Apalachicola (APA) NERR Nutrient Metadata January – December 2007 Latest Update: November 15, 2011

I. Data Set and Research Descriptors

1) Principal investigators and contact persons

a) Reserve Contact

Lee Edmiston, Research Coordinator 350 Carroll Street
Eastpoint, Fl 32328
850-670-4783 ext 107
lee.edmiston@dep.state.fl.us

Lauren Levi, Environmental Specialist II 350 Carroll Street Eastpoint, Fl 32328 850-670-4783 ext 122 lauren.levi@dep.state.fl.us

b) Laboratory Contact

Edward J. Phlips, Professor Department of Fisheries and Aquatic Sciences University of Florida 7922 N.W. 71st Street Gainesville, Florida 32653 352-392-9617 phlips@ufl.edu

Dr. William Landing Professor of Environmental and Marine Chemistry Department of Oceanography, 325 OSB Florida State University Tallahassee, FL 32306-4320

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 18 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. Other 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. Weather permitting, 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, with the exception of the East Bay Bottom (apaebnut), Cat Point (apacpnut), and Dry Bar (apadbnut) stations. Bottom measurements not contained in this dataset 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. A horizontal Van Dornstyle 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.

January and February 2007 grab sample collection methods:

Water from the sampler is delivered into two one-liter opaque polyethylene bottles. One bottle (acid washed) is designated for nutrient analysis, the other is designated for chlorophyll *a* analysis. A portion of water is also filtered in the field immediately after collection; the filtrate is collected in an acid rinsed polyethylene bottle designated for ortho-phosphate analysis. Field filtration of ortho-phosphate samples is performed using a Whatman Puradisc 25PP polypropylene 0.45 um disposable filter and a sterile disposable 30 ml BD luer lock

syringe. A new filter and syringe assembly are used for each sample and each replicate. Duplicate samples are collected at all monthly grab stations. The duplicate sample is collected with a second dip of the horizontal sampler, with the sample being split between a second set of polyethylene bottles for nutrient and chlorophyll a analysis. Polyethylene bottles designated for nutrient samples have been previously acid washed with 3% HCl and then rinsed (5x) with deionized water. Ambient rinsing is performed in the field. Bottles for chlorophyll a analysis have been thoroughly rinsed with tap water prior to use. Samples are placed in coolers of ice and kept in the dark immediately after collection. Nutrient samples remain on ice until delivery to the Florida State University Oceanography Department laboratory, which occurs within 36 hours of collection. The nutrient samples are filtered immediately upon arrival at the FSU laboratory, except samples for ortho-phosphate, which have been filtered in the field by ANERR staff. Chlorophyll a samples are filtered by ANERR staff within 6 hours of collection, frozen, and delivered to the FSU laboratory along with the nutrient samples. Nitrite has been shown to be a minor component relative to nitrate and is no longer analyzed separately.

March through December 2007 grab sample collection methods:

This method change is due to a new annual contract, beginning March 1, 2007, utilizing the University of Florida Department of Fisheries and Aquatic Sciences laboratory for nutrient sample analysis. Grab samples for nutrients and chlorophyll *a* are collected in sterile whirlpaks. Each whirlpak is labeled with the station number. The sampler spigot is flushed by discarding approximately 3 ml of water prior to filling the whirlpak. Additional samples for triplicates are obtained with additional dips of the sampler, one for each additional sample required. Triplicates are collected each month at one station, rotating through all station locations. Whirlpak samples are placed on ice in the dark immediately after collection. Samples remain on ice until return to ANERR laboratory, where all samples are filtered within 6 hours of collection. Filtrate for nutrient analysis is collected in acid washed polyethylene bottles supplied by UF laboratory and then refrigerated until shipment. Filters for Chlorophyll *a* analysis are frozen until shipment. Both filtrate and filters are shipped in a cooler with freezer packs via overnight delivery to UF laboratory. Whirlpaks are discarded after samples are processed.

Equipment QAQC and maintenance – Grab 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.

The YSI 85, pH meter, and Turbidimeter are calibrated each day of use.

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 on the same day that the bay-wide grab samples are collected. The sampler is programmed to collect a sample for nutrient and chlorophyll *a* 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 25-hour sampling period. All samples are stored on ice in the dark until laboratory filtering and analysis.

January and February 2007 diel sample handling methods:

The ISCO sampler is programmed to collect two samples, of 1000 milliliters each, every two and one-half hours. Each sample is distributed by the sampler into plastic one-liter ISCO bottles held in the base of the sampler. One of the sample bottles in each set has been acid washed with 3% HCl prior to collection and then rinsed (5x) with deionized water; this bottle is used for nutrient collection. The other bottle in each set has been thoroughly rinsed with tap water and this sample is used for chlorophyll a analysis. The nutrient samples are delivered to the Florida State University Oceanography Department laboratory within 36 hours of collection for immediate filtering. Ortho-phosphate diel samples are not filtered in the field by ANERR staff. Water for ortho-

phosphate analysis is filtered by FSU staff at the time of all other nutrient filtering. The chlorophyll *a* samples are filtered by ANERR staff immediately upon retrieval and the filters are frozen and delivered to the lab within 36 hours of collection. The ISCO sampler is deployed at the East Bay datalogger station (Figure 1). The ISCO suction strainer is deployed at a depth equivalent to the probes of the surface datalogger deployed at this station, which are 1.7 meters above the bottom sediment. Nitrite has been shown to be a minor component relative to nitrate and is no longer analyzed separately.

March through December 2007 diel sample handling methods:

This method change is due to a new annual contract, beginning March 1, 2007 utilizing the University of Florida Department of Fisheries and Aquatic Sciences laboratory for nutrient sample analysis. The ISCO sampler is programmed to collect one 1000 milliliter sample every two and one-half hours. The ISCO sample bottles are acid washed with 10% HCL and rinsed (3x) with deionized water. Samples are filtered at the ANERR lab within 3 hours of retrieval from the ISCO sampler. Filtrate for nutrient analysis is collected in acid washed polyethylene bottles supplied by UF laboratory and then refrigerated until shipment. Filters for Chlorophyll *a* analysis are frozen until shipment. Both filtrate and filters are shipped in a cooler with freezer packs via overnight delivery to UF laboratory. A field blank is run each month using an acid washed ISCO bottle as the sample container.

Equipment QAQC and maintenance – Diel Sampling Program:

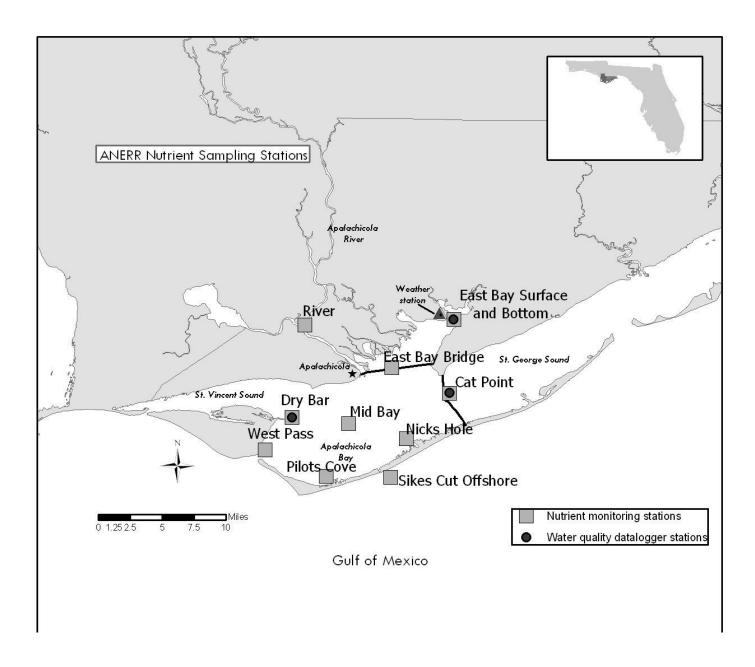
The ISCO automated sampler is flushed with tap water after each monthly sampling event. The overall condition of the pump and tubing is checked each month prior to deployment, tubing is replaced as needed.

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
apapenut	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	3-4	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 2007. 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 included as the time required to collect a grab sample is brief, on the order of three minutes from the time the sampler is dipped in the water to the time the sample is placed on ice. Time is coded based on a 2400 hour clock and is referenced to Eastern Standard Time (EST), without Daylight Savings Time adjustments.

Grab sampling (Monitoring program 1)

Site Start Date Start Time

apacpnut	1/9/2007	12:34
apacpnut	2/5/2007	10:34
apacpnut	3/6/07	11:28
apacpnut	4/9/07	9:44
apacpnut	5/8/07	8:30
apacpnut	6/5/07	8:11
apacpnut	7/10/07	8:00
apacpnut	8/7/07	8:12
apacpnut	9/10/07	10:23
apacpnut	10/9/07	9:08
apacpnut	11/5/07	13:50
apacpnut	12/4/2007	12:30
Site	Start Date	Start Time
apadbnut	1/9/2007	10:31
apadbnut	2/5/2007	12:22
apadbnut	3/6/07	9:39
apadbnut	4/9/07	9:06
apadbnut	5/8/07	10:24
apadbnut	6/5/07	9:13
apadbnut	7/10/07	9:53
apadbnut	8/7/07	10:06
apadbnut	9/10/07	11:43
apadbnut	10/9/07	11:23
apadbnut	11/5/07	12:00
apadbnut	12/4/2007	11:05
Site	Start Date	Start Time
apaebnut	1/10/2007	11:38
apaebnut	2/5/2007	9:11
apaebnut	3/6/07	14:35
apaebnut	4/9/07	10:44
apaebnut	5/8/07	12:28
apaebnut	6/5/07	10:37
apaebnut	7/10/07	11:42
apaebnut	8/7/07	13:17
apaebnut	9/10/07	8:20
apaebnut	10/9/07	8:16
apaebnut	11/5/07	9:00
apaebnut	12/4/2007	13:34
Site	Start Date	Start Time
	1/9/2007	13:06
apaegnut	1/3/200/	13.00

apaegnut	2/5/2007	9:35
apaegnut	3/5/07	13:48
apaegnut	4/9/07	11:09
apaegnut	5/8/07	12:10
apaegnut	6/5/07	10:18
apaegnut	7/10/07	11:24
apaegnut	8/7/07	12:02
apaegnut	9/10/07	8:40
apaegnut	10/9/07	13:19
apaegnut	11/5/07	9:45
apaegnut	12/4/2007	13:05
Site	Start Date	Start Time
apaesnut	1/10/2007	11:34
apaesnut	2/5/2007	9:09
apaesnut	3/5/07	14:34
apaesnut	4/9/07	10:43
apaesnut	5/8/07	12:26
apaesnut	6/5/07	10:36
apaesnut	7/10/07	11:39
apaesnut	8/7/07	13:16
apaesnut	9/10/07	8:18
apaesnut	10/9/07	8:14
apaesnut	11/5/07	8:55
apaesnut	12/4/2007	13:32
Site	Start Date	Start Time
apambnut	1/9/2007	10:25
apambnut	2/5/2007	12:39
apambnut	3/5/07	13:28
apambnut	4/9/07	8:51
apambnut	5/8/07	11:10
apambnut	6/5/07	9:26
apambnut	7/10/07	10:21
apambnut	8/7/07	10:56
apambnut	9/10/07	11:56
apambnut	10/9/07	12:02
apambnut	11/5/07	11:45
apambnut	12/4/2007	10:50
Site	Start Date	Start Time
apanhnut	1/9/2007	12:15
apanhnut	2/5/2007	10:59

apanhnut	3/6/07	11:11
apanhnut	4/9/07	11:26
apanhnut	5/8/07	9:07
apanhnut	6/5/07	8:26
apanhnut	7/10/07	8:38
apanhnut	8/7/07	8:59
apanhnut	9/10/07	10:37
apanhnut	10/9/07	10:07
apanhnut	11/5/07	13:30
apanhnut	12/4/2007	12:15
Site	Start Date	Start Time
apapcnut	1/9/2007	11:25
apapcnut	2/5/2007	11:43
apapenut	3/6/07	10:24
apapenut	4/9/07	no sample
apapenut	5/8/07	9:41
apapenut	6/5/07	8:46
apapenut	7/10/07	9:17
apapcnut	8/7/07	9:30
apapcnut	9/10/07	11:06
apapcnut	10/9/07	10:45
apapenut	11/5/07	13:00
apapenut	12/4/2007	11:50
Site	Start Date	Start Time
aparvnut	1/9/2007	14:02
aparvnut	2/5/2007	13:06
aparvnut	3/5/07	13:09
aparvnut	4/9/07	12:16
aparvnut	5/8/07	11:40
aparvnut	6/5/07	9:51
aparvnut	7/10/07	10:56
aparvnut	8/7/07	12:21
aparvnut	9/10/07	9:11
aparvnut	10/9/07	12:42
aparvnut	11/5/07	10:45
aparvnut	12/4/2007	10:07
Site	Start Date	Start Time
apascnut	1/9/2007	11:49
apascnut	2/5/2007	11:23
apascnut	3/6/07	10:50

apascnut	4/9/07	no sample
apascnut	5/8/07	9:24
apascnut	6/5/07	no sample
apascnut	7/10/07	8:59
apascnut	8/7/07	9:15
apascnut	9/10/07	10:50
apascnut	10/9/07	10:23
apascnut	11/5/07	13:20
apascnut	12/4/2007	12:00
Site	Start Date	Start Time
apawpnut	1/9/2007	11:04
apawpnut	2/5/2007	12:05
apawpnut	3/6/07	10:06
apawpnut	4/9/07	no sample
apawpnut	5/8/07	10:02
apawpnut	6/5/07	9:03
apawpnut	7/10/07	9:31
apawpnut	8/7/07	9:46
apawpnut	9/10/07	11:22
apawpnut	10/9/07	10:59
apawpnut	11/5/07	12:45
apawpnut	12/4/2007	11:30

Diel sampling (Monitoring program 2)

-			_	
Site	Start Date	Start Time	End Date	End Time
apaesnut	1/9/2007	7:00	1/10/2007	8:00
apaesnut	2/5/2007	9:30	2/6/2007	10:30
apaesnut	3/5/07	14:45	3/6/07	15:45
apaesnut	4/9/07	11:00	4/10/07	12:00
apaesnut	5/8/07	7:45	5/9/07	8:45
apaesnut	6/4/07	10:00	6/5/07	11:00
apaesnut	7/9/07	8:15	7/10/07	9:15
apaesnut	8/6/07	9:00	8/7/07	10:00
apaesnut	9/10/07	8:15	9/11/07	9:15
apaesnut	10/9/07	8:15	10/10/07	9:15
apaesnut	11/5/07	9:00	11/6/07	10:00
anaesnut	12/3/2007	11:30	12/4/2007	12:30

7) Associated researchers and projects

The Reserve conducts long-term water quality monitoring and maintains a weather station as part of the NERRS SWMP. These data can be obtained by contacting the Reserve directly, or through the CDMO's website at: http://cdmo.baruch.sc.edu/.

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/

Jennifer Putland

Florida State University Department of Oceanography

NOAA Graduate Research Fellowship

"Planktonic food web variations related to salinity and nutrient patterns

in Apalachicola Bay." PhD dissertation.

Henrieta Dulaiova

Florida State University Department of Oceanography

NOAA Graduate Research Fellowship

"Evaluation of flushing rates of estuaries and embayments via natural geochemical tracers."

PhD dissertation.

Donnato Surratt

Florida Agricultural and Mechanical University

Environmental Sciences Institute

"Historic trophic status and present trophic status for the Apalachicola Bay compared and contrasted."

PhD dissertation.

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

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.

Edmiston, HL., Wanat, J., Levi, L., Lamb, M., Selly, N., Dean, B., Wren, J., Fahrny, S.

Apalachicola National Estuarine Research Reserve. Distribution and density of fishes and benthic invertebrates in Apalachicola Bay.

Edmiston, HL., Dean, B., Lamb, M., Wanat, J., Levi, L., Selly, N., Wren, J., Fahrny, S. Apalachicola National Estuarine Research Reserve System Wide Monitoring Program Long-Term Water Quality Monitoring

Edmiston, HL., Wren, J., Fahrny, S., Wanat, J., Levi, L., Apalachicola National Estuarine Research Reserve System Wide Monitoring Program Long-Term Meteorological Monitoring

Edmiston, HL., Wren, J., Wanat, J., Levi, L., Selly, N., Apalachicola National Estuarine Research Reserve Submerged Aquatic Vegetation Monitoring

Edmiston, HL., Dean, B., Wanat, J., Wren, N., Selly, N., Levi, L., Lamb, M., Apalachicola National Estuarine Research Reserve Apalachicola Bay Oyster Growth Monitoring

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 water quality/nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Section 1. 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

General information applies to all 2007 data:

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; 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 and codes values below MDL; calculates parameters chosen by the user and automatically flags for component values below MDL and negative values; allows the user to apply QAQC flags and codes to the data; graphs selected parameters for review; append files; and export the resulting data files to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

January and February 2007 entry verification:

A hardcopy of the original ANERR Field Sample Collection logsheet accompanies the samples from ANERR to FSU Oceanography laboratory. Results data are entered into excel by FSU Oceanography laboratory staff, reviewed and signed off by the laboratory supervisor (Dr. William Landing). The excel data file is then electronically transmitted to ANERR. Lauren Levi, ANERR staff, reviews the data file for completeness and other possible anomalies. Missing data are verified by review of field logs and are denoted by a blank space in the database. The data is then processed with the NutrientQAQC Excel macro as detailed above. Calculations to determine DIN are performed by ANERR staff using the NutrientQAQC macro. Flag and code definitions are listed in sections 15 and 16 of this document.

March through December 2007 entry verification:

A hardcopy of the original ANERR Field Sample Collection logsheet accompanies the samples from ANERR to UF laboratory. Results data are entered into 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 other possible anomalies. Missing data are verified by review of field logs and are denoted by a blank space in the database. The data is then processed with the NutrientQAQC Excel macro as detailed above. Calculations to determine DIN are performed by ANERR staff using the NutrientQAQC macro. 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
i) Phosphorus:	*Orthophosphate, filtered	PO4F	mg/L as P
ii) Nitrogen:	Total Dissolved Phosphorus [#]	TDP	mg/L as P
n) i waogom	*Nitrite + Nitrate, filtered *Ammonium, filtered Dissolved Inorganic Nitrogen Total Dissolved Nitrogen [#]	NO23F NH4F DIN TDN	mg/L as N mg/L as N mg/L as N mg/L as N
iii) Plant Pigments:	*Chlorophyll a Uncorrected Chlorophyll $a^{\#}$ Phaeophytin	CHLA_N UncCHLa_N PHEA	μg/ L μg/L μg/ L
iv) Field Parameters:	Water temperature Salinity	WTEM_N SALT_N	⁰ C 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.
- 3. *Analysis for these parameters started with March 2007 sampling period.

11) Measured and Calculated Laboratory Parameters

Variables Measured Directly

Nitrogen species: NO23F, NH4F, TDN

Phosphorus species: PO4F, TDP

Other: CHLA N, UncCHLa N, PHEA, WTEMP N, SALT N, DO N,

DO S N, TURB N

Computed Variables

DIN: NO23F+NH4F

12) Limits of Detection

a) FSU Oceanography Laboratory:

The information in Table 2 is provided by FSU Oceanography Laboratory.

Analytical detection limits were established by replicate analysis of a low sample or blank, and are reported as 3SD. The analytical detection limit or method detection limit (MDL) for each analyte are reported in Table 2.

Table 2. Method Detection Limits for FSU Oceanography Laboratory

Parameter	Variable	MDL	Dates in use
Ammonium	NH4F	0.004 mg-N/l	2002- Feb 2007
Nitrate-Nitrite	NO23F	0.007 mg-N/l	2002- Feb 2007
Orthophosphate	PO4F	0.001 mg-P/l	2002- Feb 2007
Chlorophyll a	CHLA N	0.5 ug/l	2002- Feb 2007
Phaeophytin*	PHEA	0.5 ug/l	Jan – Feb 2007

^{*} Phaeophytin MDL information has not been provided by FSU Oceanography Laboratory at this time. For purposes of compiling this dataset, ANERR staff will use the Chlorophyll *a* MDL for Phaeophytin until notified otherwise by FSU staff.

b) 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	Variable	MDL	Dates in use
-----------	----------	-----	--------------

Ammonium	NH4F	0.008 mg-N/l	March – Dec 2007
Nitrate-Nitrite	NO23F	0.0014 mg-N/l	March – Dec 2007
Total Dissolved Nitrogen	TDN	0.0014 mg-N/l	March – Dec 2007
Orthophosphate	PO4F	0.002 mg-P/l	March – Dec 2007
Total Dissolved Phosphorus	TDP	0.002 mg-P/l	March – Dec 2007
Uncorrected Chlorophyll a	Unc-CHLA_N	0.01 ug/l	March – Dec 2007
Chlorophyll a	CHLA_N	0.01 ug/l	March – Dec 2007
Phaeophytin	PHEA	0.01 ug/l	March – Dec 2007

13) Laboratory Methods

a) FSU Oceanography Laboratory methods – in use dates are January and February 2007.

i) Parameter: NH4F

Method Reference: Procedure adapted from Bower and Holm-Hansen, Can. J. Fish, Aquat. Sci. 1980. V.37. pp. 794-798.

Method Descriptors:

Solutions:

Solution #1. 110 g sodium salicylate and 0.07 g sodium nitroprusside diluted to 250 ml ddH₂O, store in brown glass @ 5C

Solution #2. 18.5 g sodium hydroxide and 100 g sodium citrate diluted to 1 L dd H_2O , stable Solution #3. 1 part fresh Chlorox bleach (5.25% sodium hypochlorite), 9 parts Soln. 2. Use within 1 hour of preparation. 5 ml : 45 ml

Procedure:

Reagent addition to be carried out in the dark

To 5 ml sample, add 0.6 ml S #1, Mix, add 1 ml S #3, Mix. Stopper flask and allow color to develop for 1-3 hours in the dark. Sample can be exposed to light after color development is complete.

Read Absorbance @ 640 nm with a 1 cm path length cell

Standards:

Standards: (in mg/L), 0.0, 0.005, 0.0200, 0.0500, 0.2000, 0.5000

Primary Stock: 0.1909 g NH4Cl / 1 L = 50 mg N / L

Dilute for working stds (ul to 100ml): 0, 10, 40, 100, 400, 1000

Preservation Method: Nutrient samples are held on ice until transport to the FSU Department of Oceanography Laboratory in Tallahassee, Florida (within 36 hours). All samples are filtered through 0.45 μ m membrane filters (Pall Gelman Supor) and the filtrate is collected into new bottles and placed on ice until analysis (within 48 hours).

ii) Parameter: PO4F

Method Reference: Adapted from EPA standard method and Strickland and Parsons. Method Descriptor:

Solution #1. 78 ml conc. H₂SO₄ diluted up to 500 ml ddH₂O

Solution #2. 1.35 g C₆H ₈O₆ (Ascorbic Acid) dissolved in 25 ml ddH₂O (make new weekly, store in refrigerator)

Solution #3. 0.34 g K(SbO) $C_4H_4O_6*_{1/2}H_2O$ dissolved in 250 ml dd H_2O (store in refrigerator).

Solution #4. 7.5 g (NH₄)₆Mo₇O₂₄*H₂O dissolved in 250 ml ddH₂O (store in dark in plastic, stable, discard is see precipitate).

Solution #5. Mixed Reagent. Add in order: 62.5 ml #1, 25 ml #2, 12.5 ml #3, 25 ml #4. Solution should be light yellow, makes 125 ml. Stable < 6 hours.

Procedure:

For 10 ml samples (or 5 ml samples).

- 1. Allow samples to come to room temperature
- 2. Add 2.0 ml Soln #5 (or 1.0 ml to 5 ml samples)
- 3. Wait 30 minutes for light blue-green color to develop
- 4. **Read absorbance** @ **880 nm**, in 10 cm cell for 10 ml sample, or 1 cm cuvette If necessary, samples can be run in pairs, one set for color development and the other as a turbidity blank if necessary(no mixed reagent added). Concentration is determined by subtracting the blank from the sample and multiplying by the standard line slope.

Standards (in mg P / L): 0.0000, 0.0005, 0.0020, 0.0050, 0.0200, 0.0500

Primary Stock: 0.022 g KH2PO4 / 1 L = 5 mg P / L

Dilute for working stds (ul to 100ml): 0, 10, 40, 100, 400, 1000

Preservation Method: Nutrient samples are held on ice until transport to the FSU Department of Oceanography Laboratory in Tallahassee, Florida (within 36 hours). All samples are filtered through $0.45~\mu m$ membrane filters (Pall Gelman Supor) and the filtrate is collected into new bottles and placed on ice until analysis (within 48 hours).

iii) Parameter: CHLA_N and PHEA

Method Reference: Adapted from Parsons and Strickland, J. Marine Res., 21: 155, 1963, and from A Practical Handbook of Seawater Analysis, Chapter IV.3.

Method Descriptors:

Filtration:

Up to 1 L of sample is filtered onto Gelman AE 1 micron 47mm filter, 1 ml of magnesium carbonate solution (1 g per $100 \text{ ml } ddH_2O$) is added during final few hundred ml of filtering, desiccate the filter well under suction. The filter is placed in a 15 ml centrifuge tube and placed on ice until analysis.

Analysis:

12 ml of 90% acetone/ 10% water added, the tube is sealed and shaken vigorously.

The tubes are placed in a refrigerator (in the dark) for about 20 hours, shaking them once more at 1 or 2 hours.

Shake once more and spin the filters down for 15 minutes @ 5000 rpm.

Decant the supernatant into a 10 cm path length cell, or 1 cm cuvette (multiply the extinction values by 1.2 to normalize to values expected from 10 ml extract).

Immediately read and record absorbance @ 750nm and @ 664nm, then acidify with 100 ul (10 cm cell) or 20 ul (1 cm cell) of 1.2M HCl, mix well and read again @ 750nm and 664nm.

Make a filter blank by extracting a clean filter along with the sample filters. This measurement should be subtracted from the others OR used to zero spec.

Use Strickland and Parsons, 1972, formula to calculate concentration

Chl a = $26.7 \text{ L/g/cm} \times (664 \text{ before} - 664 \text{ acid}) \times 12 \text{ ml (extract volume)} / \text{Volume filtered (L)} \times 1.0 \text{ cm (cuvette length)} = \text{ug/L}$

Equation 664 = 664 nm measurement minus 750 nm

For Apalachicola Bay, chl a ~0.1 to 25 ug/L

Spec measurements should be ~ 0.02 to 0.20, with after acid numbers $\sim 50\text{-}75\%$ less then before acidification

mg pigment/m3 = C/V

C obtained from following equations

V is volume filtered

Pheaophytin is calculated from the same spectral data used to measure chlorophyll a.

Phaeo = $26.7 \text{ L/g/cm x} [1.7 (664 \text{ acid}) - 664 \text{ before}] \times 12 \text{ ml (extract volume)/Volume filtered (L) x 1 cm (cuvette length)} = \text{ug/L}$

Preservation Method: All samples are filtered through glass 47 mm filters at the ANERR laboratory. The filters are frozen and transported to the FSU laboratory for analysis (within 36 hours). The above methods are used at the FSU Oceanography Laboratory.

v) Parameter: NO23F

Method Reference: Adapted from Instruction manual for model 42 chemiluminescence analyzer and Braman, R.S. and S. A. Hendrix. Nanogram Nitrite and Nitrate determination in environmental and biological materials by Vanadium (III) reduction with chemiluminescence detection. Anal. Chem. 1989, 61, 2715-2718.

Method Descriptor: Nitrate (85C) and Nitrite (23C) are rapidly reduced to Nitrous Oxide in acidic Vanadium(III). The nitric oxide is removed via helium carrier gas and detected via analyzer: $NO + O_3 = NO_2 + O_2 + hv$, with the luminescence proportional to the concentration of NO.

Solutions and gases needed:

Helium, Air, Nitrogen

Isoproponyl in dry ice

2 M NaOH in ice

Reducing Reagent:

 $0.1 \text{ M Vanadium Sulfate} = 8.15 \text{ g VoSO}_{4*} \text{ nH}_2\text{O in 500 ml of } 2.0 \text{ M HCl } (2 \text{ M in 500 ml} = 83.3 \text{ ml HCl} + 416.7 \text{ ml H2O}).$

Prep: Place ~2 Tbs. Zinc pellets in a 125 ml flask.

Add 30 mls of 2% HgCl (2g in 100ml), swirl, add 70 mls more HgCl. Wait 10 min.

Dump HgCl. Add $VoSO_4$ acid solution. Cover loosely with parafilm and Bubble Nitrogen gas for 20 minutes until purple color develops (Vo(II)). Decant solution only to new flask and bubble with Oxygen (or Air) for 30+ minutes until Marine Blue color.

Apparatus setup:

Check all flow rates and connections before turning power on.

- 1) Isoproponyl in ice mixed well, with condensation trap in
- 2) Water and ice with NaOH impinger inside
- 3) Carefully connect Swagelock fittings Finger Tight Only!

Turn on power and wait 1.5 hours for analyzer to stabilize.

Push the STAT button on the front panel 4 times to attain NO_x mode.

Use the thumbwheel switches to set the range and press Enter.

Ranges include: 050, 100, 200, 500, 1000, 2000, and 5000 ppb.

Push the Stat button one more time to set the averaging time, thumb it and Enter.

Ave. times: 0.5, 1, 2, 3, 4, 5 (=0050), 6, 7, 8, 9, and 10 to 300 sec in mult. of 10.

Push the Man. (manual) button twice to be in NO_x mode.

(should read 3. with a value between 2-10)

100 ul Samples are added to the reducing solution via syringe.

Procedure: Nitrites are reduced at room temp to NO in Vo(III).

Nitrate + Nitrite: Nitrate is reduced by Vo(III) at 80-90C. The Vanadium impinger is heated to 85C and the 100 ul sample is added. Nitrites are also reduced by this method, so the Nitrite concentration measured previously is subtracted to get the Nitrate concentration.

Primary Stock: 0.425 NaNO3 / 1 L

Dilute for working stds (ul to 100ml): 0, 10, 20, 200, 400, 1000

Preservation Method: Nutrient samples are held on ice until transport to the FSU Department of Oceanography Laboratory in Tallahassee, Florida (within 36 hours). All samples are filtered through 0.45 µm membrane filters (Pall Gelman Supor) and the filtrate is collected into new bottles and placed on ice until analysis (within 48 hours).

b) UF Laboratory methods – in use dates March – December 2007.

i) Parameter: PO4

- 1) 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.

ii) 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 and stored at 4°C and run within 28 days.

iii) Parameter: NH4

- 1) Method Reference: Strickland & Parsons. 1972. A Practical Handbook of Seawater Analysis: Determination of Ammonia (Oxidation Method). Fisheries Research Board of Canada.
- 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.
- 3) Preservation Method: Samples are filtered through $0.7~\mu m$ pore size glass-fiber filters, stored at $-20^{\circ} C$ and run within 7 days.

iv) 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.
- 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 are filtered through 0.7 μm pore size glass-fiber filters, stored at -20°C and run within 48 hours.

vi) 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.
- 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, stored at -20°C and run within 28 days.

vii) Parameter: UncCHLa_N and CHLA_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. Uncorrected 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 Laboratory QAQC programs:

a) FSU Oceanography Laboratory – January and February 2007 only

i) Precision

- a) Field Variability ANERR staff collected field replicate samples from a successive grab sample. Replicate samples are collected from separate grabs at each sampling station. There were no field replicates collected during diel sampling.
- b) Laboratory Variability Laboratory duplicate sampling was performed monthly in 2007.
- c) Inter-organizational splits None

ii) Accuracy

- a) Sample Spikes FSU Oceanography lab runs an independently prepared set of internal check samples every month. The check samples are prepared using primary nutrient standards.
- b) Standard Reference Material Analysis None.
- c) Cross Calibration Exercises None.

b) UF Phlips Laboratory – March through December 2007

i) Precision

- a) Field Variability 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.
- **b)** Laboratory Variability Field blanks are run for replicate samples (every 10 samples) and sample spikes. Precision is measured by %RSD (percent relative standard deviation) and is calculated from the standard deviation and mean of seven repeat measurements. %RSD is one hundred times the standard deviation divided by the mean of the measurements.
- c) Inter-organizational splits None.

ii) Accuracy

- a) Sample Spikes Nutrient spikes are included in standard curve procedures associated with each analytical series run.
- b) Standard Reference Material Analysis Standard reference materials are used for routine evaluation of accuracy. Field blanks are included in all runs. The Florida Department of Health certification process also includes 'Blind Tests' of accuracy on an annual basis. Accuracy 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].
- c) Cross Calibration Exercises None.

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

*The -4 Outside Low Sensor Range flag was added to the 2007 dataset in August of 2011. See the Other Remarks section for more details.

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

Sensor errors

SBL	Value below minimum limit of method detection
SCB	Value calculated with a value that is below the MDL
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

CDR Sample diluted and rerun

CHB Sample held beyond specified holding time

CIP Ice present in sample vicinity
CIF Flotsam present in sample vicinity

CLE Sample collected later/earlier than scheduled

CRE Significant rain event

CSM See metadata

CUS Lab analysis from unpreserved sample

#### Record comments

CAB Algal bloom

CHB Sample held beyond specified holding time

CIP Ice present in sample vicinity
CIF Flotsam present in sample vicinity

CLE Sample collected later/earlier than scheduled

CRE Significant rain event

CSM See metadata

CUS Lab analysis from unpreserved sample

## Cloud cover

CCL clear (0-10%)

CSP scattered to partly cloudy (10-50%)

CPB partly to broken (50-90%)

COC overcast (>90%)

CFY foggy CHY hazy

CCC cloud (no percentage)

#### Precipitation

PNP none PDR drizzle

```
PLR light rain
PHR heavy rain
PSQ squally
```

PFQ frozen precipitation (sleet/snow/freezing rain)

PSR mixed rain and snow

## Tide stage

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

## Wave height

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

#### Wind direction

N from the north

NNE from the north northeast NE from the northeast ENE from the east northeast

E from the east

ESE from the east southeast SE from the southeast SSE from the south southeast

S from the south

SSW from the south southwest SW from the southwest WSW from the west southwest

W from the west

WNW from the west northwest NW from the northwest NNW from the north northwest

## Wind speed

WS0 0 to 1 knot WS1 > 1 to 10 knots WS2 > 10 to 20 knots WS3 > 20 to 30 knots WS4 > 30 to 40 knots WS5 > 40 knots

#### 17) Other remarks/notes:

a)

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 with -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.

*The 2007 dataset was updated on August of 2011 to include the -4 Outside Low Sensor Range flag. The 2007 data published prior to that time used the -3 Rejected data flag with the SBL and SCB QAQC codes to indicate that data were below the minimum detection limit. These flag code combinations were all replaced with the -4 SBL or SCB update as mandated by the Data Management Committee.

b) The Apalachicola River system has been in a record drought since 2006. This drought has been further exacerbated by upstream water uses and diversions primarily involving the explosive growth of Atlanta, Georgia. In 2007 the Apalachicola River experienced the longest continuous low flow ever recorded on the system dating back to the beginning record of 1921. Flows in the river were below 6,000 cfs for over 6 months from May through December and there was also no winter flood during the winter of 2007 as normally occurs. Nutrient levels in Apalachicola Bay are primarily influenced by river flows in the river. For more information on river flows in the Apalachicola River visit <a href="http://waterdata.usgs.gov/nwis/">http://waterdata.usgs.gov/nwis/</a>.