Chesapeake Bay National Estuarine Research Reserve in Virginia (CBV) NERR Nutrient Metadata (January-December, 2003) Latest Update: July 14, 2025

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2) Research objectives

a) Monthly Grab

Monthly grab samples are collected to quantify the spatial and temporal variability of selected nutrients and chlorophyll a in the water column along a salinity gradient within the York River estuary system.

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 25 hour period in order to quantify the short-term temporal variability of selected nutrients and chlorophyll a in the water column.

3) Research methods

a) Monthly Grab Sample 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 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 85 meter. All samples were collected in amber, widemouth, 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 chlorophyll a analysis.

b) Diel Sampling Program

Diel grab samples were taken at the Taskinas Creek long-term datasonde station. 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 (0.5m) 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 chlorophyll a.

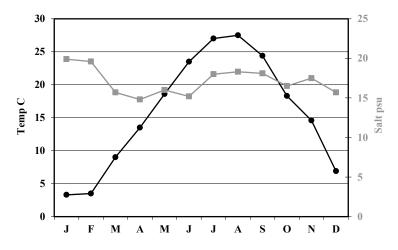
4) Site location and character

a) Goodwin Islands (37° 13' 07.63" N, 76° 23' 43.85" W)

The Goodwin Islands component of the CBNERRVA is located on the southern side of

the mouth of the York River. The Goodwin Islands are a 315 ha (777 acre) archipelago of salt-marsh islands surrounded by inter-tidal flats, extensive submerged aquatic vegetation (SAV) beds (121 ha; 300 acres). 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). Observed monthly

mean temperature and salinity values for Goodwin Islands for 2003 are presented in the following figure.



b) York River Bridge (37° 14' 41.60" N, 76° 30' 18.80" W).

The Coleman 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.

c) Catlett Islands (37° 18' N; 76° 33' W)

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

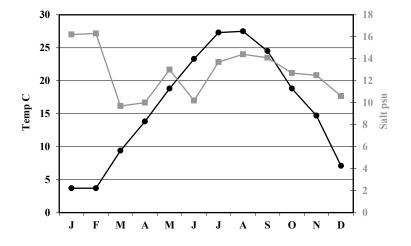
River on the eastern side of the Catlett Islands and Cedarbush Creek enters the river on the

western side. Poplar Creek bisects the two large areas of the Catlett Islands. Catlett Islands encompass 280 ha (690acres) 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.

d) Claybank (37° 20' 51.58" N, 76° 36' 37.52" W).

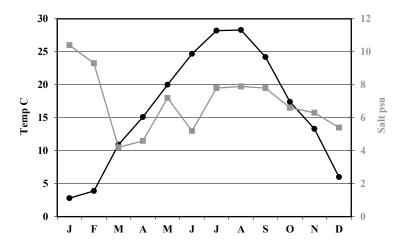
The Claybank station is with a shallow (<2m) littoral area approximated 300-400 meters wide located within the mesohaline portion of the York River estuary approximately 26 km upriver from the mouth of the estuary. The shoreline consists of a narrow fringe of salt marsh with some areas armored with bulkhead or stone. Tidal range is on the order of 0.85 meters. This station is located along the north shoreline of the estuary in an area that was vegetated with submersed aquatic vegetation prior to 1972 but has remained unvegetated since that time. The sediment consists of muddy sands. 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. The site is exposed to strong winds from the northwest and re-suspension of sediment during storm events can be high. Observed monthly mean temperature and salinity values for Claybank for 2003 are presented in the following figure.



e) Taskinas Creek (37° 24' 53.86" N, 76° 42' 51.82" W).

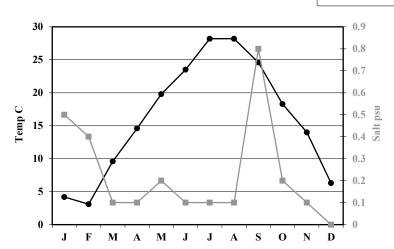
Taskinas Creek Reserve encompasses 397 ha (980acres) and is located in York River State Park near the town of Croaker, in James City County, Virginia. The small sub-estuary of the York River is located on the southern side of the river, approximately 22 km upriver from VIMS and 37 km from the mouth of 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, maplegum-ash swamps and freshwater marshes. Freshwater mixed wetlands are found in the upstream reaches of Taskinas Creek. Taskinas Creek is roughly 2 meters deep and 20 meters wide towards the lower end of the creek. Mean tide range is 0.85 m. Sub-tidal substrates are dominated by fine sediments. Wildlife populations are known to influence microbiological water quality in Taskinas Creek. Observed monthly mean temperature and salinity values for Taskinas Creek for 2003 are presented in the following figure.



f) Sweet Hall Marsh (37° 34' 16.94" N, 76° 53' 02.78" W)

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. This reserve area is 353 ha (871 acres) in area and includes 331 ha (818 acres) of emergent freshwater 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 m. Observed monthly mean temperature and salinity values for Sweet Hall Marsh for 2003 are presented in the following figure.

5) Coded variable code definitions

- a) Site/Station Names Goodwin Island (GI), Coleman Bridge (YB), Catlett Islands (CI), Clay Bank (CB), Taskinas Creek (TC), and Sweet Hall Marsh (SH)
- b) Monitoring Programs
 CBNERRVA Monthly grab sample program (1), and CBNERRVA Diel grab sample program (2)

6) Data collection period

a) Monthly Grab Sample Program (Monitoring Program 1)

| Station Code | Start Date | Start Time |
|--------------|------------|------------|
| GI | 1/14/03 | 10:20 |
| GI | 2/13/03 | 10:00 |
| GI | 3/13/03 | 10:05 |
| GI | 4/23/03 | 8:05 |
| GI | 5/21/03 | 7:42 |
| GI | 6/11/03 | 9:30 |
| GI | 7/8/03 | 9:10 |
| GI | 8/20/03 | 8:05 |
| GI | 9/4/03 | 8:25 |
| GI | 10/23/03 | 10:15 |
| GI | 11/4/03 | 9:55 |
| GI | 12/2/03 | 9:35 |

| Station Code | Start Date | Start Time |
|--------------|------------|------------|
| YB | 1/14/03 | 11:10 |
| YB | 2/13/03 | 10:54 |
| YB | 3/13/03 | 11:10 |
| YB | 4/23/03 | 8:48 |
| YB | 5/21/03 | 8:37 |
| YB | 6/11/03 | 10:15 |
| YB | 7/8/03 | 10:20 |
| YB | 8/20/03 | 8:45 |
| YB | 9/4/03 | 8:55 |
| YB | 10/23/03 | 11:07 |
| YB | 11/4/03 | 10:44 |
| YB | 12/2/03 | 10:21 |

| Station Code | Start Date | Start Time |
|--------------|------------|------------|
| CI | 1/14/03 | 11:55 |
| CI | 2/13/03 | 11:40 |
| CI | 3/13/03 | 11:55 |
| CI | 4/23/03 | 9:37 |
| CI | 5/21/03 | 9:10 |
| CI | 6/11/03 | 10:30 |
| CI | 7/8/03 | 11:05 |
| CI | 8/20/03 | 8:59 |
| CI | 9/4/03 | 9:15 |
| CI | 10/23/03 | 12:05 |
| CI | 11/4/03 | 11:23 |
| CI | 12/2/03 | 11:00 |

| Station Code | Start Date | Start Time |
|--------------|------------|------------|
| CB | 1/14/03 | 12:20 |
| CB | 2/13/03 | 12:10 |
| CB | 3/13/03 | 12:15 |
| CB | 4/23/03 | 10:02 |
| CB | 5/21/03 | 9:30 |
| CB | 6/11/03 | 10:45 |
| CB | 7/8/03 | 11:20 |
| CB | 8/20/03 | 9:15 |
| CB | 9/4/03 | 9:30 |
| CB | 10/23/03 | 12:45 |
| CB | 11/4/03 | 11:52 |
| CB | 12/2/03 | 11:25 |

| Station Code | Start Date | Start Time |
|--------------|------------|------------|
| TC | 1/14/03 | 14:19 |
| TC | 2/13/03 | 14:30 |
| TC | 3/13/03 | 12:30 |
| TC | 4/23/03 | 11:15 |
| TC | 5/21/03 | 9:18 |
| TC | 6/11/03 | 13:45 |
| TC | 7/8/03 | 11:50 |
| TC | 8/20/03 | 10:10 |
| TC | 9/4/03 | 11:20 |
| TC | 10/23/03 | 12:10 |
| TC | 11/4/03 | 14:50 |
| TC | 12/2/03 | 13:10 |

| C4-4: C- 1- | C4 1 D-4- | C44 T' |
|--------------|------------|------------|
| Station Code | Start Date | Start Time |
| SH | 1/14/03 | 16:38 |
| SH | 2/13/03 | 17:00 |
| SH | 3/13/03 | 14:25 |
| SH | 4/23/03 | 10:15 |
| SH | 5/21/03 | 11:00 |
| SH | 6/11/03 | 15:50 |
| SH | 7/8/03 | 10:55 |
| SH | 8/20/03 | 12:35 |
| SH | 9/4/03 | 10:10 |
| SH | 10/23/03 | 14:20 |
| SH | 11/4/03 | 13:55 |
| SH | 12/2/03 | 12:05 |

b) Diel Sample Program (Monitoring Program 2)

| Station Code | Start Date | Start Time | End Date | End Time |
|-----------------|------------|---------------|------------|-------------|
| TC | 1/13/2003 | 13:20 | 1/14/2003 | 14:20 |
| TC | 2/12/2003 | 13:30 | 2/13/2003 | 14:30 |
| TC | 3/11/2003 | 10:00 | 3/12/2003 | 11:00 |
| TC | 4/22/2003 | 9:50 | 4/23/2003 | 10:50 |
| TC | 5/21/2003 | 9:18 | 5/22/2003 | 10:18 |
| TC | 6/10/2003 | 12:45 | 6/11/2003 | 13:45 |
| TC | 7/7/2003 | 10:30 | 7/8/2003 | 12:30 |
| TC | 8/20/2003 | 10:00 | 8/21/2003 | 11:00 |
| TC | 9/3/2003 | 9:30 | 9/4/2003 | 10:30 |
| TC | 10/20/2003 | 12:00 | 10/21/2003 | 13:00 |
| TC | 11/3/2003 | 13:45 | 11/4/2003 | 14:45 |
| TC | 12/1/2003 | 11:00 | 12/2/2003 | 12:00 |

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. VIMS Surface Water quality Mapping Program. Since 2003, CBNERRVA has conducted monthly water quality surveys are within the York, Pamunkey and Mattaponi Rivers as part of the Chesapeake Bay Program Shallow Water Quality Monitoring Program. Utilizing a DataFlow system, sampling resolution occurs at a 50 m resolution along specified cruise tracks. Verification and nutrient samples are collected during cruises.

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.

9) Entry verification

Monthly nutrient and chlorophyll a data files, in excel format, are sent to CBNERRVA by the VIMS Analytical Service Center for Nutrients. Files consist of sampling station ID, date and time and parameter values expressed in unit concentrations. The Laboratory Supervisor verifies all parameter values in the excel file through cross comparison with laboratory data sheets. Missing data are verified through inspection of field logs, inserted into the data files and denoted by a "" (blank cell) by CBNERRVA staff. Values below the method detection limit (MDL) were replaced with the MDL and marked with a "B" as were any affected calculated values. In order to identify any obvious discrepancies in field sample replicates, replicates were plotted against each other and visually inspected.

10) Parameter Titles and Variable Names by Data Category

| Data Category | Parameter | Variable Name | Units of Measure |
|-------------------|--|--------------------|-------------------------------------|
| Phosphorus: | Orthophosphate, Filtered Dissolved Organic Phosphorus Total Dissolved Phosphorus | PO4F Dop TDP | mg/L as P mg/L as P mg/L as P |
| Nitrogen: | | | |
| | Ammonium, Filtered | NH4F | mg/L as N |
| | Nitrite, Filtered | NO2F | mg/L as N |
| | Nitrate, Filtered | NO3F | mg/L as N |
| | Nitrite + Nitrate, Filtered | NO23F | mg/L as N |
| | Dissolved Inorganic Nitrogen | DIN | mg/L as N |
| | Dissolved Organic Nitrogen | DON | mg/L as N |
| | Total Dissolved Nitrogen | TDN | mg/L as N |
| Other Lab Parame | eters: | | |
| | 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 | $^{\circ}\mathrm{C}$ |

11) Measured and Calculated Laboratory Parameters

a) Variables Measured Directly

Nitrogen species: NO2F, NO23F, NH4F, TDN

Phosphorus species: TDP, PO4F Other: CHLA N, PHEA

b) Computed Variables

NO3F: NO23F-NO2F
DIN: NO23F+NH4F
DON: TDN-DIN
DOP: TDP-PO4F

12) Limits of Detection

| Parameter | Variable Method Detection | | Method Detection Limit |
|-------------------|---------------------------|-------------------|-------------------------|
| | | Limit | |
| Ammonium | NH4F | 0.0015 mg/L as N | 1/13/2003 - 03/12/2003 |
| Allillolliulli | 111141 | 0.0054 mg/L as N | 03/13/2003 - 12/31/2003 |
| Nitrate + Nitrite | NO23F | 0.0008 mg/L as N | 1/13/2003 - 03/12/2003 |
| Miliale + Militle | NO23F | 0.0010 mg/L as N | 03/13/2003 - 12/31/2003 |
| Nitrite | NO2F | 0.0002 mg/L as N | 1/13/2003 - 12/31/2003 |
| Total Dissolved | TDN | 0.0340 mg/L as N | 1/13/2003 - 03/12/2003 |
| Nitrogen | IDN | 0.0084 mg/L as N | 03/13/2003 - 12/31/2003 |
| | | 0.0006 mg/L as P | 1/13/2003 - 03/12/2003 |
| Orthophosphate | PO4F | 0.0010 mg/L as P | 03/13/2003 - 05/20/2003 |
| | | 0.0015 mg/L as P | 05/21/2003 - 12/12/2003 |
| Total Dissolved | TDP | 0.0020 mg/L as P | 1/13/2003 - 03/12/2003 |
| Phosphorus | IDF | 0.0030 mg/L as P | 03/13/2003 - 12/31/2003 |
| Chlorophyll a | CHLA_N | 0.5 ug/L | 1/13/2003 - 12/31/2003 |
| Pheophytin | PHEA | 0.5 ug/L | 1/13/2003 - 12/31/2003 |

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 μ m 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: NO23F

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-napthylenediamine dihydrochloride to form a reddish/purple azo dye and is read colorimetrical 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. <u>Methods of Seawater Analysis</u>. Verlag Chemie, Federal Republic of Germany. 419 pp.

iii) Preservation Method: Samples are immediately filtered with a 0.45 μ m 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-napthylethylenediamine 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. <u>Methods of Seawater Analysis</u>. Verlag Chemie, Federal Republic of Germany. 419 pp.

iii) Preservation Method: Samples are immediately filtered with a 0.45 μ m 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

- <u>- 2nd Edition.</u> 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 μ m 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 catalizyed 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: <u>Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition.</u> 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 μ m 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: <u>Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition.</u> 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 μ m 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.

ii) Method Reference(s):

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

<u>TD-700 Laboratory Fluorometer Operating Manual.</u> 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. <u>Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices</u> Revision 1.2. September 1997.

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

iii) Preservation Method: Samples are immediately filtered with a $0.7~\mu m$ glass fiber filter upon return to the laboratory. The filter is drawn dry, folded, sealed in an aluminum foil packet and stored at $-20~^{\circ}\text{C}$ 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. <u>A Practical Handbook of Seawater Analysis</u>. Fish, Res. Bd. Canada 167:310.

<u>TD-700 Laboratory Fluorometer Operating Manual.</u> 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. <u>Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices</u> Revision 1.2. September 1997.

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

iii) Preservation Method: Samples are immediately filtered with a $0.7~\mu m$ glass fiber filter upon return to the laboratory. The filter is drawn dry, folded, sealed in an aluminum foil packet and stored at $-20~^{\circ}\text{C}$ until analysis. Maximum holding time is 28 days.

14) Reporting of missing data, data with concentrations lower than Method Detection Limits and other comment codes

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 | Definition |
|---------|--|
| Code | |
| A | Value above upper limit of method detection |
| В | Value below method detection limit |
| С | Calculated value |
| D | Data deleted or calculated value could not be determined due |
| | to deleted data, see metadata for details |
| Н | 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 |

Values comment coded as suspect 'S' for Chla_N were: Station cbvcbnut, 03/13/2003 at 12:15; Station cbvybnut, 12/02/2003 at 10:21. Values comment coded as suspect 'S' for Phea_N were: Station cbvcinut, 04/23/2003 at 9:37. In all cases, suspect values deviated to a large degree from replicate samples and samples taken in close association in both time and space.

15) QA/QC 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. The VIMS Analytical Service Center for Nutrients participated in the 2003 NOAA/NERRS Analytical Laboratory Intercomparison Study. Results are presented in the Table below. Overall uncertainty values are presented parenthetically.

| Parameter | Certified Seawater | VIMS Analytical | |
|-------------------|---------------------|-----------------|--|
| | Reference Material | Service Center | |
| | mg/L as P or N | mg/L as P or N | |
| Orthophosphate | $0.048 (\pm 0.002)$ | 0.048 | |
| Nitrite | $0.043~(\pm~0.002)$ | 0.042 | |
| Nitrite + Nitrate | $0.332 (\pm 0.013)$ | 0.360 | |

iii) Cross Calibration Exercises. None

16) Other Remarks

On 7/14/2025 this dataset was updated to include embedded QAQC flags and codes for anomalous/suspect, rejected, missing, and below detection limit data. System-wide monitoring data beginning in 2007 were processed to allow for QAQC flags and codes to be embedded in the data files rather than using the original single letter codes used for the nutrient and pigment dataset along with the detailed sections in the metadata document for suspect, missing, and rejected data. Please note that prior to 2007, rejected data were deleted from the dataset so they are unavailable to be used at all. Suspect, missing, rejected and below minimum detection flags and appropriate three letter codes were embedded retroactively for dataset consistency. The QAQC flag/codes corresponding to the original letter codes are detailed below.

| | | Historic | |
|---|------------|-------------|--|
| Flag/code | If also C | Letter Code | Historic Code Definition |
| <1> [SUL] | | Α | Value above upper limit of method detection |
| <-4> [SBL] | <-4> [SCB] | В | Value below method detection limit |
| no need to flag/code unless combined | | С | Calculated value |
| <-3> [GQD] | <3> [GCR] | D | Data deleted or calculated value could not be determined due to deleted data, see metadata for details |
| <1> (CHB) | | Н | Sample held beyond specified holding time |
| <0> (CSM) unless other flag | | K | Check metadata for further details |
| <-2> [GDM] | <-2> [GCM] | М | Data missing, sample never collected or calculated value could not be determined due to missing data |
| <-3> [SNV] and <1> [SCC] for components | | N | Negative calculated value |
| (CRE) or F_Record (CRE) | | Р | Significant precipitation (reserve defined, see metadata for further details) |
| <0> (CUS) | | U | Lab analysis from unpreserved sample |
| <1> (CSM) | | S | Data suspect, see metadata for further details |

Precipitation data for the sampling date and three days prior to the monthly grab and diel sampling programs. Data are presented for three meteorological stations, locations are the Virginia Institute of Marine Science at Gloucester Point (VIMS), the Sweet Hall Marsh reserve and the Taskinas Creek reserve. Data units are in mm.

| Type of Sampling | Sampling Dates | VIMS | Sweet Hall | Taskinas |
|-------------------|----------------|------|------------|----------|
| | | | | |
| Diel Sample | 1/10/2003 | 0 | NA | 0 |
| Monthly Grab/Diel | 1/11/2003 | NA | NA | 0 |
| Monthly Grab/Diel | 1/12/2003 | 0 | NA | 0 |

| Monthly Grab/Diel | 1/13/2003 | 0 | NA | 0 |
|-------------------|------------|-----|----|----|
| Monthly Grab | 1/14/2003 | 0 | NA | 0 |
| Diel Sample | 2/9/2003 | NA | 0 | 0 |
| Monthly Grab/Diel | 2/10/2003 | NA | 4 | 5 |
| Monthly Grab/Diel | 2/11/2003 | NA | 0 | 0 |
| Monthly Grab/Diel | 2/12/2003 | NA | 0 | 0 |
| Monthly Grab | 2/13/2003 | NA | 0 | 0 |
| • | | 0 | | |
| Diel Sample | 3/8/2003 | | 0 | 0 |
| Diel Sample | 3/9/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 3/10/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 3/11/2003 | 0 | 0 | 0 |
| Monthly Grab | 3/12/2003 | 0 | 0 | 0 |
| Monthly Grab | 3/13/2003 | 0 | 2 | 6 |
| Diel Sample | 4/19/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 4/20/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 4/21/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 4/22/2003 | 0 | 0 | 0 |
| Monthly Grab | 4/23/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 5/18/2003 | 11 | 25 | 22 |
| Monthly Grab/Diel | 5/19/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 5/20/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 5/21/2003 | 12 | 20 | 30 |
| Diel Sample | 6/7/2003 | 171 | 33 | 23 |
| Monthly Grab/Diel | 6/8/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 6/9/2003 | 0 | 5 | 2 |
| Monthly Grab/Diel | 6/10/2003 | 0 | 0 | 0 |
| Monthly Grab | 6/11/2003 | 2 | 2 | 0 |
| Diel Sample | 7/4/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 7/5/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | | - | _ | _ |
| • | 7/6/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 7/7/2003 | 0 | 8 | 0 |
| Monthly Grab | 7/8/2003 | 3 | 0 | 2 |
| Monthly Grab/Diel | 8/17/2003 | 27 | 0 | 0 |
| Monthly Grab/Diel | 8/18/2003 | 0 | 2 | 9 |
| Monthly Grab/Diel | 8/19/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 8/20/2003 | 0 | 0 | 0 |
| Diel Sample | 8/31/2003 | 11 | 0 | 2 |
| Monthly Grab/Diel | 9/1/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 9/2/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 9/3/2003 | 29 | 20 | 29 |
| Monthly Grab | 9/4/2003 | 13 | 88 | 39 |
| Diel Sample | 10/17/2003 | 0 | 3 | 3 |
| Diel Sample | 10/18/2003 | 0 | 0 | 0 |
| Diel Sample | 10/19/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 10/20/2003 | 0 | 0 | 0 |
| Monthly Grab | 10/21/2003 | 0 | 0 | 0 |
| Monthly Grab | 10/22/2003 | 0 | 0 | 0 |
| , - | | - | - | - |

| Monthly Grab | 10/23/2003 | 0 | 0 | 0 |
|-------------------|------------|---|---|----|
| Diel Sample | 10/31/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 11/1/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 11/2/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 11/3/2003 | 0 | 0 | 0 |
| Monthly Grab | 11/4/2003 | 0 | 0 | 0 |
| Diel Sample | 11/28/2003 | 0 | 9 | 11 |
| Monthly Grab/Diel | 11/29/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 11/30/2003 | 0 | 0 | 0 |
| Monthly Grab/Diel | 12/1/2003 | 0 | 0 | 0 |
| Monthly Grab | 12/2/2003 | 0 | 0 | 0 |
| | | | | |

b) Hurricane Isabel impacted the York River system on September 18, 2003.