Apalachicola (APA) NERR Nutrient Metadata
April – December 2002
Latest Update: December 14, 2011

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 the bay. Similar studies have determined nitrogen and phosphorus budgets for Apalachicola Bay as well as nutrient limitations related to seasonality and riverflow. There is currently a controversy between the States of Florida, Georgia, and Alabama over the upstream diversion of water. 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 during the last six years. 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. A sampling site is located in the lower Apalachicola River as well as in the coastal area, offshore of the barrier islands. 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 is utilized each month for placement of the sampler so that temporal water quality data may be compared with the nutrient/ chlorophyll *a* data collected at this site. Other studies by the Reserve have shown the influence of tidal action and runoff on other physical parameters in the bay. The sampler is programmed to collect a sample for nutrient and chlorophyll *a* every 2.5 hours, over a 25-hour period. This captures a complete lunar-tidal cycle.

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, including a station in the Apalachicola River and the offshore coastal area (Figure 1). Weather permitting, all grab samples are collected on the same day. Due to the area covered between the stations it is not always possible to collect all the samples several hours prior to low tide. Tidal condition is recorded for each station at the time of sampling. Wind direction, speed, and cloud cover are also recorded at each station at the time of sample collection. Significant weather events, such as heavy rains occurring immediately before sampling periods, are also noted. Sampling after heavy rains is avoided if at all possible. Water temperature, salinity, and dissolved oxygen are measured at each station with a YSI 85 handheld meter. pH is also recorded with a handheld meter.

Turbidity samples are also collected for analysis back at the lab using a laboratory Turbidity Meter. Turbidity is measured in NTU's. A horizontal Van Dorn-style sampler is used to collect 2.2 liters of water from a depth of 0.5 meters at all stations not associated with a SWMP datalogger site. At the Cat Point and Dry Bar SWMP datalogger stations, water samples are collected at a depth of approximately 2 and 1.5 meters (one-half meter from the bottom) respectively, a depth equivalent to the probes of the data loggers deployed at these sites. At the East Bay datalogger station water samples are collected from surface (0.5 meters) and bottom (1.5 meters) depths, equivalent to the depths of the two dataloggers deployed at this site. 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. Duplicate samples are collected at all stations, but from different grabs. The duplicate sample is collected with a second dip of the horizontal sampler, with the sample being split between a second set of one-liter polyethylene bottles for nutrient and chlorophyll *a* analysis. Duplicate samples are collected at all monthly grab stations. Polyethylene bottles designated for nutrient samples have been previously acid washed with 3% HCl. 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 laboratory, which occurs within 36 hours of collection. The appropriate samples are filtered immediately upon arrival. Chlorophyll *a* samples are filtered within 8 hours of collection, frozen, and delivered to the laboratory within the same 36 hours as the nutrients.

b) **Diel Sampling Program**

Diel sampling is performed with an ISCO 3700 Portable Automated Sampler. The ISCO is deployed on the same day that the bay-wide grab samples are collected. The sampler is programmed to collect two samples, of one-liter 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; 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 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. The nutrient samples are delivered to the lab within 36 hours of collection for immediate filtering. The chlorophyll *a* samples are filtered 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.

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.

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 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 (Nutrient station #191 & 192) the meter probes are 0.3 m above the bottom sediment. Salinity ranges from 0 to 30 ppt and the long-term average salinity is approximately 8 ppt. At the East Bay surface site (Nutrient station #181 & 182 and ISCO deployment station #'s 240-250) 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 (approximately300 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 back 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.

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 to 3 m MHW. (The site was moved approximately 600 meters south in October 1997, from 2 to 3 meters) 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 (nutrient station #221 and 222). Salinity ranges from 0 to 32 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 end of St. George Island.

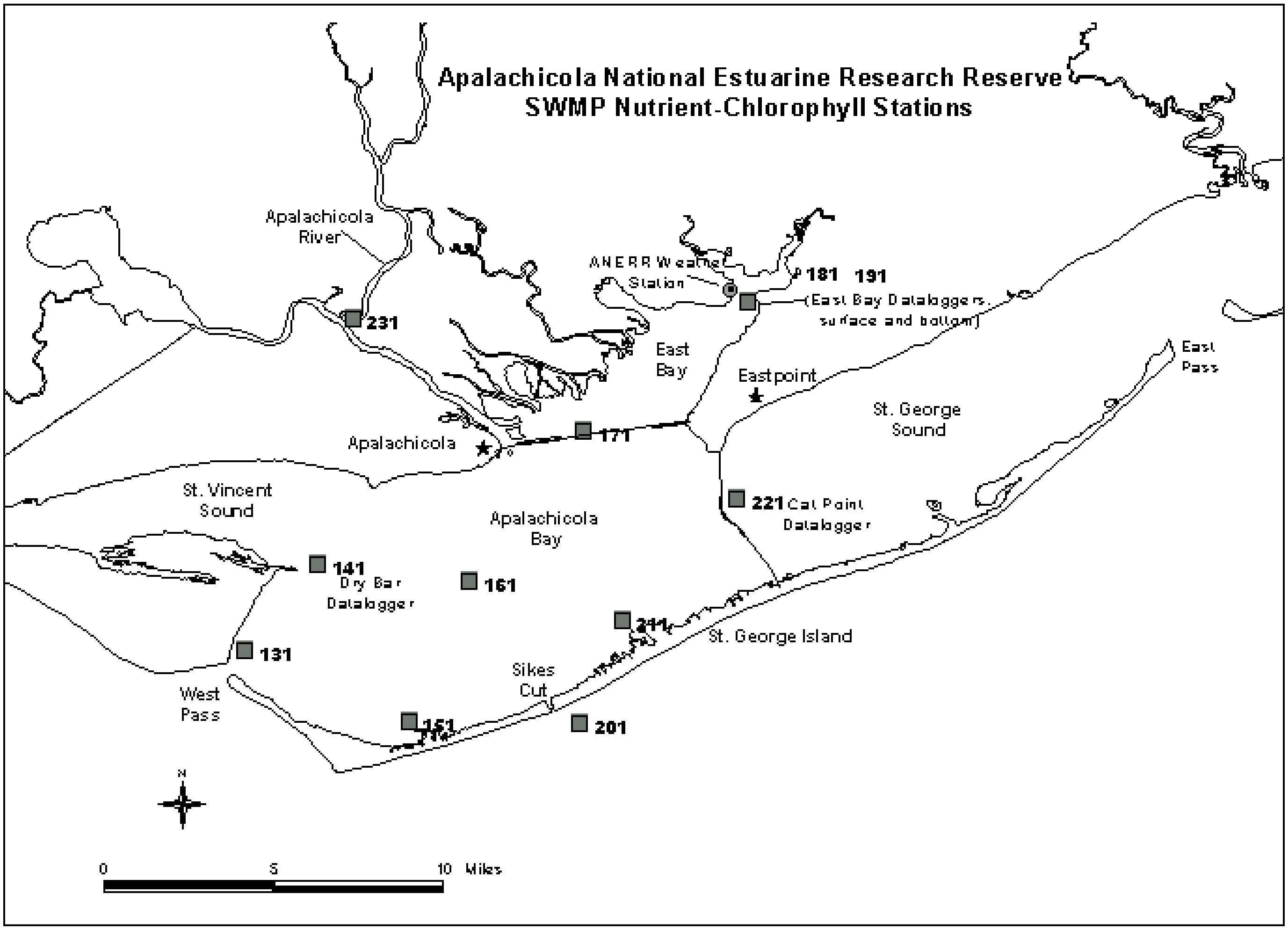
The Dry Bar datalogger and nutrient sampling site is located near St. Vincent Sound, in the western part of the Apalachicola Bay system, approximately one-half mile east of St. Vincent Island. The piling location is latitude 29° 40.48′ N and longitude 85° 3.50′ W. At the sampling site, the depth is 2 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 (nutrient station #141 & 142). The tides are mixed and range from 0.3 to 1.0 meters. Salinity ranges from 0 to 34 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 and St. Vincent National Wildlife Refuge, as well as, single family residential and commercial use in the Apalachicola area. The sampling site is influenced from the flow of the Apalachicola River and high salinity is a result of water coming through West Pass and Sikes Cut.

Information for the other 7 stations, not associated with the required sampling at the datalogger sites, as well as the datalogger sites, is included in Table 1. Duplicate samples are collected at all monthly grab stations and are denoted by a station number identical to that station except ending in the number 2 instead of 1 (ex. The duplicate sample for station #141 is labeled station #142 for laboratory analysis purposes). The 3-digit station numbers referred to in this document do not appear in the associated database. They are included in this document so that users may reference station locations to the map in Figure 1.

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

STATION NUMBER	STATION CODE	STATION NAME	LATITUDE	LONGITUDE	TIDAL RANGE AVERAGE (meters)	SALINITY RANGE	WATER DEPTH AVERAGE (meters)	BOTTOM HABITAT	DATALOGGER STATION NAME	SAMPLE DEPTH (meters)
131&132	APAWPNUT	West Pass	29 38.279	85 5.341	0.7	euryhaline	5.0	sand		0.5
141&142	APADBNUT	Dry Bar	29 40.48	85 3.50	0.7	euryhaline	1.7	oyster bar	apadbwq	1.5
151&152	APAPCNUT	Pilot's Cove	29 36.473	85 1.173	0.7	euryhaline	1.8	patchy seagrass		0.5
161&162	APAMBNUT	Mid Bay	29 40.061	84 59.641	0.7	euryhaline	2.2	sandy silt		0.5
171&172	APAEGNUT	East Bay Bridge	29 43.848	84 56.711	0.7	oligohaline	1.6	silty clay		0.5
181&182	APAESNUT	East Bay Surface	29 47.15	84 52.52	0.7	oligohaline	1.7	clayey sand	apaeswq	0.5
191&192	APAEBNUT	East Bay Bottom	29 47.15	84 52.52	0.7	oligohaline	1.7	clayey sand	apaebwq	1.5
201&202	APASCNUT	Sikes Cut Offshore	29 36.401	84 56.799	0.7	marine	>5.0	sand		0.5
211&212	APANHNUT	Nick's Hole	29 39.022	84 55.732	0.7	euryhaline	1.0	patchy seagrass		0.5
221&222	APACPNUT	Cat Point	29 42.12	84 52.81	0.7	euryhaline	1.8	oyster bar	apacpwq	2.0
231&232	APARVNUT	River	29 46.743	85 2.606	0.7	oligohaline	NA	sandy silt		0.5
240	Station Number 240 through 250 are Diel samples collected 2.5 hours apart at the East Bay Surface datalogger site, APAESNUT, with the ISCO automated water sampler. No duplicate samples are taken, however there is some overlap with monthly grabs collected at the same station at deployment of the ISCO sampler.									
241										
242										
243										
244										
245										
246										
247										
248										
249										
250										

Figure 1. Station locations.



5) **Code variable definitions**

Station code names:
West Pass (apawpnut), Dry Bar (apadbnut), Pilots Cove (apapcnut), MidBay (apambnut), East Bay Bridge (apaegnut), East Bay Surface (apaesnut), East Bay Bottom (apaebnut), Sikes Cut (apascnut), Nicks Hole (apanhnut), Cat Point (apacpnut), Apalachicola River (aparvnut).

Monitoring Programs:
Monthly grab samples (1), Diel grab sampling (2).

6) **Data collection period**

a) Grab Sampling (Monitoring program 1)

apawpnut (West Pass)

Site	Start Date	Start Time	End Date	End Time
WP	4/2/2002	13:40	4/2/2002	13:40
WP	4/30/2002	12:47	4/30/2002	12:47
WP	6/4/2002	12:35	6/4/2002	12:35
WP	7/2/2002	11:20	7/2/2002	11:25
WP	8/6/2002	13:46	8/6/2002	13:46
WP	9/10/2002	13:04	9/10/2002	13:04
WP	10/8/2002	10:32	10/8/2002	10:35
WP	11/4/2002	11:20	11/4/2002	11:25
WP	12/2/2002	13:45	12/2/2002	13:47

apadbnut (Dry Bar)

Site	Start Date	Start Time	End Date	End Time
DB	4/2/2002	13:58	4/2/2002	13:58
DB	4/30/2002	13:04	4/30/2002	13:04
DB	6/4/2002	12:50	6/4/2002	12:50
DB	7/2/2002	11:40	7/2/2002	11:42
DB	8/6/2002	14:04	8/6/2002	14:04
DB	9/10/2002	13:25	9/10/2002	13:25
DB	10/8/2002	10:58	10/8/2002	11:00
DB	11/4/2002	11:35	11/4/2002	11:37
DB	12/2/2002	14:10	12/2/2002	14:11

apapcnut (Pilots Cove)

Site	Start Date	Start Time	End Date	End Time
PC	4/2/2002	13:22	4/2/2002	13:25
PC	4/30/2002	12:28	4/30/2002	12:28
PC	6/4/2002	12:12	6/4/2002	12:12
PC	7/2/2002	11:04	7/2/2002	11:06
PC	8/6/2002	13:11	8/6/2002	13:11
PC	9/10/2002	12:35	9/10/2002	12:35
PC	10/8/2002	10:06	10/8/2002	10:08
PC	11/4/2002	10:59	11/4/2002	11:00
PC	12/2/2002	13:10	12/2/2002	13:12

apambnut (Mid Bay)

Site	Start Date	Start Time	End Date	End Time
MB	4/2/2002	14:12	4/2/2002	14:12
MB	4/30/2002	13:20	4/30/2002	13:20
MB	6/4/2002	13:08	6/4/2002	13:08
MB	7/2/2002	11:55	7/2/2002	11:57
MB	8/6/2002	14:22	8/6/2002	14:22
MB	9/10/2002	12:15	9/10/2002	12:15
MB	10/8/2002	11:16	10/8/2002	11:18
MB	11/4/2002	11:50	11/4/2002	11:52
MB	12/2/2002	14:30	12/2/2002	14:31

apaegnut (East Bay Bridge)

Site	Start Date	Start Time	End Date	End Time

EG	4/2/2002	15:03	4/2/2002	15:07
EG	4/30/2002	9:30	4/30/2002	9:30
EG	6/4/2002	10:40	6/4/2002	10:40
EG	7/2/2002	13:27	7/2/2002	13:29
EG	8/6/2002	11:55	8/6/2002	11:55
EG	9/10/2002	10:15	9/10/2002	10:15
EG	10/8/2002	8:31	10/8/2002	8:33
EG	11/4/2002	12:57	11/4/2002	12:59
EG	12/2/2002	11:45	12/2/2002	11:46

apaesnut (East Bay Surface)

Site	Start Date	Start Time	End Date	End Time
ES	4/2/2002	11:10	4/2/2002	11:11
ES	4/30/2002	9:55	4/30/2002	9:55
ES	6/4/2002	9:35	6/4/2002	9:35
ES	7/2/2002	13:53	7/2/2002	13:55
ES	8/6/2002	10:24	8/6/2002	10:24
ES	9/10/2002	10:37	9/10/2002	10:37
ES	10/8/2002	13:30	10/8/2002	13:30
ES	11/4/2002	9:35	11/4/2002	9:35
ES	12/2/2002	11:15	12/2/2002	11:16

apaebnut (East Bay Bottom)

Site	Start Date	Start Time	End Date	End Time
EB	4/2/2002	11:12	4/2/2002	11:14
EB	4/30/2002	9:55	4/30/2002	9:55
EB	6/4/2002	9:35	6/4/2002	9:35
EB	7/2/2002	13:58	7/2/2002	14:00
EB	8/6/2002	10:26	8/6/2002	10:26
EB	9/10/2002	10:39	9/10/2002	10:39
EB	10/8/2002	13:30	10/8/2002	13:30
EB	11/4/2002	9:40	11/4/2002	9:40
EB	12/2/2002	11:17	12/2/2002	11:18

apascnut (Sikes Cut Offshore)

Site	Start Date	Start Time	End Date	End Time
SC	4/2/2002	13:01	4/2/2002	13:05
SC	4/30/2002	11:49	4/30/2002	11:49
SC	6/4/2002	11:50	6/4/2002	11:50
SC	7/2/2002	10:36	7/2/2002	10:38
SC	8/6/2002	12:53	8/6/2002	12:53
SC	9/10/2002	9:39	9/10/2002	9:39
SC	10/8/2002	9:42	10/8/2002	9:44
SC	11/4/2002	10:45	11/4/2002	10:47
SC	12/2/2002	12:50	12/2/2002	12:53

apanhnut (Nicks Hole)

Site	Start Date	Start Time	End Date	End Time
NH	4/2/2002	12:50	4/2/2002	12:52

NH	4/30/2002	11:32	4/30/2002	11:32
NH	6/4/2002	11:30	6/4/2002	11:30
NH	7/2/2002	10:17	7/2/2002	10:19
NH	8/6/2002	12:40	8/6/2002	12:40
NH	9/10/2002	9:16	9/10/2002	9:16
NH	10/8/2002	9:18	10/8/2002	9:20
NH	11/4/2002	10:30	11/4/2002	10:30
NH	12/2/2002	12:32	12/2/2002	12:33

apacpnut (Cat Point)

Site	Start Date	Start Time	End Date	End Time
CP	4/2/2002	11:55	4/2/2002	11:56
CP	4/30/2002	11:15	4/30/2002	11:15
CP	6/4/2002	11:03	6/4/2002	11:03
CP	7/2/2002	9:53	7/2/2002	9:55
CP	8/6/2002	12:13	8/6/2002	12:13
CP	9/10/2002	9:00	9/10/2002	9:00
CP	10/8/2002	8:55	10/8/2002	8:57
CP	11/4/2002	10:05	11/4/2002	10:06
CP	12/2/2002	12:10	12/2/2002	12:11

aparvnut (River)

Site	Start Date	Start Time	End Date	End Time
RV	4/2/2002	14:40	4/2/2002	14:40
RV	4/30/2002	14:10	4/30/2002	14:10
RV	6/4/2002	13:44	6/4/2002	13:44
RV	7/2/2002	12:50	7/2/2002	12:52
RV	8/6/2002	14:55	8/6/2002	14:55
RV	9/10/2002	14:10	9/10/2002	14:10
RV	10/8/2002	12:10	10/8/2002	12:12
RV	11/4/2002	12:35	11/4/2002	12:37
RV	12/2/2002	15:05	12/2/2002	15:07

b) Diel Sampling (Monitoring program 2)

apaesnut (East Bay Surface)

Site	Start Date	Start Time	End Date	End Time
ES	4/8/2002	9:10	4/9/2002	10:10
ES	4/29/2002	9:00	4/30/2002	10:00
ES	6/3/2002	9:00	6/4/2002	10:00
ES	7/1/2002	10:00	7/2/2002	11:00
ES	8/5/2002	9:30	8/6/2002	10:30
ES	9/9/2002	9:30	9/10/2002	10:30
ES	10/7/2002	10:00	10/8/2002	11:00
ES	11/4/2002	9:30	11/5/2002	10:30
ES	12/2/2002	11:30	12/3/2002	12:30

Note: Time is coded based on a 2400 hour clock and is referenced to Eastern Standard Time (EST).

7) Associated researchers and projects

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

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

Northwest Florida Water Management District
Tate's Hell Restoration Project
Apalachicola Bay Freshwater Needs Study

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."

Donnato Surratt
Florida Agricultural and Mechanical University
Environmental Sciences Institute
"Historic trophic status and present trophic status for the Apalachicola Bay compared and contrasted."

Edmiston,HL., Wanat, J., Levi, L., Miller, K., Stewart, J. /Apalachicola
National Estuarine Research Reserve.
Distribution and density of fishes and benthic invertebrates in Apalachicola Bay.

Edmiston,HL., Stewart, J., Miller, K., Wanat, J., Levi, L.
Apalachicola National Estuarine Research Reserve
System Wide Monitoring Program
Long-Term Water Quality Monitoring

Edmiston,HL., Wanat, J., Levi, L., Miller, K., Stewart, J.
Apalachicola National Estuarine Research Reserve
System Wide Monitoring Program
Long-Term Meteorological Monitoring

Edmiston,HL., Miller, K., Wanat, J., Levi, L., Stewart, J.
Apalachicola National Estuarine Research Reserve
Submerged Aquatic Vegetation 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 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, Microsoft Excel spreadsheet format, and comma-delimited format.

II. Physical Structure Descriptors

9) Entry verification

A hardcopy of the original 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. The Excel data file is then electronically transmitted to ANERR. ANERR staff review the data file for completeness, MDL flags, and other possible anomalies. Missing data are verified by review of field logs and are denoted by a blank space in the database. Values below the method detection limit (MDL) are replaced with the MDL value and flagged with a "B". Affected calculated values are flagged with a "B"' as well. ANERR staff then formatted the file in Excel to meet the CDMO standards. After review by ANERR staff the data are electronically transmitted to the CDMO. Research Coordinator Lee Edmiston and Environmental Specialist Lauren Levi are responsible for these tasks.

10) Parameter Titles and Variable Names by Data Category

Data Category	Parameter	Variable Name	Units of Measure
i) Phosphorus:			
	Orthophosphate, filtered	PO4F	mg/L as P
ii) Nitrogen:			
	Nitrite + Nitrate, filtered	NO23F	mg/L as N
	Nitrite, filtered	NO2F	mg/L as N
	Nitrate	NO3F	mg/L as N
	Ammonium, filtered	NH4F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
iii) Other Lab Parameters:			
	Chlorophyll *a*	CHLA_N	µg/L
iv) Field Parameters:			
None			

11) Measured and Calculated Laboratory Parameters

Variables Measured Directly

Nitrogen species:	NO2F, NO23F, NH4F
Phosphorus species:	PO4F
Other:	CHLA_N

Computed Variables

NO3F:	NO23F-NO2F
DIN:	NO23F+NH4F

12) Limits of Detection

Analytical detection limits were established by replicate analysis of a low sample or blank, and are reported as 3SD. This evaluation was conducted monthly over the last 7 months of the project period (April 2002-March 2003). The analytical detection limits for each analyte are reported in Table 2.

Table 2. Analytical Detection Limits

Parameter	Variable	MDL	Dates in use
Ammonium	NH4F	0.004 mg-N/L	2002
Nitrite	NO2F	0.002 mg-N/L	2002
Nitrate-Nitrite	NO23F	0.007 mg-N/L	2002
Orthophosphate	PO4F	0.001 mg-P/L	2002
Chlorophyll a	CHLA_N	0.5 µg/L	2002

13) Laboratory Methods

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 ddH$_2$O, store in brown glass @ 5C

Solution #2. 18.5 g sodium hydroxide and 100 g sodium citrate diluted to 1 L ddH$_2$O, 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:

$(NH_4)_2SO_4$ MW = 132.14

1.5 mM NH_4 = 0.75 mM $(NH_4)_2SO_4$
0.75mM x 1M/1000mM x 132.14/1 mole = 0.0991 g/L
Standards: (in mg/L), 0.0, 0.0028, 0.0056, 0.0140, 0.0280, 0.2800

Preservation Method: Nutrient samples are collected monthly via Van Dorn bottle grabs and placed into 1L bottles on ice until transport to the FSU Department of Oceanography Laboratory in Tallahassee, Florida (within 36 hours). 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).

ii) **Parameter: PO4F**

Method Reference: Adapted from EPA standard method
Method Descriptor:
Solutions:
Solution #3. 78 mL conc. H_2SO_4 diluted up to 500 mL ddH_2O
Solution #6. 7.5 g $(NH_4)_6Mo_7O_{24}*H_2O$ dissolved in 250 mL ddH_2O (store in dark in plastic, stable, discard is see precipitate).
Solution #7. 5.4 g $C_6H_8O_6$ (Ascorbic Acid) dissolved in 100 mL ddH_2O (make new weekly, store in refrigerator, can also be aliquoted out and stored in freezer)
Solution #8. 0.34 g $K(SbO)C_4H_4O_6 *_{1/2}H_2O$ dissolved in 250 mL ddH_2O (store in refrigerator).
Solution #9. Mixed Reagent.. 25 mL #6, 62.5 mL #3, 25 mL #7, 12.5 mL #8. Solution should be light yellow, makes 125 mL. Stable < 6 hours.
Procedure:
For 10 mL samples.

a. Allow samples to come to room temperature
b. Add 2.0 mL S #9 to one tube of each pair
c. Wait 30 minutes
d. Read absorbance @ 880 nm.

Samples should be run in pairs, one set for color development and the other as a turbidity blank I(no mixed reagent added). The concentration is determined by subtracting the blank from the sample and multiplying by the slope of the standard curve.
Standard:
136.09 g/L = 1 M, 1.3609 g/L = 10 mM KH2PO4
Standards: (in mg/L), 0.000, 0.0015, 0.00375, 0.0075, 0.0150

Preservation Method: Nutrient samples are collected monthly via Van Dorn bottle grabs and placed into 1L bottles on ice until transport to the FSU Department of Oceanography Laboratory in Tallahassee, Florida (within 36 hours). 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).

iii) **Parameter: CHLA_N**

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

A 1 L sample is filtered using a Gelman AE 1 micron 47mm filter, 1 mL of magnesium carbonate solution (1 g per 100 mL ddH_2O) is added during final few hundred mL of filtering, desiccate the filter well under suction. The filter is stored on ice until analysis.
The filter is placed in a 15 mL centrifuge tube, and 12 mL of 90% acetone is added, the tube is sealed and shaken vigorously until the filter is disintegrated.
The tubes are placed into a refrigerator in the dark for about 20 hours, shaking them once more at 1 or 2 hours. Remove the tubes and place at room temperature in the dark. Add 90% acetone to fill up to exactly 12 mL. Centrifuge 10 minutes @ 3000-4000 rpm.
Decant the supernatant into a 10 cm path length cell (multiply the extinction values by 1.2 to normalize to values expected from 10 mL extract).
Immediately read absorbance @ 750nm and @ 664nm, then acidify with 100 ul of 1.2M HCl, wait a few minutes 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 L/g/cm x (664 before – 664 acid) x 12 mL (extract volume) / Volume filtered (L) x 8.5cm (cuvette length) = ug/L
Equation 664 = 664 nm measurement minus 750 nm
For Apalachicola Bay, chl a ~0.1 to 10 ug/L
Spec measurements should be ~ 0.02 to 0.20, with after acid numbers ~ 50-75% less then before acidification
mg pigment/m3 = C/V
C obtained from following equations
V is volume filtered

Preservation Method: Chlorophyll a samples are collected monthly via Van Dorn bottle grabs and placed into 1L bottles on ice until transport to ANERR laboratory (2-4 hours). 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.

iv) **Parameter: NO2F**

Method Descriptor:

Solutions:

Standard Nitrite Solution, Primary Standard: 5 mM = 0.345 g Anhydrous analytical reagent grade Sodium Nitrite in 1000 mL of nano H_2O
Sulphanilamide solution: 5 g Sulphanilamide in a mixture of 50 mL concentrated HCl and approximately 300 mL nano H_2O. Dilute up to 500 mL with nano H_2O
-N-(1-Naphthyl)-Ethylenediamine dihydrochloride solution: 0.50 g Dihydrochloride in 500 mL nano H_2O. Store in a dark brown bottle. Renew Monthly.
On day of analysis:
Secondary Nitrite standard: 5 mL of primary into 500 mL nano H_2O
Working standards: 0.50 umol: 0.5 mL secondary into 500 mL nano H_2O
1.0 umol: 1.0 mL secondary into 500 mL nano H_2O
Procedure:
Label Erlenmeyer flasks: 4 flasks – BLK; 3 flasks – 0.5; 3 flasks – 1.0
Pour 25 mL nano H_2O into the 4 BLK flasks
Pour 25 mL 0.5 umol std into 0.5 labelled, 50 mL 1.0 umol into 1.0 labelled flasks
Add 0.5 mL sulphanilamide solution to each flask, swirl, allow 2-8 minutes to react
Add 0.5 mL dihydrochloride solution to each flask, swirl, wait at least 10 minutes

Read the Blanks and standards @ 543 nm (in 10 cm cell)
If readings give good std curve, prepare and run samples, if not, prepare new stds.
Analysis of Samples:
25 mL each sample into properly labeled flask
Add 0.5 mL sulphanilamide, swirl, 2-8 minutes
Add 0.5 mL dihydrochloride, swirl quickly, at least 10 minutes
Read Absorbance @ 543 nm
Stds: (in mg/L), 0.00, 0.00079, 0.00158, 0.00316, 0.00790

Preservation Method: Nutrient samples are collected monthly via Van Dorn bottle grabs and placed into 1L bottles on ice until transport to the FSU Department of Oceanography Laboratory in Tallahassee, Florida (within 36 hours). 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).

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, Oxygen, Air, Nitrogen
Isoproponyl in dry ice
2 M NaOH in ice
Reducing Reagent: 0.1 M Vanadium Sulfate = 8.15 g $VoSO_4 * nH_2O$ (FW = 163) in 500 mL of 2.0 M HCl.
Preparation: 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 10 minutes until Marine Blue color.
The Vanadium(III) is stable for several months.
Apparatus:
Check all flow rates and connections as in Figure 1 before turning power on.
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 of the analyzer.
Ave. times include: 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 to 300 sec in mult.of 10.
To enter the averaging time of 5 sec., set the thumbwheel to 0050 and press Ent.
Push the Man. (manual) button twice to be in NO_x mode.
Procedure: Nitrites are reduced at room temp to NO in Vo(III).
100 ul Samples are added to the reducing solution via syringe and degassed until all is removed.

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.

Preservation Method: Nutrient samples are collected monthly via Van Dorn bottle grabs and placed into 1L bottles on ice until transport to the FSU Department of Oceanography Laboratory in Tallahassee, Florida (within 36 hours). 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).

14) Reporting of Missing Data, Data with Concentrations Lower than Method Detection Limits

Nutrient/Chla comment codes and definitions are provided in the following table. Missing data are denoted by a blank cell “ ” and commented coded with an “M”. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDL’s for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 14) of this document. Measured concentrations that are less than this limit are replaced with the minimum detection limit value and comment coded with a “B” in the variable code comment column. For example, the measured concentration of NO23F was 0.0005 mg/L as N (MDL=0.0008), the reported value would be 0.0008 with a “B” placed in the NO23F comment code column. Calculated parameters are comment coded with a “C” and if any of the components used in the calculation are below the MDL, the calculated value is removed and also comment coded with a “B”. If a calculated value is negative, the value is removed and comment coded with an “N”.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2002-2006 were also coded with a B, but replaced with -9999 place holders. Any 2002-2006 nutrient/pigment data downloaded from the CDMO prior to December November of 2011 will contain -9999s representing below MDL concentrations.

Comment Code	Definition
A	Value above upper limit of method detection
B	Value below method detection limit
C	Calculated value
D	Data deleted or calculated value could not be determined due to deleted data, see metadata for details
H	Sample held beyond specified holding time
K	Check metadata for further details
M	Data missing, sample never collected or calculated value could not be determined due to missing data
P	Significant precipitation (reserve defined, see metadata for further details)
U	Lab analysis from unpreserved sample
S	Data suspect, see metadata for further details

b) **Occurrences of code "K"**
The following anomaly occurred during deployment of the automated ISCO sampler at the East Bay station 181/191 (apaesnut, monitoring program 2)**.**

4/9/2002 apaesnut Rep 1 Time 0900 This sample was preserved with sulfuric acid at the time of collection.

c) Occurrences of code "M"
The following anomalies occurred during deployment of the automated ISCO sampler at the East Bay station 181/191 (apaesnut, monitoring program 2).

4/9/2002 apaesnut Rep 1 Time 1010 No sample was collected because the deployment period of this instrument was ended early due to approaching severe weather.
4/29/2002 apaesnut Rep 1 Time 0000 No sample was collected due to the strainer being out of the water during extreme low tide.
4/30/2002 apaesnut Rep 1 Time 0230 No sample was collected due to the strainer being out of the water during extreme low tide.
7/2/2002 apaesnut Rep 1 Time 0330 No sample was collected due to the strainer being out of the water during extreme low tide.

15) QA/QC Programs

a) Precision

i) Field Variability – Field replicate samples are collected from a successive grab sample. Replicate samples were collected from each grab sampling station (monitoring program 1) during the first year to assess the sampling and analytical reproducibility. Field replicate samples comprise 33% of the total field samples (monitoring program 1 + monitoring program 2) collected, including diel samples (monitoring program 2). There were no field replicates collected during diel sampling. The results for replicate samples are shown in Figure 2, where the analysis of each duplicate pair is plotted on a 1:1 plot. Perfect sampling and analytical replication would result in values falling exactly on the 1:1 line. As the sample concentrations approach the analytical detection limit, one expects to see more divergence from the 1:1 line. While the replicate agreement is extremely good for most samples, we observed deviations among the replicate samples that exceeded our analytical precision. Additional sources of variance include: true environmental variance, sample bottle cleanliness (and field rinsing), and low-level contamination during filtration. The samples we have collected thus far do not permit an evaluation of these other sources of variance; although we believe that natural phytoplankton patchiness may be responsible for the replicate variability at high chlorophyll-a concentrations.
ii) Laboratory Variability – No laboratory duplicate sampling was performed in 2002.
iii) Inter-organizational splits – No split sampling was performed in 2002.

b) Accuracy

i) Sample Spikes – not performed in 2002
ii) Standard Reference Material Analysis -
Accuracy was determined by analysis of external nutrient QA/QC samples. In 2002, the FSU laboratory participated in the NRC/CNRC NOAA/NRC Second Intercomparison for Nutrients in Seawater project. Two "unknown" samples were provided, which were analyzed in duplicate for nitrate, nitrate+nitrite, nitrite, and Soluble Reactive Phosphorus (SRP). The results are reported in Table 3. In general, analyses were within 1SD of the mean values reported for the intercomparison project. FSU Oceanography Laboratory will continue to participate in these intercalibration exercises when they are offered.

Table 3. Laboratory Intercomparison

	Analytical accuracy determined in the 2002 NOAA/NRC Second Intercomparison for Nutrients in Seawater			
	MOOS-1		NOAA/NRC Test	
	Reported	Detected	Reported	Detected
Soluble Reactive Phosphorus (SRP; mg-P/L)	0.050 ± 0.007	0.055 0.056	0.029 ± 0.006	0.034 0.033
Nitrate+Nitrite (mg-N/L)	0.337 ± 0.024	0.360 0.367	0.214 ± 0.020	0.234 0.235
Nitrite (mg-N/L)	0.043 ± 0.003	0.046 0.046	0.027 ± 0.003	0.031 0.031

iii) Cross Calibration Exercises – none performed in 2002

16) Other Remarks

Locally significant rain events in excess of 50 mm during a 24 hour period occurred on the following dates:
3/2/2002
6/23/2002
8/31/2002
9/14/2002 (Tropical Storm Hannah in the Gulf of Mexico)
9/24/2002
However, they were not within 3 days prior to nutrient sampling periods.

Apalachicola NERRS Nutrient Project
Replicate Analyses: 2002-2003

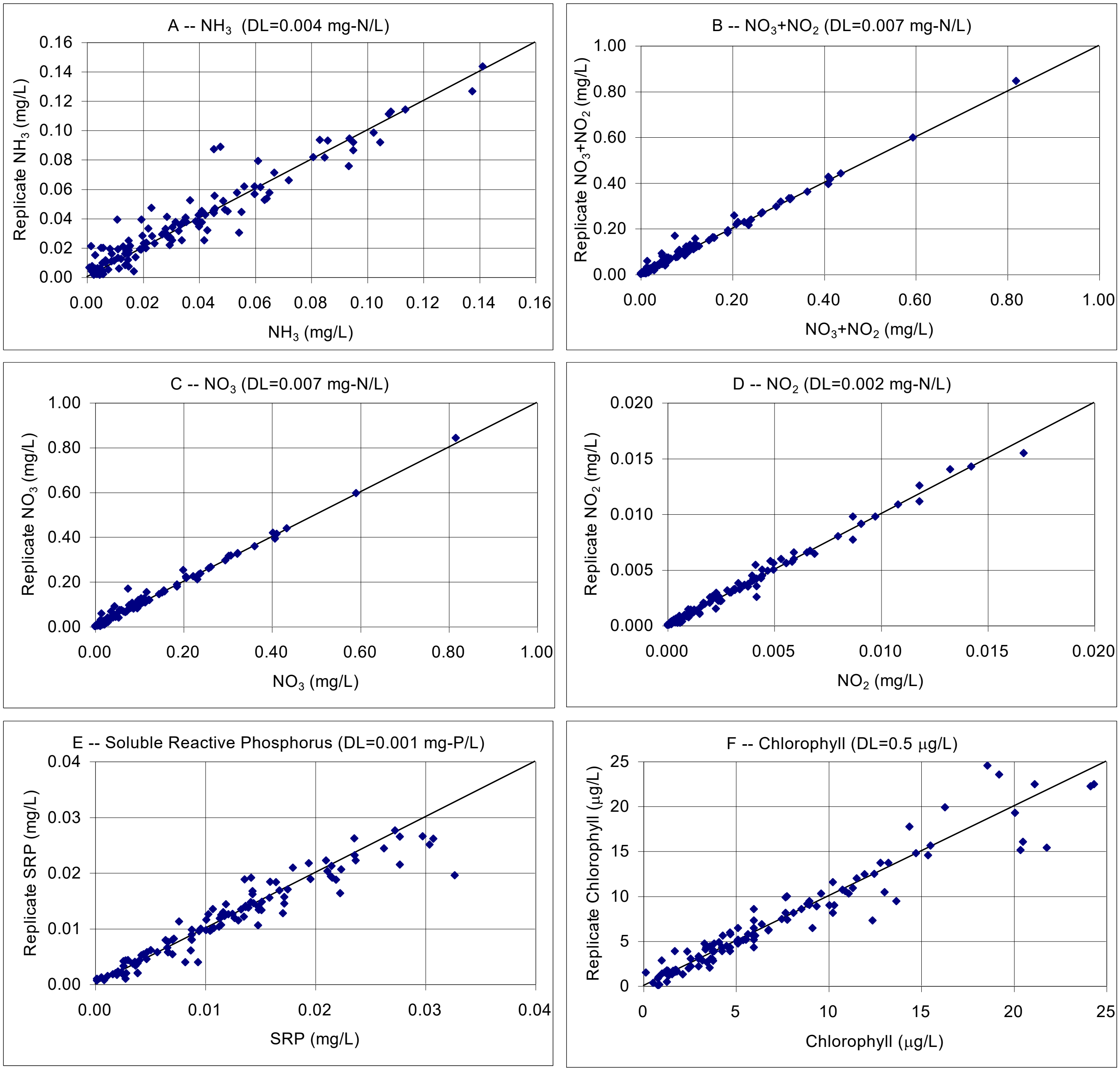


Figure 1. Analysis of duplicate samples collected during the 2002-2003 sampling period. The lines represent 1:1 (perfect) agreement. As expected, the scatter from the 1:1 line increases when the in-situ concentrations approach the analytical detection limits. For Chlorophyll-a, the scatter increases at very high concentrations due to natural phytoplankton patchiness. Detection Limits are reported for each analyte on a 3SD basis.