

Chesapeake Bay National Estuarine Research Reserve in Virginia (CBV)
January-December, 2009
Latest Update: March 18, 2014

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons

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2) Research objectives

a) Monthly Grab Sampling Program

Monthly grab samples are collected to quantify the spatial and temporal variability of selected nutrients and plant pigments in the water column along a salinity gradient within the York River estuary system. The Chesapeake Bay, Virginia National Estuarine Research Reserve (CBV NERR) began collecting monthly grab samples on January 16, 2002.

b) Diel Sampling Program

On a monthly basis, samples are collected at Taskinas Creek, a small tributary of the York River, every two and one-half hours throughout a complete tidal cycle in order to quantify the short-term temporal variability of selected nutrients and plant pigments in the water column.

3) Research methods

a) Monthly Grab Sampling Program

Monthly grab samples were taken at six stations within the York River estuary. Samples were taken at the four principal CBNERRVA datasonde stations (Goodwin Islands, Clay Bank, Taskinas Creek and Sweet Hall Marsh and two other stations which were the York River Bridge, located at Gloucester Point, and Catlett Islands. All grab samples were taken on the same day between +3 hrs before or after slack low-water. No distinction was made between neap and spring tide conditions. Efforts were made to allow for an antecedent dry period of 72 hours prior to sampling. Replicate (N=2) samples were collected by hand at an approximate depth of 10 cm. At the time of sample collection, water temperature, salinity and dissolved oxygen was measured with a YSI Model 600 XL meter. All samples were collected in amber, wide-mouth, nalgene sample bottles that were previously acid washed (10% HCl), rinsed (3x) with distilled deionized water, dried and followed by rinsing (3x) of ambient water prior to collection of the sample. Samples were immediately placed on ice, in the dark and returned to the laboratory. Once in the laboratory, samples were shaken and processed for nutrient and plant pigment analysis.

b) Diel Sampling Program

Diel grab samples were taken at the Taskinas Creek long-term datasonde station. Eleven samples were collected over a lunar day (24hr:48min) time period at 2.5 hour intervals using an ISCO auto-sampler. Collection of samples began at predicted slack low water. Samples were collected at a fixed depth (0.25m) from the bottom which reflected the water mass sampled by the datasonde. No distinction was made between neap and spring tide conditions. Efforts were made to allow for an antecedent dry period of 72 hours prior to sampling. Samples were collected in 1000 ml bottles that were previously acid washed (10% HCl), rinsed (3x) with distilled-deionized water and dried. Prior to sample collection, the ISCO sampler including all sample tubing was rinsed with ambient water. Samples were collected and stored inside a ISCO sampler that contained ice. Once in the laboratory, samples were shaken and processed for nutrient and plant pigments.

4) Site location and character

- a) **Goodwin Islands** (station was moved slightly on 3/25/2009 to **Lat 37.215796, Long -76.392675**; previous location was Lat 37.21739, Long -76.3954)

The Goodwin Islands component of CBNERRVA is located on the southern side of the mouth of the York River. The station is located approximately 400 meters from shore, with an average water depth on the order of 1 meter. MHW depth at the sample location is approximately 1.70 meters. Goodwin Islands are a 315 ha (777 acre) archipelago of salt-marsh islands surrounded by inter-tidal flats and extensive beds of submerged aquatic vegetation dominated by eelgrass (*Zostera marina*) and Widgeon grass (*Ruppia maritima*). Water circulation patterns around the island are influenced by York River discharge and wind patterns of the Chesapeake Bay. Tides at the Goodwin Islands are semi-diurnal and display an average range of 0.7 m (range: 0.4 - 1.1 m). Mean seasonal water temperature values ranged from 13.7-15.6 °C for spring (March-May), 25.7-27.2 °C for summer (June-August), 18.0-19.2 °C for fall (September-November), and 4.7-8.2 °C for winter (January-February, and December). Mean seasonal salinity values ranged from 13.9-23.0 psu for spring, 17.2-23.0 psu for summer, 16.5-24.0 for fall, and 15.9-23.3 psu for winter. Summary water quality statistics were derived from 15-minute interval data for the years 1998-2004. The data logger probes are located 0.5 m above the sandy substrate bottom. Potential activities that could impact the site included, light recreational and commercial boating activity.

- b) **York River Bridge (Lat 37.24489, Long 76.50522)**

The York River Bridge station is located in the mid-channel approximately 9 km from the mouth of the York River estuary between Gloucester Point and Yorktown, Virginia. The sampling station is located within the polyhaline region with a mean depth of 21 meters and a tidal range of 0.75 meters. Mean salinity at this site is 17.4 ppt and the salinity range is 8.2 to 25.1 ppt (taken from the 2002-2005 monthly nutrient data). Depth at the sample location ranges from 13.7 to 22.9 meters. The bottom type is a mixture of sand and fine sediments and there are no known pollutants.

- c) **Catlett Islands (Lat 37.30000, Long 76.55000)**

The Catlett Islands are located approximately 20 km from the mouth and on the North side of the York River in Gloucester County, Virginia. Timberneck Creek flows into the York River on the eastern side of the Catlett Islands and Cedarbush Creek enters the river on the western side. Poplar Creek bisects the two large areas of the Catlett Islands. Catlett Islands encompass 280 ha (690 acres) and displays a ridge-and-swale geomorphology. The islands consist of multiple parallel ridges of forested wetland hammocks, forested upland hammocks, emergent wetlands and tidal creeks surrounded by shallow subtidal areas that once supported beds of submerged aquatic vegetation. Water quality ranges listed here are based on weekly volunteer citizen water quality monitoring has been ongoing since the incorporation of the site in 1990. Surface water temperatures range from 5.4 °C to 27.4 °C. Salinity is indicative of mesohaline conditions, ranging from 14-18 ppt in the fall to 8.2-12 ppt in the spring. Dissolved oxygen concentration ranges from 4.2 to 14.0 mg/L. Tidal range is on the order of 0.75 meters and depth at the sample location is from 1.0 to 1.5 meters. The bottom type is a mixture of sand and fine sediments and there are no known pollutants.

- d) **Claybank** (station was moved slightly on 3/25/2009 to **Lat 37.346665, Long -76.611263**; previous location was Lat 37.34855, Long 76.61123)

The Claybank station is located within a shallow (<2m) littoral area approximately 300-400 meters wide along the mesohaline portion of the York River estuary. The site is approximately 26 km upriver from the mouth of the estuary. The shoreline consists of a narrow fringe of salt marsh with some areas armored with bulkhead or stone. Tidal range is on the order of 0.85 meters and depth at MHW is approximately

2.25 meters. This station is located along the north shoreline of the estuary in an area that historically (prior to 1972) supported submersed aquatic vegetation. The sampling station is influenced by a secondary turbidity maximum that moves back and forth in a region of about 20-40 km from the mouth of the York River estuary. Substrate within the region varies from fine sediments to sand. The site is exposed to strong winds from the northwest and re-suspension of sediment during storm events can be high. There is no fresh water input at this site. Seasonal water quality conditions described here are from 2001 through 2003 (Spring: March-May; Summer: June-August; Fall: September-November; Winter: December-February). Mean seasonal water temperature ranged between 14.0-16.2 for spring, 26.1-27.7 for summer, 17.5-19.4 for fall, and 4.9-8.0 °C in winter. Mean seasonal salinity ranged between 15.7-20.3 for spring, 16.5-21.3 for summer, 13.2-21.6 for fall, and 14.3-20.0 ppt in winter. Potential activities that could impact the site include, light recreational and commercial boating activity.

e) Taskinas Creek (Station was rebuilt on 5/19/2009 and moved to **Lat 37.414986, Long -76.71442**; previous location was Lat 37.41497, Long 76.71441)

Taskinas Creek Reserve, component of CBNERRVA, encompasses 397 ha (980 acres) and is located within the boundaries of York River State Park near the town of Croaker, Virginia. The small sub-estuary of the York River is located on the southern side of the river, approximately 37 km up river from the mouth of the York River. The Taskinas Creek watershed is representative of an inner coastal plain, rural watershed within the southern Chesapeake Bay system. The watershed is dominated by forested and agricultural land uses with an increasing residential land use component. The non-tidal portion of Taskinas Creek contains feeder streams that drain oak-hickory forests, maple-gum-ash swamps and freshwater marshes. Freshwater mixed wetlands are found in the upstream reaches of Taskinas Creek. The creek is roughly 2 meters deep and 20 meters wide towards the lower end of the creek where substrate is dominated by fine sediment. MHW depth at the sample location is approximately 2.0 meters and mean tide range is 0.85 meters. Mean seasonal water temperature values ranged from 15.2-19.0 °C for spring, 26.8-28.2 °C for summer, 15.7-18.3 °C for fall, and 3.6-9.0 °C for winter. Located within the meso-polyhaline region of the York River estuary, mean seasonal salinity values ranged from 4.0-14.0 psu for spring, 7.0-18.2 psu for summer, 6.9-17.0 for fall, and 5.8-15.3 psu for winter. Summary water quality statistics were derived from 15-minute interval data for the years 1998-2004. Potential activities that could impact the site include residential development, selective hardwood logging, and light recreational boating activity. Wildlife populations have been shown to influence microbiological water quality within the watershed.

f) Sweet Hall Marsh (Lat 37.57138; Long 76.88424)

Sweet Hall Marsh is the most downriver extensive tidal freshwater marsh located in the Pamunkey River, one of two major tributaries of the York River. The marsh is located approximately 77 km upriver from the mouth of the York River estuary. The reserve is 353 ha (871 acres) in area and includes 331 ha (818 acres) of emergent fresh-water marsh, 14 ha (35 acres) of permanently flooded broad-leaved forested wetlands and approximately 4 ha (9 acres) of scrub-shrub. The marsh community is classified as freshwater mixed. Mean tidal range at Sweet Hall Marsh is on the order of 0.9 meters and MHW depth at the sample location is approximately 1.5 meters. The Pamunkey River, which surrounds Sweet Hall Marsh, can reach depths up to 15 meters. Substrate within the littoral zone and channel is dominated by fine sediment. Mean seasonal water temperature values ranged from 14.7-16.7 °C for spring, 26.7-27.9 °C for summer, 18.6-19.1 °C for fall, and 4.7-6.3 °C for winter. Located within the oligohaline, lower freshwater reaches of the Pamunkey River, mean seasonal salinity values ranged from 0.1-3.4 psu for spring, 0.1-8.4 psu for summer, 0.3-8.4 psu for fall, and 0.1-3.2 psu for winter. Summary water quality statistics were derived from 15-minute interval data for the years 2002-2004. Potential activities that could impact the site include minor municipal point source discharges above and below river of Sweet

Hall Marsh, a major industrial discharge site (pulp mill) in the town of West Point and significant groundwater withdrawal near the confluence of the Pamunkey and York Rivers.

5) Coded variable definitions

cbvcbnut = Chesapeake Bay Virginia Claybank nutrients
cbvcinut = Chesapeake Bay Virginia Catlett Island nutrients
cbvginut = Chesapeake Bay Virginia Goodwin Island nutrients
cbvshnut = Chesapeake Bay Virginia Sweet Hall Marsh nutrients
cbvtcnut = Chesapeake Bay Virginia Taskinas Creek nutrients
cbvybnut = Chesapeake Bay Virginia York River Bridge nutrients

Monitoring program codes:

monthly grab sample program = 1
 diel grab sample program = 2

6) Data collection period

a) Monthly Grab Sample Program (Monitoring Program 1)

Field replicate samples (n=2) were collected within a few minutes of the first sample unless otherwise noted.

Station Code	Start Date	Start Time
GI	01/22/2009	09:50
GI	02/18/2009	09:41
GI	03/19/2009	08:10
GI	04/20/2009	09:20
GI	05/20/2009	08:58
GI	06/15/2009	07:53
GI	07/15/2009	07:12
GI	08/13/2009	07:20
GI	09/14/2009	07:46
GI	10/12/2009	07:32
GI	11/16/2009	11:55
GI	12/14/2009	11:46
Station Code	Start Date	Start Time
YB	01/22/2009	10:06
YB	02/18/2009	10:00
YB	03/19/2009	08:29
YB	04/20/2009	09:44
YB	05/20/2009	09:32
YB	06/15/2009	08:13
YB	07/15/2009	07:48
YB	08/13/2009	07:39
YB	09/14/2009	08:16
YB	10/12/2009	07:56

YB	11/16/2009	12:27
YB	12/14/2009	12:06
Station Code	Start Date	Start Time
CI	01/22/2009	10:26
CI	02/18/2009	10:12
CI	03/19/2009	08:42
CI	04/20/2009	10:00
CI	05/20/2009	10:04
CI	06/15/2009	08:28
CI	07/15/2009	08:21
CI	08/13/2009	07:52
CI	09/14/2009	08:35
CI	10/12/2009	08:11
CI	11/16/2009	12:39
CI	12/14/2009	12:17

Station Code	Start Date	Start Time
CB	01/22/2009	10:41
CB	02/18/2009	10:26
CB	03/19/2009	08:59
CB	04/20/2009	10:25
CB	05/20/2009	10:21
CB	06/15/2009	08:43
CB	07/15/2009	08:39
CB	08/13/2009	08:04
CB	09/14/2009	08:49
CB	10/12/2009	08:23
CB	11/16/2009	12:51
CB	12/14/2009	12:30
Station Code	Start Date	Start Time
TC	01/22/2009	12:08
TC	02/18/2009	10:13
TC	03/19/2009	09:20
TC	04/20/2009	12:01
TC	05/20/2009	12:08
TC	06/15/2009	08:33
TC	07/15/2009	08:45
TC	08/13/2009	08:06
TC	09/14/2009	09:43
TC	10/12/2009	09:14
TC	11/16/2009	14:12
TC	12/14/2009	13:57

Station Code	Start Date	Start Time
SH	01/22/2009	14:01
SH	02/18/2009	12:30
SH	03/19/2009	12:30
SH	04/20/2009	12:58

SH	05/20/2009	12:59
SH	06/15/2009	09:51
SH	07/15/2009	10:31
SH	08/13/2009	09:29
SH	09/14/2009	12:16
SH	10/12/2009	11:46
SH	11/16/2009	16:03
SH	12/14/2009	15:06

b) Diel Sample Program (Monitoring Program 2)

Station Code	Start Date	Start Time	End Date	End Time
TC	01/29/2009	06:30	01/30/2009	07:30
TC	02/18/2009	12:07	02/19/2009	13:07
TC	03/19/2009	12:30	03/20/2009	13:30
TC	04/20/2009	14:00	04/21/2009	15:00
TC	05/19/2009	13:15	05/20/2009	14:15
TC	06/15/2009	10:45	06/16/2009	11:45
TC	07/15/2009	10:40	07/16/2009	11:40
TC	08/13/2009	10:15	08/14/2009	11:15
TC	09/15/2009	13:20	09/16/2009	14:20
TC	10/13/2009	13:07	10/14/2009	14:37
TC	11/17/2009	04:30	11/18/2009	05:30
TC	12/15/2009	03:00	12/16/2009	04:00

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

7) Associated researchers and projects

Additional water quality monitoring programs within the York River system include:

a) USEPA Chesapeake Bay Mainstem and Tributary Monitoring Program. Since 1984, biweekly to monthly water quality sampling at a series of sites located along the mid-river channel has been conducted as part of the Chesapeake Bay Program (www.chesapeakebay.net). Station ID's: York River proper (WE4.2, LE4.3, LE4.2, LE4.1, RET4.3), the Pamunkey River (RET4.1, TF4.2) and Mattaponi River (RET4.2 and TF4.4).

b) VIMS Shoal Survey. Since 1984, biweekly to monthly water quality sampling at a series of sites located along the shoal areas of the lower York River estuary has been conducted by the Biological Sciences Department at the Virginia Institute of Marine Science. Station ID's include: Guinea Marsh, Goodwin Island, VIMS, Yorktown, Mumfort Islands, Catlett Islands and Clay Bank.

c) Alliance for the Chesapeake Bay Volunteer Monitoring Program. Physical and chemical (limited nutrients) data are collected by a volunteer network along the York River system (www.Acb-online.org). Station ID's include: Thorofare Creek, Wormley Creek, Blackwell Landing, Pamunkey Trail, Timberneck

Creek, Yorktown Naval Weapons Station, Gloucester Point, West Point and Croaker Landing. Note: Some stations may be inactive.

d) VIMS Juvenile Abundance Monitoring Survey. As part of their Juvenile Abundance Monitoring Surveys, water quality and hydrographic data has been collected since 1968 along a series of sites in the York River estuary (includes the Mattaponi and Pamunkey River systems) by the Fisheries Science Department (www.fisheries.vims.edu/research.html) at the Virginia Institute of Marine Science. Surveys include the VIMS Trawl Survey, the Striped Bass Seine Survey and the Juvenile Shad/River Herring Pushnet Survey.

e) Virginia Department of Health. The Virginia Department of Health, Division of Shellfish Sanitation's (www.vdh.state.va.us/shellfish) Seawater Sampling Program collects microbial and general water quality and hydrographic data along a series of sites in the York River estuary (includes lower portions of the Mattaponi and Pamunkey River systems).

f)) USEPA Chesapeake Bay Shallow Water Monitoring Program. Since May 2003, CBNERRVA has maintained additional continuous (15 minute) fixed water monitoring stations within the York, Piankatank, James River, Rappahannock River, and Potomac River estuary systems using YSI 6600 EDS Datasondes. Measurements for this program include: temperature, specific conductivity, dissolved oxygen, pH, turbidity, insitu fluorescence, and depth. York River stations are located at Gloucester Point and White House (Pamunkey River). Piankatank River stations are located at Burton's Point, Bland's Wharf, and Dragon Run. James River stations are located at Wythe Point, James River Country Club, 4H Club, Chickahominy Haven, Rice Center, Appomattox, and Osborne Landing. Rappahannock River stations are located at Hicks Landing, Kendale Farms, Bowler's Wharf, Christ Church, and Corrotoman River. Potomac River stations are located Potomac Creek, Colonial Beach, Yeocomico River, and Nomini Bay. An additional surface water quality mapping program, which monitors the above stated parameters, at sub-surface depths of approximately 0.25 m along continuous cruise tracts, occurs on a monthly basis in the York River estuary (see www.VECOS.org). This sub-surface continuous sampling of water quality has been conducted since May 2003 on the York River until present, and for the Pamunkey and Mattaponi Rivers from May 2003 through October 2005.

g) Chesapeake Bay National Estuarine Research Reserve (CBV) Water Quality Monitoring Program. The Chesapeake Bay Virginia NERR maintains a long-term water quality monitoring stations at Goodwin Island, Claybank, Sweet Hall Marsh, and Taskinas Creek within the York River estuary. Goodwin Island station was established in 1997, Claybank in 2001, Sweet Hall Marsh in 2000, and Taskinas Creek in 1997. Using YSI 6600 EDS Datasondes, measurements for this program include: temperature, specific conductivity, dissolved oxygen, pH, turbidity, insitu fluorescence, and depth.

h) Chesapeake Bay National Estuarine Research Reserve (CBV) Meteorological Monitoring Program. Since 2001, CBNERR-VA has maintained a meteorological monitoring station located at Taskinas Creek within the York River estuary system. Measurements for this program include: Air Temperature (degrees C), Relative Humidity (%), Barometric Pressure (mb), Wind speed (m/s), Wind Direction (degrees), PAR (mmol/m²), and Precipitation (mm) data.

8) Distribution

NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature,

including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal Resource Management, National Ocean Service, National Oceanic and Atmospheric Administration. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

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

II. Physical Structure Descriptors

9) Entry Verification

Monthly nutrient and Chlorophyll a data files, in excel format, are sent to CBNERRVA by the VIMS Analytical Service Center, Carol Pollard, for Nutrients. Files consist of sampling station ID, date and time and parameter values expressed in unit concentrations. The Laboratory Supervisor, Joy Austin, verifies all parameter values in the excel file through cross comparison with laboratory data sheets. In order to identify any obvious discrepancies in field sample replicates, replicates were plotted against each other and visually inspected.

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.

10) Parameter titles and variable names by category

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

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus:	Total Dissolved Phosphorus	TDP	mg/L as P
	*Orthophosphate, Filtered	PO4F	mg/L as P
	Dissolved Organic Phosphorus	DOP	mg/L as P

Nitrogen:	Total Dissolved Nitrogen	TDN	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Ammonium, Filtered	NH4F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Dissolved Organic Nitrogen	DON	mg/L as N

Other Lab Parameters:

*Chlorophyll a	CHLA_N	µg/L
Phaeophytin	PHEA	µg/L

Field Parameters:

Dissolved Oxygen	DO_N	mg/L
%Dissolved Oxygen Saturation	DO_S_N	%
Salinity	SALT_N	ppt
Water Temperature	WTEM_N	°C

Notes:

1. Time is coded based on a 2400 clock and is referenced to Standard Time.
2. Reserves have the option of measuring either NO2 and NO3 or they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3.

11) Measured or calculated laboratory parameters

a) Parameters measured directly

Nitrogen species:	NH4, NO2, NO23, TDN
Phosphorus species:	PO4F, TDP
Other:	CHLA, PHEA

b) Calculated parameters

DOP	TDP-PO4F
NO3	NO23-NO2
DIN	NO23+NH4
DON	TDN-DIN

12) Limits of detection

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the VIMS Nutrient Analytical Laboratory. The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. These values are reviewed and revised periodically.

Parameter	Start Date	End Date	MDL
CHLA_N	01/01/09	12/31/09	0.50
NH4F	01/01/09	12/31/09	0.0054
NO23F	01/01/09	12/31/09	0.0010
PO4F	01/01/09	12/31/09	0.0015
NO2F	01/01/09	12/31/09	0.0002
TDN	01/01/09	12/31/09	0.0084

TDP	01/01/09	12/31/09	0.0030
PHEA	01/01/09	12/31/09	0.50

13) Laboratory methods.

a) Parameter: NH₄F

i) Method Summary: Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside. Reaction is heat catalyzed at 37°C and is measured colorimetrically at 660 nm.

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

ii) Method Reference(s):

U.S. EPA. 1974. Methods for Chemical Analysis of Water and Wastes, pp. 168-174.

Standard Methods for the Examination of Water and Wastewater, 14th edition. p 410. Method 418A and 418B (1975).

Annual Book of ASTM Standards, Part 31. "Water", Standard 1426-74, Method A, p 237 (1976).

EPA 600/R-97/072 Method 349.0. Determination of Ammonia in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis. In: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.

iii) Preservation Method: Samples are immediately filtered with a 0.45 µm membrane filter upon return to the laboratory from the field and stored at -20 °C until analysis. Maximum holding time is 28 days.

b) Parameter: NO₃F

i) Method Summary: Nitrate is reduced to nitrite by a copper/cadmium reductor column. The nitrite ion then reacts with sulfanilimide to form a diazo compound. This compound then couples with n-1-naphthylenediamine dihydrochloride to form a reddish/purple azo dye and is read colorimetrically at 540 nm. Nitrate concentration is obtained by subtracting the corresponding nitrite value from the NO₃⁻ + NO₂⁻ concentration. The color development chemistry is the same as that used in Nitrite.

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

ii) Method Reference(s):

EPA 600/R-97/072 Method 353.4. Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. In: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.

U.S. EPA. 1974 Methods for Chemical Analysis of Water and Wastes, pp. 207 -212.

Wood, E.D., F.A.G. Armstrong and F.A. Richards. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. J. Mar. Biol. Assoc. U.K. 47: 23.

Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. Methods of Seawater Analysis. Verlag Chemie, Federal Republic of Germany. 419 pp.

iii) Preservation Method: Samples are immediately filtered with a 0.45 µm membrane filter upon return to the laboratory from the field and stored at –20 °C until analysis. Maximum holding time is 28 days.

c) Parameter: NO₂F

i) Method Summary: An adaptation of the diazotization method. Under acidic conditions, nitrite ion reacts with sulfanilimide to yield a diazo compound that couples with N-1-naphthylethylenediamine dihydrochloride to form a soluble dye that is measured **colorimetrically at 540nm**. **Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.**

ii) Method Reference(s):

EPA 600/R-97/072 Method 353.4. Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. In: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.

U.S. EPA. 1974 Methods for Chemical Analysis of Water and Wastes, pp. 207 -212.

Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. Methods of Seawater Analysis. Verlag Chemie, Federal Republic of Germany. 419 pp.

iii) Preservation Method: Samples are immediately filtered with a 0.45 µm membrane filter upon return to the laboratory from the field and stored at –20 °C until analysis. Maximum holding time is 28 days.

d) Parameter: TDN

i) Method Summary: The sample is autoclaved in the presence of alkaline potassium persulfate. Following digestion, the sample is then buffered and analyzed for nitrate. It should be noted that this is an adaption of D'Elia's method of 1977.

ii) Method Reference(s):

D'Elia, C.F., P.A. Steudler, and N. Corwin. 1977. Determination of Total Nitrogen in Aqueous Samples using Persulfate Digestion. Limnology and Oceanography 22: 760-764.

EPA 600/R-97/072 Method 353.4. Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. In: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio 45268.

iii) Preservation Method: Samples are immediately filtered with a 0.45 µm membrane filter upon return to the laboratory from the field and stored at –20 °C until analysis. Maximum holding time is 28 days.

e) Parameter: PO4F

i) Method Summary: Ammonium molybdate and antimony potassium tartrate react in a sulfuric acid environment to form an antimony-phospho-molybdo complex, which is reduced to a blue colored complex by ascorbic acid. Reaction is heat catalyzed at 40°C and measured colorimetrically at 880nm. Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

ii) Method Reference(s):

SKALAR Method: O-Phosphate/Total Phosphate Catnr. 503-365.1 Issue 042993/MH/93-Demo1.

EPA 600/R-97/072 Method 365.5. Determination of Orthophosphate in Estuarine and Coastal Waters by Automated Colorimetric Analysis. In: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development . U.S. EPA, Cincinnati, Ohio 45268.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chim. Acta* 27 : 31-36.

iii) Preservation Method: Samples are immediately filtered with a 0.45 µm membrane filter upon return to the laboratory from the field and stored at –20 °C until analysis. Maximum holding time is 28 days.

f) Parameter: TDP

i) Method Summary: The sample is autoclaved in the presence of alkaline potassium persulfate. Following digestion, the sample is then buffered and analyzed for orthophosphate. It should be noted that this is an adaptation of D'Elia's method of 1977.

ii) Method Reference(s):

EPA 600/R-97/072 Method 365.5 Determination of Orthophosphate in Estuarine and Coastal Waters by Automated Colorimetric Analysis. In: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development . U.S. EPA, Cincinnati, Ohio 45268.

D'Elia, C.F., P.A. Steudler, and N. Corwin. 1977. Determination of Total Nitrogen in Aqueous Samples using Persulfate Digestion. *Limnology and Oceanography* 22: 760-764.

iii) Preservation Method: Samples are immediately filtered with a 0.45 µm membrane filter upon return to the laboratory from the field and stored at –20 °C until analysis. Maximum holding time is 28 days.

g) Parameter: CHLA_N

i) Method Summary: The method used requires filtering a known quantity of water through a glass fiber filter (4.7 cm GF/F). This filter is later ground with a tissue grinder made of teflon/glass. Approximately 1-3 ml of 90% acetone is added to the filter before grinding. Acetone is also used to wash the filter into 17 x 150 test tube with tight fitting cap. The sample is steeped at least 2 hours and not exceeding 24 hours at 4°C, in the dark. The samples are centrifuged and read on fluorometer. If the samples cannot be read within that time period, storage in the freezer at -20°C for a few days is acceptable. Instrumentation: Turner Designs TD-700 fluorometer.

iii) Method Reference(s):

Strickland, J.D.H., and Parson, T.R. 1972. A Practical Handbook of Seawater Analysis. Fish. Res. Bd. Canada 167:310.

TD-700 Laboratory Fluorometer Operating Manual. Version 1.8. July 7, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

EPA /600/ R-97/072 - Method 445.0. *In Vitro* Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices Revision 1.2. September 1997.

Using the Turner Designs Model 10 Analog, The 10AU Digital, Or the TD-700 Fluorometer with EPA Method 445.0. January 19, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

iii) Preservation Method: Samples are immediately filtered with a 0.7 µm glass fiber filter upon return to the laboratory. The filter is drawn dry, folded, sealed in an aluminum foil packet and stored at -20 °C until analysis. Maximum holding time is 28 days.

h) Parameter: PHEA

i) Method Summary: The method used requires filtering a known quantity of water through a glass fiber filter (4.7 cm GF/F). This filter is later ground with a tissue grinder made of teflon/glass. Approximately 1-3 ml of 90% acetone is added to the filter before grinding. Acetone is also used to wash the filter into 17 x 150 test tube with tight fitting cap. The sample is steeped at least 2 hours and not exceeding 24 hours at 4°C, in the dark. The samples are centrifuged and read on fluorometer. For pheophytin measurements, the sample is acidified and read again. If the samples cannot be read within that time period, storage in the freezer at -20°C for a few days is acceptable. Instrumentation: Turner Designs TD-700 fluorometer.

ii) Method Reference(s):

Strickland, J.D.H., and Parson, T.R. 1972. A Practical Handbook of Seawater Analysis. Fish. Res. Bd. Canada 167:310.

TD-700 Laboratory Fluorometer Operating Manual. Version 1.8. July 7, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

EPA /600/ R-97/072 - Method 445.0. *In Vitro* Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluoresence. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices Revision 1.2. September 1997.

Using the Turner Designs Model 10 Analog, The 10AU Digital, Or the TD-700 Fluorometer with EPA Method 445.0. January 19, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

iii) **Preservation Method:** Samples are immediately filtered with a 0.7 µm glass fiber filter upon return to the laboratory. The filter is drawn dry, folded, sealed in an aluminum foil packet and stored at –20 °C until analysis. Maximum holding time is 28 days.

14) Field and Laboratory QAQC programs

a) Precision

- i) **Field variability** – CBNERRVA collects two successive grab samples for the monthly grab sample program.
- ii) **Laboratory variability** – The VIMS Analytical Service Center for Nutrients analyzes a laboratory duplicate once for every ten samples.
- iii) **Inter-organizational splits** – None

b) Accuracy

- i) **Sample spikes** – The VIMS Analytical Service Center for Nutrients analyzes a matrix spike once for every ten samples.
- ii) **Standard reference material analysis.** CBNERRVA has participated in the 2004, 2005, 2006, 2007, 2008, and 2009 NOAA/NERR Interlaboratory Comparison Studies. VIMS Analytical Service Center results have all fallen within acceptable control limits. For details, contact the Reserve Research Coordinator.
- iii) **Cross calibration exercises** - CBNERRVA participates in cross calibration exercises. Cross calibration exercises include the Chesapeake Bay Quarterly Split Sample Program and the US EPA Method Validation Studies.

15) QAQC flag definitions

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

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

16) QAQC code definitions

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

General errors

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

Sensor errors

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

Parameter Comments

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

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 NO₃F 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) Precipitation data for the sampling date and three days prior to the monthly grab and diel sampling programs. Data are presented for two meteorological stations, locations are the Sweet Hall Marsh reserve and the Taskinas Creek reserve. Data units are in mm.

Type of Sampling	Previous Dates	Sweet Hall	Taskinas
Monthly Grab	01/19/2009	0.0	0.0
Monthly Grab	01/20/2009	0.0	0.0
Monthly Grab	01/21/2009	0.0	0.0
Monthly Grab	01/22/2009	0.0	0.0
Diel	01/27/2009	8.4	10.0
Diel	01/28/2009	12.0	7.3
Diel	01/29/2009	0.0	0.0
Diel	01/30/2009	0.3	0.0
Monthly Grab	02/15/2009	0.0	0.0
Monthly Grab	02/16/2009	0.0	0.0
Monthly Grab	02/17/2009	0.0	0.0
Monthly Grab	02/18/2009	5.9	7.9
Diel	02/16/2009	0.0	0.0
Diel	02/17/2009	0.0	0.0
Diel	02/18/2009	5.9	7.9
Diel	02/19/2009	0.0	0.3
Monthly Grab	03/16/2009	8.7	7.6
Monthly Grab	03/17/2009	6.7	8.4
Monthly Grab	03/18/2009	0.0	0.0
Monthly Grab	03/19/2009	2.8	5.6
Diel	03/17/2009	6.7	8.4
Diel	03/18/2009	0.0	0.0
Diel	03/19/2009	2.8	5.6
Diel	03/20/2009	0.0	0.0
Monthly Grab	04/17/2009	0.0	0.0
Monthly Grab	04/18/2009	0.0	0.0
Monthly Grab	04/19/2009	0.0	0.0

Monthly Grab	04/20/2009	13.0	21.8
Diel	04/18/2009	0.0	0.0
Diel	04/19/2009	0.0	0.0
Diel	04/20/2009	13.0	21.8
Diel	04/21/2009	5.9	1.1
Monthly Grab	05/17/2009	11.4	2.6
Monthly Grab	05/18/2009	0.9	1.5
Monthly Grab	05/19/2009	0.0	0.0
Monthly Grab	05/20/2009	0.0	0.0
Diel	05/17/2009	11.4	2.6
Diel	05/18/2009	0.9	1.5
Diel	05/19/2009	0.0	0.0
Diel	05/20/2009	0.0	0.0
Monthly Grab	06/12/2009	12.5	6.7
Monthly Grab	06/13/2009	0.0	0.0
Monthly Grab	06/14/2009	0.0	0.0
Monthly Grab	06/15/2009	10.8	1.8
Diel	06/13/2009	0.0	0.0
Diel	06/14/2009	0.0	0.0
Diel	06/15/2009	10.8	1.8
Diel	06/16/2009	0.0	0.0
Monthly Grab	07/12/2009	3.0	0.0
Monthly Grab	07/13/2009	19.8	0.0
Monthly Grab	07/14/2009	0.0	0.0
Monthly Grab	07/15/2009	0.0	0.0
Diel	07/13/2009	19.8	0.0
Diel	07/14/2009	0.0	0.0
Diel	07/15/2009	0.0	0.0
Diel	07/16/2009	4.4	3.3
Monthly Grab	08/10/2009	0.0	0.0
Monthly Grab	08/11/2009	4.8	0.0
Monthly Grab	08/12/2009	0.3	3.4
Monthly Grab	08/13/2009	0.0	19.6
Diel	08/11/2009	4.8	0.0
Diel	08/12/2009	0.3	3.4
Diel	08/13/2009	0.0	19.6
Diel	08/14/2009	0.0	0.0
Monthly Grab	09/11/2009	1.2	0.3
Monthly Grab	09/12/2009	0.0	0.0
Monthly Grab	09/13/2009	0.0	0.0
Monthly Grab	09/14/2009	0.0	0.0
Diel	09/13/2009	0.0	0.0
Diel	09/14/2009	0.0	0.0
Diel	09/15/2009	0.0	0.0
Diel	09/16/2009	0.0	0.0
Monthly Grab	10/09/2009	0.0	0.0
Monthly Grab	10/10/2009	1.5	0.9
Monthly Grab	10/11/2009	0.0	0.0

Monthly Grab	10/12/2009	0.8	0.5
Diel	10/11/2009	0.0	0.0
Diel	10/12/2009	0.8	0.5
Diel	10/13/2009	0.0	0.0
Diel	10/14/2009	0.3	0.3
Monthly Grab	11/13/2009	6.3	6.3
Monthly Grab	11/14/2009	0.3	0.9
Monthly Grab	11/15/2009	0.0	0.0
Monthly Grab	11/16/2009	1.0	1.3
Diel	11/15/2009	0.0	0.0
Diel	11/16/2009	1.0	1.3
Diel	11/17/2009	0.0	0.0
Diel	11/18/2009	0.0	0.0
Monthly Grab	12/11/2009	0.0	0.0
Monthly Grab	12/12/2009	0.0	0.0
Monthly Grab	12/13/2009	24.0	32.5
Monthly Grab	12/14/2009	0.3	0.0
Diel	12/13/2009	24.0	32.5
Diel	12/14/2009	0.3	0.0
Diel	12/15/2009	0.0	0.3
Diel	12/16/2009	0.0	0.0