using a simplified equation based on the extinction coefficient for chlorophyll <u>a</u> in ethanol solvent.
- 3) Preservation Method: Samples are filtered onto 0.7 μm pore size glass-fiber filters, wrapped in aluminum foil, stored in plastic bags in the dark at –20°C, and run within 28 days.

14) Field and UF Laboratory QAQC programs:

a) Precision

- i) Field Variability Field Blanks are included in all runs. ANERR staff collected field triplicate samples from a successive grab sample. Triplicate samples are collected from separate grabs at one sampling station each month, rotating through all stations. There were no field triplicates collected during diel sampling.
- **ii)** Laboratory Variability Method blanks (MB) and duplicate samples are run at least every 20 samples. Precision is measured by Relative Percent Difference (RPD). It is calculated by multiplying the difference between two determinations of the same sample by two, dividing that result by the sum of the same values, and multiplying by 100 [RPD= 2((A-B)/(A+B)) X 100].
- iii) Inter-organizational splits None.

b) Accuracy

- i) Sample Spikes Samples spike recoveries (SR).
- **ii)** Standard Reference Material Analysis NIST traceable check standards (QC) are included in each run at least every 20 samples. The Florida Department of Health certification process also includes 'Blind Tests' of accuracy on a semi-annual basis. Accuracy is measured by percent recovery (% R), the measured value divided by the expected value, multiplied by 100.
- **iii)** Cross Calibration Exercises Participation in the NOAA/NERRS Analytical Laboratory Intercomparison Study for 2011.

15) QAQC flag definitions:

QAQC flags provide documentation of the data and are applied to individual data points by insertion into the parameter's associated flag column (header preceded by an F_). QAQC flags are applied to the nutrient data during secondary QAQC to indicate data that are out of sensor range low (-4), rejected due to QAQC checks (-3), missing (-2), optional and were not collected (-1), suspect (1), and that have been corrected (5). All remaining data are flagged as having passed initial QAQC checks (0) when the data are uploaded and assimilated into the CDMO ODIS as provisional plus data. The historical data flag (4) is used to indicate data that were submitted to the CDMO prior to the initiation of secondary QAQC flags and codes (and the use of the automated primary QAQC system for WQ and MET data). This flag is only present in historical data that are exported from the CDMO ODIS.

- -4 Outside Low Sensor Range
- -3 Data Rejected due to QAQC
- -2 Missing Data
- -1 Optional SWMP Supported Parameter
- 0 Data Passed Initial QAQC Checks
- 1 Suspect Data
- 4 Historical Data: Pre-Auto QAQC
- 5 Corrected Data

16) QAQC code definitions:

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

General errors

GCM	Calculated value could not be determined due to missing data
GCR	Calculated value could not be determined due to rejected data
GDM	Data missing or sample never collected
GQD	Data rejected due to QA/QC checks
GQS	Data suspect due to QA/QC checks

Sensor errors

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

Parameter Comments

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

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.

January 201: Diel sampler not deployed due to extreme low tide conditions.

April 2011: Diel sampler not deployed due to rough water conditions.

December 2011: Diel sampler deployed however no samples were collected due to tubing failure.

April 2011: Field parameter sampling is incomplete. The handheld meter used to collect field parameters was malfunctioning.

April 2011: Field salinity data was obtained from a refractometer after samples were returned to the ANERR laboratory.

2011 entire year: TDN and NO23 analysis were performed from filtered unpreserved samples within 48 hours of collection. This method change was necessary to avoid interferences from acid preservation as described in Standard Methods.

Various grab sample sites were not sampled during 2011 due to rough conditions and/or inclement weather.

There were no major named tropical systems impacting Apalachicola Bay in 2011.