Apalachicola (APA) NERR Nutrient Metadata
January – December 2022
Latest Update: May 25, 2023

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

I. Data Set and Research Descriptors

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2) Research objectives –

Previous studies have shown the importance of river flow and flushing rates on nutrients and primary productivity in Apalachicola Bay. Similar studies have determined nitrogen and phosphorus budgets as well as nutrient limitations related to seasonality and river flow (Elder and Mattraw 1982, Frick et al. 1996, Mortazavi 1998, Twilley et al. 1999, Mortazavi 2000a, b, Mortazavi et al. 2001, Putland 2005, Edmiston 2008, Caffrey et al. 2013). There has been an ongoing controversy between the states of Florida, Georgia, and Alabama over the upstream diversion of water for 25 years. Approximately 88% of the Apalachicola River and Bay drainage basin is in Georgia and Alabama and historical flows are being threatened by upstream use. 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 and the compact expired. In late 2014, the US Supreme Court agreed to hear the case and legal proceedings are currently underway. The research objectives of this study are to investigate short-term variability, long-term change, and the relationship of other environmental factors to the productivity of the Apalachicola Bay system as well as try to separate natural from man-made variability. Data from this monitoring project has also been used by Florida DEP in support of Numeric Nutrient Criteria development.

a) Monthly Grab

Monthly grab samples are collected at 11 sites located across Apalachicola Bay to monitor spatial and temporal fluctuations in nutrient and chlorophyll-*a* concentrations across the bay. The stations were chosen to help determine the influence of the river, local rainfall, adjacent habitats, and anthropogenic impacts on the Bay. Sampling sites are in the lower Apalachicola River, in the coastal area, offshore of the barrier islands, at the SWMP datalogger locations (primary SWMP stations), and throughout the bay. Seasonal, climatic, and anthropogenic factors all impact river flow, which in turn affects nutrient and chlorophyll-*a* concentrations in the bay. Nutrient and chlorophyll-*a* concentrations are also influenced by biological activity, 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 and chlorophyll-*a* concentration. 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 and 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 (Estabrook 1973, Livingston 1978, Livingston and Duncan 1979, Edmiston 2008). Diel samples are collected over a 25-hour period thereby covering the lunar day of 24 hours 48 minutes.

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. Because of the distance between the stations it is not always possible to collect all the samples several hours prior to low tide. Tidal condition, wave height, wind direction, speed, precipitation, 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 Apalachicola National Estuarine Research Reserve (ANERR) weather station is available online at www.nerrsdata.org. Sampling after heavy rains is avoided if possible. Water temperature, salinity, specific conductivity, dissolved oxygen, pH, total dissolved solids, and turbidity are measured at surface and bottom for each station with a YSI Pro DSS handheld meter. Surface measurements only are included in this dataset for temperature, salinity, pH, and dissolved oxygen (except for the East Bay Bottom station). Bottom measurements for temperature, salinity, specific conductivity, dissolved oxygen, pH, total dissolved solids, and turbidity are available on request. Secchi data is also included in this dataset. In addition to readings taken by the hand-held instrument, turbidity samples are collected at each site and are analyzed in the ANERR lab with a HR Scientific DRT-15CE Turbidimeter. Biochemical oxygen demand was measured from whole water samples for the months of March, June, September, and December

(quarterly) at all stations except for apaebnut. These data are not included in the dataset but are available by contacting the Reserve directly. All grab samples are analyzed at the Florida Department of Environmental Protection laboratory (FLDEP).

Additional samples are collected in conjunction with ANERR's nutrient grab sampling monthly at the West Pass (apawpnut), Dry Bar (apadbnut), Mid Bay (apambnut), East Bay Bridge (apaegnut), Sikes Cut (apascnut), and Cat Point (apacpnut) stations for the Florida Fish & Wildlife Conservation Commission (FWC) Red Tide Monitoring Program. Results may be obtained by contacting FWC directly at RTOMP_coordinator@myfwc.com.

i) Grab sample collection:
A submersible pump and flexible clear plastic tubing is used to collect 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 1.5 meters below the surface to match the approximate depth of 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, approximating the depths of the two dataloggers deployed at this site. Triplicate samples are collected every other month at one randomly selected primary SWMP station.

ii) Grab sample filtration and handling:
Water from the submersible pump is delivered directly into the appropriate sample bottles. For samples requiring filtration, an in-line filter is attached to the end of the flexible tubing, and water filtered in this manner is delivered directly to the appropriate sample bottles. Necessary preservatives are added prior to water sample according to appropriate EPA protocols for nutrient sampling. Whole water samples for chlorophyll-*a* analysis are filtered at the FLDEP laboratory. All samples are placed on ice in the dark until delivery to the FLDEP laboratory. The submersible pump and tubing are flushed with ambient water prior to sample collection at each station. If an additional filter is needed at a site, either a new filter holder and filter will be used, or the current filter holder is rinsed with DI prior to addition of a new filter. A field blank is also run each month, using deionized water (DI) water for sample blank. The field blank is delivered using the pump, tubing and filter as described above. All grab samples are delivered to the FLDEP laboratory 24 to 36 hours after collection.

b) Diel Sampling Program
Diel sampling is performed with an ISCO 3700 Portable Automated Sampler at the East Bay surface (apaesnut) station. The ISCO is deployed on a fixed platform located at the East Bay surface site. Generally, the ISCO is deployed at the beginning of the grab sample collection trip and retrieved the following morning. In some months, adverse weather conditions result in deployment of the ISCO sampler during a week other than the week of grab sample collection. The sampler is programmed to collect two 1000 ml water samples every 2.5 hours, over a 25-hour period at the same depth as the East Bay surface datalogger probes (0.5 m below surface). This captures a complete 24 hour 48-minute 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 on ice upon retrieval of the ISCO sampler at the end of the sampling period. Nutrient sample filtration is performed at ANERR laboratory within one hour of retrieval from the ISCO sampler. Whole water samples for chlorophyll-*a* analysis are filtered at the FLDEP laboratory. All diel samples are delivered to the FLDEP laboratory within 36 hours of the first sample collection time. Note: No duplicate diel samples are taken, however there is some overlap with monthly grabs collected at the East Bay Surface station and deployment of the ISCO sampler.

c) Equipment QAQC and maintenance – Grab and Diel Sampling Program:
The submersible pump, tubing, and filter holders used in the field are acid rinsed with 10% Hydrochloric Acid and triple rinsed with ultra-pure DI water after each sampling trip. Laboratory items such as the filtration funnels and receivers are acid washed with 10% Hydrochloric Acid and triple rinsed with ultra-

pure DI water after each sampling event. Diel sample collection bottles used in the ISCO automated sampler are acid washed and triple rinsed with ultra-pure DI water after each sampling event. The ISCO automated sampler tubing is acid washed and triple rinsed with ultra-pure DI water after each sampling event. The overall condition of the pump and tubing is checked each month prior to deployment and tubing is replaced as needed, and per the CDMO SOP replacement schedule. New, unused sample bottles are supplied by FLDEP laboratory for each grab sampling event. The YSI Pro DSS and Turbidimeter are calibrated before each sampling event.

4) Site location and character –

The Apalachicola Drainage Basin encompasses over 50,700 square kilometers 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 freshwater 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. ANERR is in the northwestern part of Florida, generally called the panhandle. It is located adjacent to the Cities of Apalachicola and Eastpoint, and encompasses most of the Apalachicola Bay system, including 84 kilometers of the lower Apalachicola River. Passes, both natural and manmade, connect Apalachicola Bay to the northeastern Gulf of Mexico. Nutrient discharge and pollutant runoff surrounding the city of Apalachicola is elevated, compared to minimal pollution draining to Apalachicola Bay from the undeveloped panhandle.

Monthly grab samples are collected at all SWMP and nutrient monitoring stations. A map of station locations is given in Figure 1.

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. East 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 in the upper reaches of East Bay. The tower location for the two East Bay dataloggers (ES and EB) is 29.7858 N, 84.8752 W. At the sampling site, the depth is 2.2 m MHW and the width of the bay is 1.0 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 1.5 meters below the surface (or 0.3 m off the bottom sediment). Salinity ranges from 0 to 30 psu and the long-term (1995 – 2017) average salinity is 11.2 psu. At the East Bay surface site the meter probes are 0.5 meters below the surface (or 1.7 m off the bottom sediment) and salinity ranges from 0 psu to 30 psu with a long term (1995 – 2017) average salinity of 9.9 psu. 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 needlerush grass (*Juncus roemerianus*) and swamp sawgrass (*Cladium jamaicense*) and smooth cordgrass (*Spartina alterniflora*). The dominant upland vegetation is primarily pineland forests which includes slash pine (*Pinus elliotii*), saw palmetto (*Serenoa repens*), and sand pine (*Pinus clausa*). 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 effect 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 in St. George Sound, approximately 400 meters east of the St. George Island Bridge. The piling location is 29.7021 N, 84.8802 W. The tides at Cat Point are mixed

and range from 0.3 m to 1.0 m (average 0.5 m). At the sampling site, the depth is 2.5 meters MHW, and the width of the bay is 6.4 km. At the Cat Point site the datalogger probes are located 1.5 meters below the surface (or 0.3 m off the bottom sediment). This is also the approximate depth where nutrients are collected monthly. Salinity ranges from 0 to 34 psu with a long-term (2002 – 2017) average salinity of 21.9 psu. 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 (*Pinus elliotii*), saw palmetto (*Serenoa repens*), and sand pine (*Pinus clausa*). 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 0.8 kilometer east of St. Vincent Island. The tower location is 29.6747 N, 85.0584 W. The tides are mixed and range from 0.3 to 1.0 meters. At the sampling site, the depth is 2.0 meters MHW and the width of the bay is 11.2 km. At the Dry Bar site, the datalogger probes are located 1.5 meters below the surface (or 0.3 m off the bottom sediment). This is also the approximate depth where nutrients are collected monthly. Salinity ranges from 0 to 34 psu with a long-term (2002 – 2017) average salinity of 21.9 psu. Flows vary with local rainfall and are not quantified because the sampling site is influenced by the flow of the Apalachicola River and high salinity water coming through West Pass and Sikes Cut. 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 (*Pinus clausa*) flatwoods with various combinations of gallberry (*Ilex glabra*), smooth cordgrass (*Spartina alterniflora*), fetterbush (*Leucothoe racemosa*), cabbage palm (*Sabal palmetto*), saw palmetto (*Serenoa repens*), magnolia (*Magnolia grandiflora*), 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.

d) Secondary SWMP stations

Detailed information for an additional 7 nutrient (secondary SWMP) stations, not associated with the required sampling at the primary SWMP datalogger sites, as well as the datalogger sites, is included in Table 1.

<u>West Pass</u>
29.6379 N, 85.0890 W
Salinity average = 22.5 psu, range = 1.8 – 36.0 psu
This site is in the pass between two uninhabited barrier islands, the state owned and managed Cape St. George Island and St. Vincent National Wildlife Refuge. The sampling site is influenced by the flow of the Apalachicola River and high salinity water coming through West Pass.

<u>Pilots Cove datalogger and nutrient station</u>
29.60133 N, 85.02765 W
Salinity average = 22.9 psu, range = 1.3 – 35.5 psu
This site is located near state owned and managed Cape St. George Island, an uninhabited barrier island. The sampling site is influenced by the flow of the Apalachicola River and high salinity water coming through West Pass.

<u>Mid Bay</u>
29.6677 N, 84.9940 W
Salinity average = 16.3 psu, range = 0.2 – 35.2 psu
This sampling site is in central Apalachicola Bay. The site is roughly equidistant from state owned and managed Cape St. George Island (four miles distant), St. Vincent National Wildlife Refuge (six miles distant), and single family residential and commercial use in the Apalachicola area (four miles distant). This site is approximately 2.5 kilometers from the intercoastal waterway channel. The sampling site is influenced by the flow of the Apalachicola River and high salinity water coming through Sikes Cut and West Pass.

East Bay Bridge
29.7308 N, 84.9452 W
Salinity average = 7.9 psu, range = 0 – 30.7 psu
This site is located near the western section of the US Highway 98 bridge connecting Apalachicola and Eastpoint. The bridge also serves as the boundary line between East Bay and Apalachicola Bay. Nearby upland areas consist of residential and commercial use in the areas surrounding the cities of Apalachicola and Eastpoint. The sampling site is influenced by flows from the Apalachicola River and distributaries including the Little St. Marks River, St. Marks River, and East River.

Sikes Cut offshore
29.6067 N, 84.9467 W
Salinity average = 31.9 psu, range 21.7 – 35.8 psu
This site is selected to characterize true marine water and is located south of Sikes Cut in the Gulf of Mexico. The site is near the eastern portion of state owned and managed Cape St. George Island and near the western end of St. George Island in an area consisting of single family and vacation homes. Sikes Cut allows tidal exchange of high salinity water from the Gulf of Mexico and lower salinity water from Apalachicola Bay. Sikes Cut is an important pass utilized by commercial and recreational vessels.

Nicks Hole
29.6504 N, 84.9289 W
Salinity average = 19.0 psu, range = 0.5 – 35.4 psu
This site is near single family and vacation home use on St George Island. A small airport utilized by private aircraft is also located near Nicks Hole. The site is tidally influenced by high salinity water from Sikes Cut and by flows from the Apalachicola River.

River
29.7791 N, 85.0434 W
Salinity average = 0.1 psu, range = 0 – 0.1 psu
This site is selected to characterize fresh water in the Apalachicola River. The site is in the central channel of the river approximately 9.5 kilometers north and upstream of the river mouth and the residential and commercial areas of Apalachicola. Adjacent areas are state owned and managed forested floodplain. The site is influenced by Apalachicola River flow.

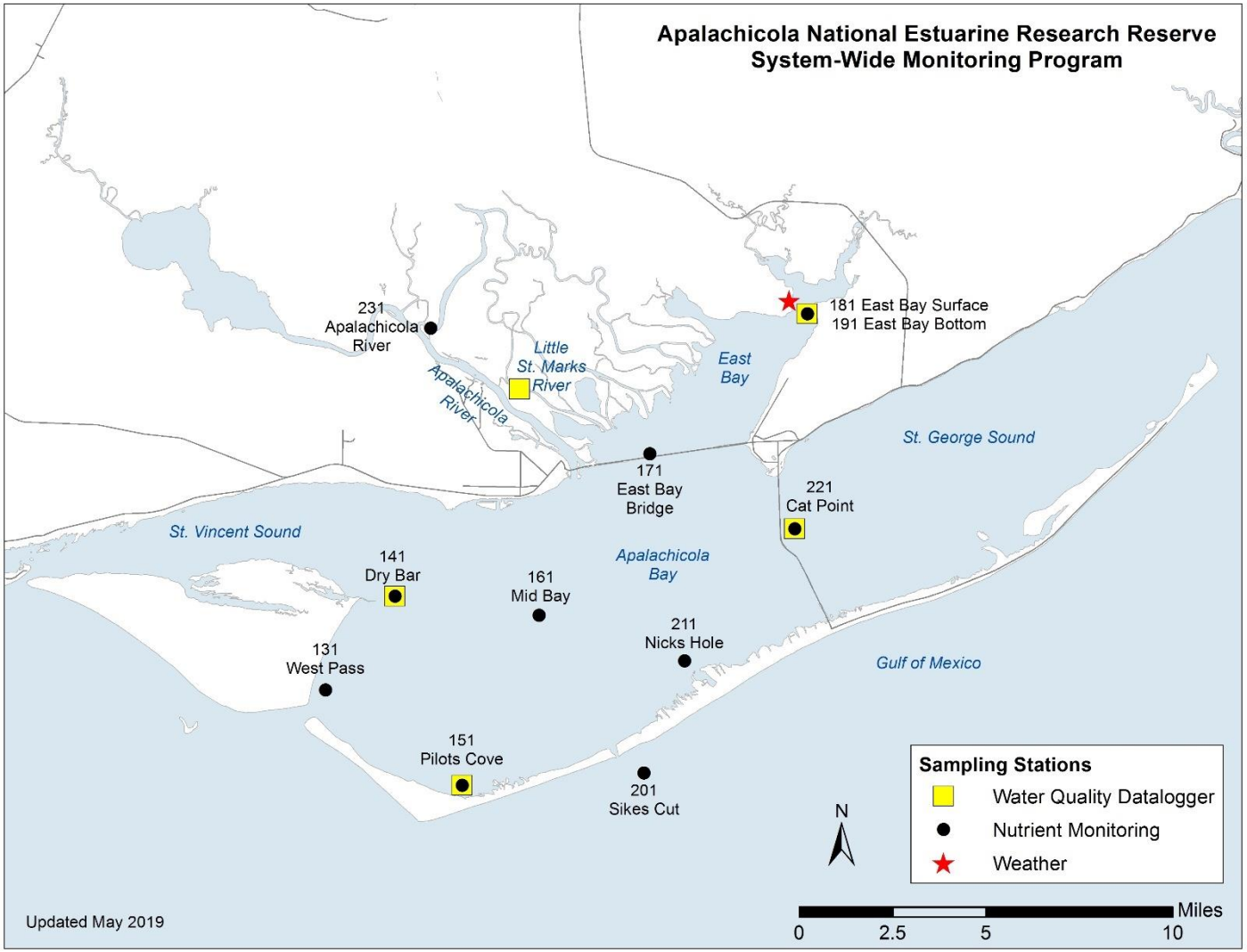
Table 1. Nutrient and chlorophyll-*a* sampling sites for the Apalachicola NERR SWMP.

Station code	SWMP Status	Station name	Location	Active Dates	Tidal Range Average (meters)	Salinity Range	Water Depth Average (meters)	Bottom Habitat	Datalogger Station Name	Sample Depth (meters)	Reason Decommissioned	Notes
apawpnut	S	West Pass	29° 38' 16.44 N, 85° 5' 20.40 W	04/01/2002 - current	0.7	euryhaline	5.0	sand		0.5	NA	NA
apadbnut	P	Dry Bar	29° 40' 28.92 N, 85° 3' 29.88 W	04/01/2002 - current	0.7	euryhaline	1.7	oyster bar	apadbwq	1.5	NA	NA
apapcnut	S	Pilot's Cove	29° 36' 28.44 N, 85° 1' 10.56 W	04/01/2002 – 11/27/2017	0.7	euryhaline	1.8	patchy seagrass		0.5	*See note	NA
apapcnut	S	Pilot's Cove	29° 36' 4.79 N, 85° 1' 39.54 W	1/10/2018 - current	0.7	euryhaline	2.2	patchy seagrass	apapcwq	1.5	NA	NA
apambnut	S	Mid Bay	29° 40' 3.72 N, 84° 59' 38.40 W	04/01/2002 - current	0.7	euryhaline	2.2	sandy silt		0.5	NA	NA
apaegnut	S	East Bay Bridge	29° 43' 50.88 N, 84° 56' 42.72 W	04/01/2002 - current	0.7	euryhaline	1.6	silty clay		0.5	NA	NA
apaesnut	P	East Bay Surface	29° 47' 8.88 N, 84° 52' 30.72 W	04/01/2002 - current	0.7	euryhaline	1.7	clayey sand	apaeswq	0.5	NA	NA
apaebnut	P	East Bay Bottom	29° 47' 8.88 N, 84° 52' 30.72 W	04/01/2002 - current	0.7	euryhaline	1.7	clayey sand	apaebwq	1.5	NA	NA
apascnut	S	Sikes Cut Offshore	29° 36' 24.12 N, 84° 56' 48.12 W	04/01/2002 - current	0.7	marine	>5.0	sand		0.5	NA	NA
apanhnut	S	Nick's Hole	29° 39' 1.44 N, 84° 55' 44.04 W	04/01/2002 - current	0.7	euryhaline	1.0	patchy seagrass		0.5	NA	NA
apacpnut	P	Cat Point	29° 42' 7.68 N, 84° 52' 48.72 W	04/01/2002 - current	0.7	euryhaline	1.8	oyster bar	apacpwq	1.5	NA	NA

aparvnut	S	River	29° 46' 44.76 N, 85° 2' 36.24 W	04/01/2002 - current	0.7	oligohaline	3-4	sandy silt		0.5	NA	NA

*The Pilot's Cove nutrient station was moved from its old location to the Pilots Cove water quality datalogger station, 1.2 km away that was approved by DMC as a secondary SWMP station in fall of 2016. The reason for the move is to have both the nutrients and water quality sampled at the same location, allowing us to more closely couple the nutrient data with the water quality readings that are now being collected at the new water quality site. ANERR sampled all nutrient and p-chem parameters at both stations monthly during 2017 to show that there is no statistically measurable difference in parameters between the locations, which is why the new location retained the Pilot's Cove station name and number rather than becoming a new station. This station move was approved by the CDMO Data Management Committee in late 2017 and took effect in January 2018.

Figure 1: ANERR SWMP Station locations.



5) Coded 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 2020. The Start and End date and times listed below 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. 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) Samples date/times Monitoring Program 1 (Grab Samples)

Site	Date	Time	Site	Date	Time	Site	Date	Time
apacpnut	2/21/2022	10:04	apadbnut	2/21/2022	12:52	apaebnut	2/21/2022	8:55
apacpnut	3/1/2022	10:03	apadbnut	3/1/2022	12:52	apaebnut	3/1/2022	8:57
apacpnut	4/18/2022	8:30	apadbnut	3/1/2022	12:54	apaebnut	4/18/2022	7:50
apacpnut	5/3/2022	8:58	apadbnut	3/1/2022	12:56	apaebnut	5/3/2022	8:09
apacpnut	5/3/2022	9:33	apadbnut	4/18/2022	9:55	apaebnut	5/31/2022	7:45
apacpnut	5/3/2022	9:36	apadbnut	5/3/2022	11:08	apaebnut	6/28/2022	8:23
apacpnut	5/31/2022	9:01	apadbnut	5/31/2022	12:00	apaebnut	8/2/2022	7:17
apacpnut	6/28/2022	9:15	apadbnut	6/28/2022	11:32	apaebnut	9/6/2022	7:34
apacpnut	8/2/2022	8:02	apadbnut	8/2/2022	10:13	apaebnut	10/4/2022	7:52
apacpnut	9/6/2022	8:50	apadbnut	9/6/2022	11:45	apaebnut	11/1/2022	7:33
apacpnut	10/4/2022	8:39	apadbnut	10/4/2022	10:27	apaebnut	11/1/2022	7:35
apacpnut	11/1/2022	8:26	apadbnut	11/1/2022	10:41	apaebnut	11/1/2022	7:37
apacpnut	12/13/2022	10:14	apadbnut	12/13/2022	13:26	apaebnut	12/13/2022	8:39

Site	Date	Time	Site	Date	Time	Site	Date	Time
apaegnut	2/21/2022	9:46	apaesnut	2/21/2022	8:53	apambnut	2/21/2022	13:36
apaegnut	3/1/2022	9:37	apaesnut	3/1/2022	8:55	apambnut*	3/1/2022	13:30
apaegnut	4/18/2022	8:13	apaesnut	4/18/2022	7:45	apambnut*	4/18/2022	10:30
apaegnut	5/3/2022	8:41	apaesnut	5/3/2022	8:07	apambnut	5/3/2022	11:47
apaegnut	5/31/2022	8:30	apaesnut	5/31/2022	7:43	apambnut	5/31/2022	12:44
apaegnut	6/28/2022	8:50	apaesnut	6/28/2022	8:23	apambnut	6/28/2022	12:06
apaegnut	8/2/2022	7:45	apaesnut	8/2/2022	7:11	apambnut	8/2/2022	10:50
apaegnut	9/6/2022	8:20	apaesnut	8/2/2022	7:13	apambnut	9/6/2022	12:23
apaegnut	10/4/2022	8:21	apaesnut	8/2/2022	7:15	apambnut	10/4/2022	10:51
apaegnut	11/1/2022	8:08	apaesnut	9/6/2022	7:32	apambnut	11/1/2022	11:18
apaegnut	12/13/2022	9:38	apaesnut	9/6/2022	7:36	apambnut	12/13/2022	14:12
			apaesnut	9/6/2022	7:38			
			apaesnut	10/4/2022	7:50			
			apaesnut	11/1/2022	7:31			
			apaesnut	12/13/2022	8:37			

Site	Date	Time	Site	Date	Time	Site	Date	Time
apanhnut	2/21/2022	10:34	apapcnut	2/21/2022	11:22	aparvnut	2/21/2022	13:56
apanhnut	3/1/2022	10:38	apapcnut	3/1/2022	11:40	aparvnut*	3/1/2022	14:00
apanhnut	4/18/2022	8:50	apapcnut	4/18/2022	9:12	aparvnut*	4/18/2022	11:30
apanhnut	5/3/2022	9:31	apapcnut	5/3/2022	10:18	aparvnut	5/3/2022	12:28
apanhnut	5/31/2022	9:38	apapcnut	5/31/2022	10:42	aparvnut	5/31/2022	13:25
apanhnut	6/28/2022	9:36	apapcnut	6/28/2022	10:31	aparvnut	6/28/2022	12:46
apanhnut	8/2/2022	8:27	apapcnut	8/2/2022	9:11	aparvnut*	8/3/2022	11:30
apanhnut	9/6/2022	9:20	apapcnut	9/6/2022	10:29	aparvnut	9/6/2022	13:02
apanhnut	10/4/2022	8:54	apapcnut	10/4/2022	9:36	aparvnut	10/4/2022	11:20
apanhnut	11/1/2022	8:52	apapcnut	11/1/2022	9:36	aparvnut	11/1/2022	12:00
apanhnut	12/13/2022	11:00	apapcnut	12/13/2022	11:48	aparvnut	12/13/2022	14:54

Site	Date	Time	Site	Date	Time
apascnut	2/21/2022	10:56	apawpnut	2/21/2022	12:21
apascnut*	3/1/2022	11:00	apawpnut	3/1/2022	12:13
apascnut*	4/18/2022	9:00	apawpnut	4/18/2022	9:30
apascnut	5/3/2022	9:53	apawpnut	5/3/2022	10:45
apascnut	5/31/2022	10:09	apawpnut	5/31/2022	11:21
apascnut	6/28/2022	10:02	apawpnut	6/28/2022	11:04
apascnut	8/2/2022	8:46	apawpnut	8/2/2022	9:46
apascnut	9/6/2022	9:54	apawpnut	9/6/2022	11:09
apascnut	10/4/2022	9:13	apawpnut	10/4/2022	10:03

apascnut	11/1/2022	9:13	apawpnut	11/1/2022	10:13
apascnut*	12/13/2022	11:20	apawpnut	12/13/2022	12:39

*Samples marked with an * were not collected due to poor weather conditions.

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

Site	Start Date	Start Time	End Date	End Time
apaesnut	2/23/2022	8:45	2/24/2022	9:45
apaesnut	3/1/2022	9:00	3/2/2022	10:00
apaesnut	4/18/2022	8:00	4/19/2022	9:00
apaesnut	5/3/2022	8:15	5/4/2022	9:15
apaesnut	5/31/2022	8:00	5/31/2022	23:00
apaesnut	6/1/2022	1:30	6/1/2022	9:00
apaesnut	7/18/2022	7:00	7/19/2022	8:00
apaesnut	8/2/2022	7:15	8/3/2022	8:15
apaesnut	9/6/2022	7:45	9/7/2022	8:45
apaesnut	10/4/2022	8:00	10/5/2022	9:00
apaesnut	11/1/2022	7:45	11/2/2022	8:45
apaesnut	12/13/2022	8:45	12/14/2022	9:45

7) Associated researchers and projects–

As part of the SWMP long-term monitoring program, the Apalachicola (APA) NERR also monitors 15-minute meteorological and water quality data which may be correlated with this nutrient/pigment dataset. These data are available at www.nerrsdata.org.

Other ongoing projects or data that relate to the nutrient monitoring project include:

Apalachicola Bay Oyster Situation Report TP200. UF/IFAS, Sea Grant Florida. April 24, 2013.

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

Bourque, E., Jackson, E. Garwood, J., Lamb, M., Harper, J., Apalachicola National Estuarine Research Reserve, System Wide Monitoring Program, Long-Term Water Quality Monitoring. Ongoing.

Caffrey, J. University of West Florida. Effect of diurnal and weekly water column hypoxic events on nitrification and nitrogen transformations in estuarine sediments. 2008.

Cannonier, S. Florida Agricultural and Mechanical University School of the Environment, Doctoral Dissertation, HAB Biotoxin Concentration in two NERR sites in correlation to nutrient concentrations. Ongoing.

Florida Fish and Wildlife Conservation Commission. Red Tide Monitoring Program. Ongoing.

Garwood, J., Lamb, M., Bourque, E., Jackson, E. Apalachicola National Estuarine Research Reserve, Distribution and density of fishes and benthic invertebrates in Apalachicola Bay. Ongoing.

Garwood, J., Lamb, M., Bourque, E., Jackson, E. Apalachicola National Estuarine Research Reserve, Effects of River Flow on Estuarine Primary Productivity and Macrozooplankton Communities. Ongoing.

Garwood, J., Bourque, E. Apalachicola National Estuarine Research Reserve, System Wide Monitoring Program, Long-Term Meteorological Monitoring. Ongoing.

Geyer, N. Florida State University, Doctoral Dissertation, Spatio-temporal dynamics of phytoplankton distribution in Apalachicola Bay. 2017.

Geyer, N., Huettel, M., Wetz, M. Biogeochemistry of a River-Dominated Estuary Influenced by Droughts and Storms. Estuaries and Coasts 41: 2009-2023.

Harper, J., Wren, K., Garwood, J., Snyder, C., Bourque, E., Lamb, M., Jackson, E. NERRS Sentinel Sites Program for Understanding Climate Change Impacts on Estuaries. Ongoing.

Hagen, S., DeLorme, D., Walters, L., Wang, D., Weishampel, J., Yeh, G., Huang, W., Slinn, D., Morris, J. Predicting impacts of sea level rise in the northern Gulf of Mexico. 2015.

Kimbro, D., Garland, H., Christopher, M., Cox, N., Yuan, S., Peter, K., Lamb, M., Harper, J. Apalachicola National Estuarine Research Reserve, Oyster reef research in Apalachicola Bay provided for the ACF lawsuit. 2013-2016.

Martínez-Colón, Michael. Florida Agricultural and Mechanical University. Benthic foraminifera and their microbiomes in oxic/anoxic estuaries. Ongoing.

Site-Specific Information in Support of Establishing Numeric Nutrient Criteria in Apalachicola Bay, Nutrient Criteria Technical Support Document. Division of Assessment and Restoration, Florida Department of Environmental Protection, July 2013.

Tucker, K., Florida Agricultural and Mechanical University Department of Civil and Environmental Engineering, Master's Thesis, Effects of river flow and rainfall on chlorophyll a in Apalachicola River. 2011.

Tucker, K., Florida Agricultural and Mechanical University Department of Civil and Environmental Engineering, Doctoral Dissertation, Nutrient input effects on *Karenia brevis* and *Pseudo-nitzschia* and subsequent marine mortalities in the Gulf of Mexico, Ongoing.

Viveros, P., NOAA Graduate Research Fellowship, University of Florida, Phytoplankton composition and abundance in relation to salinity, nutrient and light gradients in the Apalachicola National Estuarine Research Reserve. 2011.

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.

8) Distribution –

NOAA retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The NERRS retains the right to be fully credited for having

collected and process the data. Following academic courtesy standards, the NERR site where the data were collected should be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

Requested citation format:
NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; *accessed* 12 October 2022.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page www.nerrsdata.org. Data are available in comma separated version format.

II. Physical Structure Descriptors

9) Entry verification –

ANERR personnel download data from the FLDEP laboratory roughly a month after sampling, following notification from the laboratory that sample results are available. Data and final reports are downloaded through the laboratory's in-house LIMS software program. Raw data and sample hold times are downloaded as Microsoft Excel 1997-2003 workbooks (.xls) files and final laboratory reports are downloaded as .pdf documents. Data are verified for completeness and notes are made of any communications with the laboratory regarding suspect data. On a quarterly basis, raw nutrient and chlorophyll-*a* data is copied and pasted into quarterly files and hand-held physical chemistry readings taken at the time of sampling are added to these files. Preliminary QAQC and samples falling below MDLs are noted on a quarterly basis. Units are consistent with those used by CDMO so unit conversion is not necessary. At the end of the calendar year, quarterly files are compiled and this data is copied into a single working file for secondary QAQC using the CDMO Nutrient QAQC Excel macro.

Nutrient data are entered into a Microsoft Excel worksheet and processed using the NutrientQAQC Excel macro. The NutrientQAQC macro sets up the data worksheet, metadata worksheets, and MDL worksheet; adds chosen parameters and facilitates data entry; allows the user to set the number of significant figures to be reported for each parameter and rounds using banker's rounding rules; allows the user to input MDL values and then automatically flags/codes measured values below MDL and inserts the MDL; calculates parameters chosen by the user and automatically flags/codes for component values below MDL, negative calculated values, and missing data; allows the user to apply QAQC flags and codes to the data; produces summary statistics; graphs selected parameters for review; and exports the resulting data file to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

From January 2018 to present, Ethan Bourque was responsible for these tasks.

10) Parameter titles and variable names by category –

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

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:			
	*Orthophosphate	PO4F	mg/L as P
	Total Phosphorus	TP	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Total Kjeldahl Nitrogen whole	TKN	mg/L as N
	Total Nitrogen	TN	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
	Uncorrected Chlorophyll-*a*	UncCHLA_N	µg/ L
Other Lab Parameters:			
	Total Suspended Solids	TSS	mg/L
Field Parameters:			
	Water Temperature	WTEM_N	ºC
	Salinity	SALT_N	ppt
	Dissolved oxygen	DO_N	mg/L
	% Saturated dissolved oxygen	DO_S_N	%
	pH	PH_N	SU
	Turbidity	TURB_N	NTU
	Secchi Disk Depth	SECCHI	meters

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 or calculated laboratory parameters –

a) **Parameters measured directly**

Nitrogen species:	NH4F, NO23F, TKN
Phosphorus species:	PO4F, TP
Other:	UncCHLA_N, CHLA_N, PHEA, TSS

b) **Calculated parameters**

TN	NO23F + TKN
DIN	NO23F+NH4F

12) Limits of detection –

All information in this section is provided by FLDEP laboratory.

a) FLDEP laboratory MDL determination:

The MDL is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from the method blank result. MDLs are determined using the method specified in the Federal Register, 40 CFR Part 136 Appendix B Revision 2, using LCSs prepared near the estimated detection limit as surrogates to estimate methodological noise for actual method blanks to directly measure methodological noise. If none of the method blanks give numerical results for an individual analyte, method blanks are not required for the determination of the MDL. Where the possibility exists for significant systematic bias from sample preparation and handling or from the analytical determinative step (typically inorganic analyses), bias is considered when calculating detection limits. Published MDLs may be set higher than experimentally determined MDLs to (1) avoid observed positive interferences from matrix effects or common reagent contaminants or (2) for reporting convenience (i.e., to group common compounds with similar but slightly different experimentally determined MDLs). MDLs are determined in a suitable analyte-free matrix when possible. For certain analytes and matrices, no suitable, analyte-free matrix may be available. In those cases, MDLs are determined in the absence of any matrix, but in the presence of all preparatory reagents carried through the full preparatory and determinative steps. LOD verification procedures may be found in SOP LB-031, Limit of Detection Verification. (From page 42 of FLDEP Laboratory Quality Manual 2022. The most current version of the manual and individual method SOPs can be accessed at: https://floridadep.gov/dear/florida-dep-laboratory/content/dep-laboratory-quality-assurance-manual-and-sops).

b) 2022 base MDLs for Orthophosphate (PO4F), Nitrate + Nitrate (NO23F), ammonium (NH4F), Total Kjeldahl Nitrogen whole (TKN), and Total Suspended Solids (TSS), as reported by FLDEP laboratory. FLDEP SOPs state that the reported MDL for a sample may vary based on sample dilution. base MDLs for Total Phosphorus (TP) as reported by FLDEP laboratory. FLDEP SOP states that "the applicable range for" the SEAL Analytical AQ2 "method is from the practical quantitation limit (PQL) of 0.050 to 1.0 mg P/L. The method detection limit (MDL) is 0.005 mg P/L. The range may be extended by dilution. All samples with concentrations below the PQL on the AQ2 are analyzed using the" Bran Luebbe "segmented flow analyzer (see DEP SOP NU-082)." FLDEP SOPs state that the reported MDL for a sample may vary based on sample dilution.

Parameter	Start Date	End Date	Nominal (Base) MDL	MDL Range	Date Revisited	SOP Name
PO4F	4/2/2021	8/10/2021	0.004	0.004	4/1/2021	NU-070-1.21
PO4F	8/11/2022	12/31/2022	0.004	0.004	8/4/2022	NU-070-1.22
NO23F	2/21/2020	12/26/2021	0.004	0.004 - 0.008	2/20/2020	NU-066-1.23
NO23F	12/27/2021	12/31/2022	0.004	0.004 - 0.008	12/20/2021	NU-066-1.24
NH4F	3/10/2021	10/9/2022	0.002	0.002	3/9/2021	NU-104-1.2
NH4F	10/10/2022	12/31/2022	0.002	0.002	8/31/2022	NU-104-1.3
TKN	12/30/2020	1/31/2021	0.080 to 4.0	0.08	12/30/2020	NU-092-1.11
TKN	2/1/2022	12/31/2022	0.080 to 4.0	0.08	1/27/2022	NU-092-1.12
TSS	1/4/2021	1/25/2022	2.0 or 3.0*	2.0 - 3.0	1/4/2021	NU-051-3.24
TSS	1/26/2022	10/2/2022	2.0 or 3.0*	2.0 - 3.0	11/23/2021	NU-051-3.25
TSS	10/3/2022	12/31/2022	2.0 or 3.0*	2.0 - 3.0	10/3/2022	NU-051-3.26
TP	2/14/2020	12/26/2021	0.002	0.002	2/13/2020	NU-082-1.15
TP	12/27/2021	12/31/2022	0.002	0.002	12/27/2021	NU-082-1.16

* FLDEP laboratory SOP statement regarding Total Suspended Solid (TSS) MDLs: "The practical range of determination is from the method detection limit (MDL) 2 mg/L (3.0 mg/L for samples with conductivity ≥ 15,000 µmhos/cm) to 20,000 mg/L."

c) FLDEP MDLs for the chlorophyll suite of components may change by station and month based on the need to dilute samples during processing. The base MDL listed in the FLDEP SOP is based on the maximum filtration volume and minimum extract volume and will therefore be the lowest MDL.

Base MDL values for ANERR 2022 plant pigment parameters:

Parameter	FLDEP SOP version	SOP Valid Dates		MDL	Units	Revisited
		Start Date	End Date			
Chlorophyll-*a* (Chla_N)	BB-029-2.8	2/15/2021	2/15/2022	0.82	ug/L	2/15/2021
Chlorophyll-*a* (Chla_N)	BB-029-2.9	2/16/2022	12/31/2022	0.82	ug/L	2/16/2022
Uncorrected Chlorophyll-*a* (UncChla_N)	BB-029-2.8	2/15/2021	2/15/2022	0.6	ug/L	2/15/2021
Uncorrected Chlorophyll-*a* (UncChla_N)	BB-029-2.9	2/16/2022	12/31/2022	0.6	ug/L	2/16/2022
Phaeophytin (PHEA)	BB-029-2.8	2/15/2021	2/15/2022	0.9	ug/L	2/15/2021
Phaeophytin (PHEA)	BB-029-2.9	2/16/2022	12/31/2022	0.9	ug/L	2/16/2022

The sample MDL is calculated based on the number of times a sample must be diluted. For example, if a CHL_A sample must be diluted to twice its volume, the base MDL of 0.55 ug/L is multiplied by a dilution factor of two (0.55 ug/L x 2) thus resulting in an MDL of 1.10 ug/L. For samples that fall below the MDL and their MDL is greater than the base MDL, individual sample MDLs are listed in the table below. These data have been flagged and coded as -4 SBL in the dataset.

2022 MDLs for Chlorophyll-*a* (CHLA_N), Uncorrected Chlorophyll-*a* (UncCHLA_N), and Phaeophytin (PHEA), as reported by FLDEP laboratory when values differ from base MDL values:

Paramter	SateTimeStamp	Site	MDL	UNITS
PHEA	2/21/2022 9:46	apaegnut	2.1	ug/L
PHEA	2/21/2022 10:56	apascnut	0.98	ug/L
PHEA	2/21/2022 11:22	apapcnut	1.6	ug/L
PHEA	2/21/2022 12:21	apawpnut	0.98	ug/L
PHEA	2/23/2022 8:45	apaesnut	2.4	ug/L
PHEA	2/23/2022 11:15	apaesnut	2.2	ug/L
PHEA	2/23/2022 13:45	apaesnut	1.8	ug/L
PHEA	2/23/2022 16:15	apaesnut	1.4	ug/L
PHEA	2/23/2022 18:45	apaesnut	1.7	ug/L
PHEA	2/23/2022 21:15	apaesnut	1.8	ug/L
PHEA	2/23/2022 23:45	apaesnut	1.8	ug/L
PHEA	3/1/2022 10:38	apanhnut	0.98	ug/L
PHEA	3/1/2022 11:30	apaesnut	3	ug/L

PHEA	3/1/2022 11:40	apapcnut	1.2	ug/L
PHEA	3/1/2022 12:56	apadbnut	2.2	ug/L
PHEA	3/1/2022 16:30	apaesnut	1.8	ug/L
PHEA	3/1/2022 19:00	apaesnut	1.4	ug/L
PHEA	3/2/2022 10:00	apaesnut	5.1	ug/L
PHEA	4/18/2022 9:50	apanhnut	1.4	ug/L
PHEA	4/18/2022 10:12	apapcnut	1.2	ug/L
PHEA	4/18/2022 10:30	apawpnut	1.5	ug/L
PHEA	5/3/2022 9:07	apaesnut	1.8	ug/L
PHEA	5/3/2022 9:41	apaegnut	1.6	ug/L
PHEA	5/3/2022 10:31	apanhnut	1	ug/L
PHEA	5/3/2022 10:33	apacpnut	1.6	ug/L
PHEA	5/3/2022 11:18	apapcnut	2.4	ug/L
PHEA	5/3/2022 12:47	apambnut	0.98	ug/L
PHEA	5/3/2022 21:45	apaesnut	6.5	ug/L
PHEA	5/31/2022 9:30	apaegnut	2	ug/L
PHEA	5/31/2022 10:01	apacpnut	1.6	ug/L
PHEA	5/31/2022 10:38	apanhnut	1	ug/L
PHEA	5/31/2022 11:09	apascnut	1	ug/L
PHEA	5/31/2022 12:21	apawpnut	1.6	ug/L
PHEA	5/31/2022 13:00	apadbnut	3	ug/L
PHEA	5/31/2022 13:44	apambnut	1.8	ug/L
PHEA	5/31/2022 14:00	apaesnut	3.4	ug/L
PHEA	5/31/2022 14:25	aparvnut	1.7	ug/L
PHEA	5/31/2022 16:30	apaesnut	1.7	ug/L
PHEA	5/31/2022 19:00	apaesnut	2.2	ug/L
PHEA	6/28/2022 9:50	apaegnut	1.7	ug/L
PHEA	6/28/2022 10:15	apacpnut	4.5	ug/L
PHEA	6/28/2022 10:36	apanhnut	1.2	ug/L
PHEA	6/28/2022 11:02	apascnut	1	ug/L
PHEA	6/28/2022 11:31	apapcnut	1.6	ug/L
PHEA	6/28/2022 12:04	apawpnut	1.1	ug/L
PHEA	6/28/2022 12:32	apadbnut	1.6	ug/L
PHEA	6/28/2022 13:06	apambnut	2.3	ug/L
PHEA	8/2/2022 9:46	apascnut	0.98	ug/L
PHEA	8/2/2022 11:13	apadbnut	0.98	ug/L
PHEA	9/6/2022 9:20	apaegnut	1.5	ug/L
PHEA	9/6/2022 10:20	apanhnut	1.8	ug/L

PHEA	9/6/2022 11:29	apapcnut	1	ug/L
PHEA	9/6/2022 12:09	apawpnut	1.5	ug/L
PHEA	9/6/2022 12:45	apadbnut	1.5	ug/L
PHEA	9/6/2022 21:15	apaesnut	3.6	ug/L
PHEA	9/7/2022 9:45	apaesnut	3	ug/L
PHEA	10/4/2022 8:50	apaesnut	1.8	ug/L
PHEA	10/4/2022 8:52	apaebnut	1.6	ug/L
PHEA	10/4/2022 10:13	apascnut	1.5	ug/L
PHEA	10/4/2022 10:36	apapcnut	1.8	ug/L
PHEA	10/4/2022 11:03	apawpnut	1.8	ug/L
PHEA	10/4/2022 11:30	apaesnut	1.8	ug/L
PHEA	11/1/2022 11:15	apaesnut	1.8	ug/L
PHEA	12/13/2022 8:37	apaesnut	2.2	ug/L
PHEA	12/13/2022 14:54	aparvnut	1.8	ug/L

13) Laboratory methods –

a) Parameter: PO4

Method Reference: EPA Method 365.1, Rev. 2.0 (1993), the Seal AutoAnalyzer3 method G-146-95 Rev. 3, and the Seal AutoAnalyzer 500 method A-036-19 Rev. 1.

Method Description: Orthophosphate reacts with molybdenum (VI) and antimony (III) in an acid medium to form an antimony-phospho-molybdate complex. The complex is reduced with ascorbic acid to form a blue complex that absorbs at 880 nm.

Preservation Method: Samples are filtered in the field, placed on ice (not frozen), and analyzed within 48 hours of sample collection.

b) Parameter: TP

Method Reference: This SOP is based on EPA Method 365.1, Rev. 2.0 (1993) and Seal Method G-146-95 Rev. 3.

Method Description: Prior to analysis the samples are prepared by autoclave digestion (DEP SOP NU-049) in which all phosphate containing compounds, both organic and inorganic, are hydrolyzed to generate orthophosphate ion (PO4 3-). During analysis orthophosphate forms a complex with molybdenum and antimony in an acid medium. This phosphoantimony/molybdenum complex is reduced with ascorbic acid and generates a blue colored solution. The intensity of this color is measured at 880 nm for total phosphate analysis.

Preservation Method: Samples are acidified in the field to pH <2, placed on ice (not frozen), and analyzed within 28 days of sample collection.

c) Parameter: NH4

Method Reference: This SOP is based upon EPA Method 350.1, Rev. 2.0 (1993) and SEAL Auto Analyzer Method G-427-14 Rev. 3.

Method Description: The sample is air-segmented and made alkaline in the donor stream. The ammonia molecules generated at this pH flow into the dialysis block holding the gas diffusion membrane. On the other side of the gas diffusion membrane is an acidic acceptor stream that the ammonia gas diffuses into. The ammonia reacts with salicylate and dichloro-isocyanuric acid at 37˚C to produce a blue-green color proportional to the ammonia concentration. Sodium nitroprusside is used as a catalyst. The absorbance is measured at 660 nm.

Preservation Method: Samples are filtered in the field, acidified to pH <2, placed on ice in the dark and analyzed within 28 days.

d) Parameter: NO23

Method Reference: This method is based on EPA method 353.2, Rev 2.0 (1993) and Lachat method10-107-04-1-C. Diethylenetriaminepentaacetic acid (DTPA) is used ascomplexing agent instead of ethylenediamine tetraacetic acid (EDTA).

Method Description: A sample is passed through a column containing granular copper-cadmium catalyst, which reduces nitrate to nitrite. The nitrite originally present plus the reduced nitrate can then are determined by colorimetry. The nitrite is diazotized with sulfanilamide and coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to form a highly colored azo dye, which is measured at a wavelength of 520 nm.

Preservation Method: Samples are filtered in the field, acidified to pH <2, placed on ice in the dark and analyzed within 28 days.

e) Parameter: TKN

Method Reference: This SOP is based on EPA method 351.2, Rev. 2.0 (1993) and Seal AQ2 method EPA-111-A Rev. 4.

Method Description: Prior to analysis, digestion converts free ammonia and organic nitrogen compounds to ammonium sulfate (DEP SOP NU-091). Ammonium reacts with salicylate and hypochlorite in a buffered, alkaline solution in the presence of sodium nitroferricyanide (pH = 12.4-12.7) to form the salicylic acid analog of indophenol blue. The blue-green color produced is measured at 660 nm.

Preservation Method: Whole water is acidified in the field to pH <2, placed on ice in the dark and analyzed within 28 days.

f) Parameter: CHLA_N and UncCHLA_N and PHEA

Method Reference: This method is based on Standard Methods 10200H and EPA Method 446.0.

Method Description: This method is used to determine the amount of chlorophyll-*a* and pheophytin-*a* in marine and freshwater algae by visible spectrophotometry. Uncorrected chlorophyll-*a* is calculated using the trichromatic equation. Corrected chlorophyll-*a* and pheophytin are calculated using the monochromatic equation. The absorption-peak-ratio (chlorophyll/pheophytin) is also determined. A sample is vacuum filtered onto a glass fiber filter. The filter is then macerated with a tissue grinder and steeped in 90% acetone to extract chlorophyll from the algal cells. The sample is clarified through centrifugation. The absorbance of the clarified extract is then measured on a spectrophotometer at 750, 665, 664, 647 and 630 nm wavelengths before and after a 90 second Hydrochloric acid acidification step.

Preservation Method: Whole water is collected in brown Nalgene bottles, placed on ice in the dark, and delivered to the FLDEP lab within 36 hours for filtration.

g) Parameter: TSS

Method Reference: This method is based on Standard Methods 2540 D-2011.

Method Description: A well-mixed sample is filtered through a pre-weighed glass fiber filter. The filter and any residue are then dried to a constant weight at 103-105 °C. The filter is cooled in a desiccator, weighed and the result used to compute the TSS of the sample.

Preservation Method: Whole water is placed on ice in the dark for analysis within 7 days.

14) Field and Laboratory QAQC programs –

a) Precision

i. **Field Variability** – Field blanks (using deionized water) are included in all monthly sampling events. ANERR staff collect field triplicate samples from a successive grab sample. Triplicate

samples are collected from separate grabs at one primary SWMP sampling station selected at random every other month. There are no field triplicates collected during diel sampling, though the first diel sample is taken at a similar time frame to the grab sample at that station and can be compared for similarity.

ii. **Laboratory Variability** – Method blanks and duplicate samples are run with every sample batch. Batches are groups of 20 or less samples that are analyzed concurrently. Precision is measured by Relative Percent Difference (RPD).

iii. **Inter-organizational splits** – None.

b) Accuracy

i. **Sample Spikes** – At least two sample spikes are performed with each sample batch. The acceptance limits for sample or spike duplicates is a RPD of less than 20% if both results are above the PQL. Laboratory fortified blanks are run with each sample batch, acceptance limits for recovery are 85-115%.

ii. **Standard Reference Material Analysis** – Check standards are included in each batch and at the beginning and end of each run. Check standard acceptance limits are 85-115% recovery. (FLDEP Central Laboratory NU-043-2.24)**.**

iii. **Cross Calibration Exercises** – FDEP laboratory participated in two rounds of performance testing (PT) in 2020. The studies are performed by many labs around the nation to and are required to maintain the lab's TNI certification. In addition to the PT studies the lab also participated in a round robin organized by North Carolina DEQ for chlorophyll analysis. In 2020, the round robin occurred at the end of July/beginning of August and the lab analyzed 8 split samples.

15) QAQC flag definitions –

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

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

16) QAQC code definitions –

QAQC codes are used in conjunction with QAQC flags to provide further documentation of the data and are also applied by insertion into the associated flag column. There are three (3) different code categories, general, sensor, and comment. General errors document general problems with the sample or sample collection, sensor errors document common sensor or

parameter specific problems, and comment codes are used to further document conditions or a problem with the data. Only one general or sensor error and one comment code can be applied to a particular data point. However, a record flag column (F_Record) in the nutrient data allows multiple comment codes to be applied to the entire data record.

General errors

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

Sensor errors

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

Parameter Comments

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

Record comments

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

Cloud cover

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

Precipitation

PNP	none
PDR	drizzle

PLR	light rain
PHR	heavy rain
PSQ	squally
PFQ	frozen precipitation (sleet/snow/freezing rain)
PSR	mixed rain and snow
Tide stage	
TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide
Wave height	
WH0	0 to <0.1 meters
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.6 meters
WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters
Wind direction	
N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest
Wind speed	
WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) Other remarks/notes –

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of NO23F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL.

In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected, and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the Reserve submitting the data.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2007-2010 were also flagged/coded, but either reported as the measured value or a blank cell. Any 2007-2011 nutrient/pigment data downloaded from the CDMO prior to November of 2011 will reflect this difference.

a) Information about flagged data and additional notes

January 2022:

- Sampling canceled due to Covid restrictions at the DEP laboratory and marine conditions.

February 2022:

- H_2SO_4 preservative in apaesnut grab sample expired 10/2021, laboratory flagged analytes with "Y" qualifier indicating sample wasn't properly preserved (<2 pH) and results may not accurately represent the composition of sample at time of sampling: NCR (Non-Conformance Report) due to expired H_2SO_4

April 2022:

- Last apaesnut diel sample not collected, stopped deployment early due to worsening marine conditions

June 2022:

- Several apaesnut diel sample bottles had stuff stuck to the bottom that would not resuspend or rinse out

July 2022:

- Triplicates at apaesnut not collected, collection moved to August

August 2022:

- Aparvnut not collected due to lightning

October 2022:

- ISCO stopped sampling early, power disconnect then reconnect error messages found, unit drawing more power than normal sent in for repair

November 2022:

- New ISCO collected all apaesnut diel samples

December 2022:

- ISCO stopped sampling early, determined that the battery had been damaged by ISCO that was sent for repair

b) Sample hold times

	Date Analyzed						
Sample descriptor	**NH4F**	**NO23F**	**PO4F**	**CHLA_N, UncCHLA_N, PHEA**	**TKN**	**TP**	**TSS**
02/21/2022 all grab samples, 02/23/2022 all diel samples	2/25/2022, 3/1/2022, 3/3-4/2022, 3/18/2022	2/25/2022, 3/1/2022, 3/3-4/2022, 3/7-8/2022, 3/15/2022	2/22/2022, 2/24/2022	2/28/2022, 3/2/2022	2/25/2022, 3/1-2/2022, 3/8/2022, 3/10/2022	2/24/2022, 2/28/2022, 3/4/2022, 3/7/2022, 3/11/2022, 3/21/2022	2/23/2022, 2/28/2022
03/01/2022 all grab samples, 03/01-02/2022 all diel samples	3/4/2022, 3/9-10/2022	3/10-11/2022, 3/15/2022	3/2/2022	3/9/2022	3/7-8/2022, 3/10/2022, 3/21-24/2022	3/11/2022, 3/16/2022	3/7/2022
04/18/2022 all grab samples, 04/18-19/2022 all diel samples	4/22/2022, 4/28/2022	4/21/2022, 4/25/2022, 4/27/2022	4/19/2022	4/20-21/2022	4/28/2022, 5/2/2022, 5/5/2022, 5/9/2022	4/27-28/2022, 5/3-4/2022, 5/10/2022	4/22/2022
05/03/2022 all grab samples, 05/03-04/2022 all diel samples	5/12-13/2022, 5/16/2022, 5/18-19/2022	5/9-10/2022, 5/12/2022, 5/16/2022, 5/18/2022	5/4-5/2022	5/11/2022	5/17-20/2022, 5/23/2022	5/13/2022, 5/19/2022, 5/20/2022	5/9/2022
05/31/2022 all grab samples, 05/31/2022-06/01/2022 all diel samples	6/17/2022	6/10/2022, 6/13/2022, 6/17/2022	6/1/2022	6/6-7/2022	6/8/2022, 6/10/2022, 6/13/2022	6/6-7/2022, 6/10/2022	6/3/2022
06/28/2022 all grab samples, 07/18-19/2022 all diel samples	7/1/2022, 7/13/2022, 7/26/2022, 7/28/2022	7/7/2022, 7/18/2022, 7/25/2022, 7/27/2022, 8/1/2022	6/29/2022, 7/19-20/2022	7/6/2022, 7/22/2022, 7/25/2022	7/6/2022, 7/14-15/2022, 7/20/2022, 7/26/2022, 7/28/2022	7/7-8/2022, 7/25/2022, 7/28-29/2022	6/30/2022, 7/22/2022

08/02/2022 all grab samples, 08/02-03/2022 all diel samples	8/4/2022, 8/9/2022 8/16/2022	8/5/2022, 8/9/2022, 8/11-12/2022	8/3/2022	8/9-10/2022	8/9/2022, 8/11/2022, 8/16/2022, 8/22/2022	8/11/2022, 8/22/2022	8/5/2022
09/06/2022 all grab samples, 09/06-07/2022 all diel samples	9/14/2022, 9/16/2022, 9/19/2022	9/9/2022, 9/13-14/2022	9/7/2022	9/15/2022, 9/19/2022	9/13-16/2022	9/14-15/2022, 9/19/2022	9/9/2022
10/04/2022 all grab samples, 10/04-05/2022 all diel samples	10/12-13/2022, 10/17-18/2022	10/6-7/2022, 10/12/2022	10/5/2022	10/17/2022	10/10/2022, 10/12-13/2022	10/10/2022, 10/13/2022	10/7/2022
11/01/2022 all grab samples, 11/01-02/2022 all diel samples	11/8/2022, 11/14-16/2022	11/8/2022, 11/14-15/2022	11/2/2022	11/3/2022, 11/8/2022	11/8/2022, 11/10/2022, 11/16/2022	11/9/2022, 11/14/2022, 11/17-18/2022	11/7/2022
12/13/2022 all grab samples, 12/13-14/2022 all diel samples	12/21/2022, 1/3/2023	12/19-20/2022, 1/6/2023	12/14/2022	12/19-20/2022	12/16/2022, 12/19-20/2022, 1/4/2023	1/3/2023, 1/5/2023	12/19/2022

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