

**Delaware (DEL) National Estuarine Research Reserve Nutrient Metadata
(January 2006-December 2006)
Latest Update: May 16, 2025**

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

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c) Other Contacts and Programs: None

2) Research objectives –

a) Monthly Grab Program:

The objective of this monitoring program is to provide baseline information on inorganic nutrient and Chla water quality status in the Delaware NERR while also contributing to

baseline information nationally. The five sites chosen for monitoring will assist in understanding the impacts of both urban and agricultural impacts on the watersheds.

b) Diel Sampling Program:

The objective of this monitoring program is to provide baseline information on inorganic nutrient and Chla water quality status in the Delaware NERR. The diel sampling program attempts to capture a more comprehensive view by assessing fluctuating nutrient amounts throughout a lunar tidal cycle. The site chosen for monitoring will assist in understanding the impacts of both urban and agricultural impacts on the watersheds.

3) Research methods –

a) Monthly Grab Sampling Program:

Monthly grab samples are taken at 3 sites in the St. Jones River watershed and 2 sites in the Blackbird watershed. These sites coincide with the five datasonde sites: Scotton Landing, Lebanon Landing, Division Street, Blackbird Landing, and Beaver Branch (non-SWMP water quality site). All grab samples are taken on the same day between +/- 3 hours slack-low tide. No distinction is made between neap and spring tide conditions. Efforts are made to allow for an antecedent dry period of 72 hours prior to sampling, however this was not always possible due to staffing limitations and extensive periods of inclement weather. Sampling events are staggered 30 days apart to the best of the research staff's ability. Replicate (N=2) samples are collected with a Wildco grab sampler at an approximate depth of 30 cm above the bottom. All samples are collected in wide-mouth, nalgene sample bottles that were previously acid washed (10%), rinsed (3x) with distilled-deionized water, dried, and rinsed (2x) with ambient water prior to collection of the sample. Samples are immediately placed on ice, in a dark cooler and returned to the laboratory.

Once in the DNERR laboratory, samples are shaken and processed for nutrient and Chla analysis. Sample processing includes the filtration of samples since all analysis takes place at the Virginia Institute for Marine Science (VIMS). The filtering methods differ between samples for Chla analysis and other nutrient parameter analysis. Chl-a processing included filtering a 100ml sample through a 47mm Whatman GF/F filters using a vacuum-pump and filter flask apparatus. The Whatman type GF/F filter is folded immediately after sample filtering, enclosed in tinfoil, placed in a sealed bag, and placed in the freezer until it is sent off for analysis the following day. Sample processing for other parameters includes filtering 100ml of a sample through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47mm GF/C filter may be used to filter the sample prior to filtering through the 0.45um Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day. All lab glassware is acid washed (10% HCl) and rinsed (6x) using distilled-deionized water between samples to avoid any contamination.

b) Diel Sampling Program:

Diel samples are collected once a month at Scotton Landing, a site located along the St. Jones River. An Isco 6700 automated sampler takes samples at 2.5-hour intervals over a 25-hour cycle, thus resulting in 11 samples per event. Diel sampling starts between +/- 3 hours slack-low tide. No distinction is made between neap and spring tide conditions. Efforts are made to allow for an antecedent dry period of 72 hours prior to starting the sampler, however this was

not always possible due to staffing limitations and extensive periods of inclement weather. Sampling events are staggered 30 days apart to the best of the research staff's ability. Samples are collected at an approximate depth of 30 cm coinciding with the vertical placement of the data sonde. All samples are collected in wide-mouth, Nalgene sampler bottles that were previously acid washed (10%), rinsed (3x) with distilled-deionized water, and dried. Samples are immediately placed on ice, inside the ice-filled sampler. Samples are processed in the same manner illustrated in the "Monthly Grab Sampling Program" portion of this section.

4) Site location and character –

The Delaware National Estuarine Research Reserve is comprised of two component sites, the St. Jones River and Blackbird Creek components. Both components are located along the Delaware Bay Coast. The St. Jones River Component is located in central Kent County Delaware, east of the State Capitol City, Dover. The Blackbird Creek component is located in the unincorporated area of Southern New Castle County. There are five sampling sites, three located in the St. Jones component and two in the Blackbird Creek component.

1) Scotton Landing (SL) - is located in the Lower St. Jones River at the Scotton Landing Public Fishing Pier, just up stream of Delaware Route 113. The river is 22.3 km long (mainstream linear dimension), has an average depth of 4m MHW and the width is 50 m. At the sampling site, the depth is 3.2 m MHW and the width is 40 m. The sediment is clayey silt with no bottom vegetation. The watershed-draining site is 19778 ha. The site is influenced by freshwater runoff from the relatively urbanized area upstream. Pollutants in the area include PCB's.

Salinity ranges from 1- 30 ppt.

Tidal Range: Spring Mean (m) – 1.26

Neap Mean (m) – 1.13

Position: Latitude 39 degree 05' 05.9160" N

Longitude 75 degree 27' 38.1049" W

2) Blackbird Landing (BL) - is located in the upper Blackbird Creek at Blackbird Landing Road. The creek is 25.8 km long (mainstream linear dimension), has an average depth of 3 m MHW, and an average width of 90 m. At the sampling site, the depth is 1.8 m MHW and width is 110 m. The sediment is silty clay with no bottom vegetation. The watershed draining site is 4694 ha. The site is influenced by freshwater runoff from unimpacted forested areas intermixed with agricultural land uses and a small amount of low-density development. There is very little pollutant presence in the area.

Salinity ranges from 0-9 ppt.

Tidal Range: Spring Mean (m) – 1.12

Neap Mean (m) – 1.13

Position: Latitude 39 degree 23' 19.5196" N

Longitude 75 degree 38' 09.5882" W

3) Lebanon Landing (LL) - is located in the mid portion of the St. Jones River at the Lebanon Landing Public Fishing Pier, farther upstream from the Scotton Landing monitoring site. The St. Jones River is 22.3 km long (mainstream linear dimension), has an average depth of 4m MHW and the width is 50 m. At the sampling site, the depth is 3.0 m MHW and the width is 28 m. The sediment

is clayey silt with no bottom vegetation. The watershed-draining site is 19778 ha. The site is influenced by freshwater runoff from the relatively urbanized area upstream. Pollutants in the area include PCB's.

Salinity ranges from 0 to 28ppt.

Tidal Range: Spring Mean (m) – 0.855

Neap Mean (m) – 0.671

Position: Latitude 39° 06' 51.8" N

Longitude 75° 29' 57.1" W

4) Division Street (DS) - is located in the upper portion of the St. Jones River near the USGS station on Division Street. The site is influenced by runoff from the urbanized surroundings. The St. Jones River is 22.3 km long (mainstream linear dimension), has an average depth of 4m MHW and the width is 50 m. At the sampling site, the depth is 0.6m MHW and the width is 26 m. The sediment is clayey silt with no bottom vegetation. The site is fresh water and is influenced by urban freshwater runoff.

Salinity Range: Fresh water (0.1 ppt)

Tidal Range: Not Applicable, freshwater

Position: Latitude 39° 09' 49.4" N

Longitude 75° 31' 08.7" W

5) Beaver Branch (BB) - is located in the upper Blackbird Creek. . The sampling site is situated on the south side of a Union Church Road bridge. The creek is 1.5 km long (mainstream linear dimension), has an average depth of 1.5m MHW, and an average width of 37m. At the sampling site, the depth is 1.4m MHW and width is 12.8 m. The site is influenced by freshwater runoff from unimpacted forested areas intermixed with agricultural land uses and increasing amounts of development. The sediment is silty clay with no bottom vegetation. Some emergent vegetation exists near the western bank. The watershed draining site is 4694 ha. There is very little pollutant presence in the area.

Salinity Range: 0.5-10.0 ppt

Tidal Range: Spring Mean (m) – 0.82

Neap Mean (m)-0.72

Position: Latitude 39 degree 24' 08.6" N

Longitude 75 degree 37' 40.7" W

5) Code variable definitions –

Each individual sample is given a 3 part name code in addition to other codes. The 3 part name code, “delslnut” for example, gives the reserve name (del = Delaware), station name (sl = Scotton Landing, etc), and SWMP program code (nut = nutrient monitoring program).

Sampling Site Codes:

delslnut = Delaware Reserve nutrient data for Scotton Landing

delblnut = Delaware Reserve nutrient data for Blackbird Landing

delllnut= Delaware Reserve nutrient data for Lebanon Landing

deldsnut = Delaware Reserve nutrient data for Division Street

delbbnut= Delaware Reserve nutrient data for Beaver Branch

The monitoring codes are set as “1” to indicate grab samples and “2” to indicate diel samples. Replicates are also given specific codes. Grab samples in which duplicates sample are taken utilize a “1” for the first sample and a “2” for the second sample. Diel samples are always labeled with a “1” since only one sample is taken at each 2.5 hr interval.

6) Data collection period –

Diel Sampling (All times in EST)

Site	Start Date	Start Time	End Date	End Time
SL	01/30/2006	0930	01/31/2006	1030
SL	02/27/2006	0900	02/28/2006	1000
SL	03/21/2006	1000	03/22/2006	1100
SL	04/26/2006	0430	04/27/2006	0530
SL	05/23/2006	0100	05/24/2006	0200
SL	06/19/2006	1130	06/20/2006	1230
SL	07/20/2006	1130	07/21/2006	1230
SL	08/14/2006	0730	08/15/2006	0830
SL	09/27/2006	0930	09/28/2006	1030
SL	10/31/2006	1000	11/01/2006	1100
SL	11/20/2006	0930	11/21/2006	1030
SL	12/27/2006	0900	12/28/2006	1000

Grab Sampling (All times in EST)

Site	Start Date	Start Time	End Date	End Time
SL	01/04/2006	0922	01/04/2006	0926
SL	02/02/2006	0849	02/02/2006	0852
SL	03/03/2006	0701	03/03/2006	0704
SL	04/12/2006	0614	04/12/2006	0617
SL	05/01/2006	0735	05/01/2006	0737
SL	06/01/2006	0743	06/01/2006	0746
SL	07/11/2006	0632	07/11/2006	0636
SL	08/01/2006	0622	08/01/2006	0627
SL	09/11/2006	0726	09/11/2006	0728
SL	10/16/2006	0753	10/16/2006	0757
SL	11/02/2006	0926	11/02/2006	0930
SL	12/06/2006	0825	12/06/2006	0829

Site	Start Date	Start Time	End Date	End Time
LL	01/04/2006	0939	01/04/2006	0942
LL	02/02/2006	0905	02/02/2006	0907
LL	03/03/2006	0718	03/03/2006	0721
LL	04/12/2006	0631	04/12/2006	0633
LL	05/01/2006	0752	05/01/2006	0755
LL	06/01/2006	0800	06/01/2006	0802
LL	07/11/2006	0651	07/11/2006	0653
LL	08/01/2006	0656	08/01/2006	0700
LL	09/11/2006	0739	09/11/2006	0741
LL	10/16/2006	0815	10/16/2006	0820

LL 11/02/2006	0952	11/02/2006	0955
LL 12/06/2006	0847	12/06/2006	0851

Site	Start Date	Start Time	End Date	End Time
DS	01/04/2006	0957	01/04/2006	0959
DS	02/02/2006	0923	02/02/2006	0926
DS	03/03/2006	0737	03/03/2006	0740
DS	04/12/2006	0649	04/12/2006	0651
DS	05/01/2006	0813	05/01/2006	0815
DS	06/01/2006	0819	06/01/2006	0822
DS	07/11/2006	0714	07/11/2006	0716
DS	08/01/2006	0717	08/01/2006	0721
DS	09/11/2006	0755	09/11/2006	0757
DS	10/16/2006	0846	10/16/2006	0849
DS	11/02/2006	1014	11/02/2006	1016
DS	12/06/2006	0918	12/06/2006	0920

Site	Start Date	Start Time	End Date	End Time
BL	01/04/2006	1033	01/04/2006	1036
BL	02/02/2006	1003	02/02/2006	1005
BL	03/03/2006	0818	03/03/2006	0821
BL	04/12/2006	0724	04/12/2006	0727
BL	05/01/2006	0853	05/01/2006	0855
BL	06/01/2006	0902	06/01/2006	0909
BL	07/11/2006	0749	07/11/2006	0751
BL	08/01/2006	0808	08/01/2006	0812
BL	09/11/2006	0824	09/11/2006	0826
BL	10/16/2006	0932	10/16/2006	0935
BL	11/02/2006	1055	11/02/2006	1057
BL	12/06/2006	0953	12/06/2006	0955

Site	Start Date	Start Time	End Date	End Time
BB	01/04/2006	1041	01/04/2006	1044
BB	02/02/2006	1014	02/02/2006	1016
BB	03/03/2006	0829	03/03/2006	0831
BB	04/12/2006	0736	04/12/2006	0739
BB	05/01/2006	0915	05/01/2006	0917
BB	06/01/2006	0917	06/01/2006	0921
BB	07/11/2006	0807	07/11/2006	0810
BB	08/01/2006	0822	08/01/2006	0825
BB	09/11/2006	0833	09/11/2006	0835
BB	10/16/2006	0946	10/16/2006	0949
BB	11/02/2006	1107	11/02/2006	1110
BB	12/06/2006	1006	12/06/2006	1018

7) Associated researchers and projects –

The DNERR water quality monitoring program occurs at the corresponding nutrient sample sites. A YSI 6600 datasonde is deployed at each site measuring: dissolved oxygen, salinity, water temperature, depth, turbidity, and pH. Weather data is collected in both the St. Jones River and Blackbird Creek watershed near nutrient/water quality sites as another portion of the NERRS

SWMP program. An additional stormwater sampling program is underway to analyze the impact of agricultural BMP's at sites in the Blackbird Creek Watershed, St. Jones River Watershed.

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 –

Excel data files containing measured values received from the VIMS Analytical Laboratory are used to generate calculated parameter values and create a yearly Excel file. Both directly measured and calculated values were entered into this document by Michael G. Mensinger. Once the yearly file is complete, the “Nutrient Rounding Macro”, developed by the CDMO staff, is run on the file to ensure proper significant figures and decimal places exist. The yearly file is imported into EQ Win using the nutrient import (.EQI) file. Various graphs and queries are used to verify data validity. Michael G. Mensinger is also responsible for a visual QA/QC to verify no entry errors are present. The original Excel files received from VIMS are archived on the State of Delaware server. Edited files containing additional calculated parameters are archived on the State of Delaware server and sent to the CDMO for additional archiving.

10) Parameter Titles and Variable Names by Data Category –

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

Data Category	Parameter	Variable Name	Units of Measure
i) Phosphorus:	*Orthophosphate, Filtered	PO4F	mg/L as P

ii) Nitrogen:	*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
iii) Plant Pigments:	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
iv) Other Lab Parameters:			
	Silicate, Filtered	SiO4F	mg/L as SI
iv) Field Parameters: none			

Notes:

1. Time is coded based on a 2400 hour clock and is referenced to Eastern Standard Time (EST).
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 and Calculate Laboratory Parameters –

i) Variables Measured Directly:

Nitrogen Species:	NO2F, NO23F, NH4F
Phosphorus:	PO4F
Other:	CHLA_N, PHEA, SiO4F

ii) Computed Variables:

Nitrogen Species:	NO3: (NO23F-NO2F)
	DIN: (NO23F+NH4F)

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. Table 1 presents the current MDL's; these values are reviewed and revised periodically.

Table 1. Method Detection Limits (MDL) for measured water quality parameters.

Parameter	Variable	Method Detection Limit	Dates in Use
Ammonium	NH4F	0.0015 mg/L as N	2002-2006
Nitrite	NO2F	0.0002 mg/L as N	2002-2006
Orthophosphate	PO4F	0.0006 mg/L as P	2002-2006
Nitrite + Nitrate, filtered	NO23F	0.0008 mg/L as N	2002-2006
Chlorophyll a	CHLA	0.5000	2002-2006
Phaeophytin	PHEA	0.5000	2002-2006
Silica	SiO4F	0.008 mg/L	2003-2006

13) Laboratory Methods –

i) Parameter: Orthophosphate

Method References:

Virginia Institute of Marine Science Analytical Service Center.

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

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.

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.

Method Descriptor:

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

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. The range is 1-50 ppb.

Preservation Method:

100ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47mm GF/C filter may be used to filter the sample prior to filtering through the 0.45um Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day.

ii) Parameter: Nitrite

Method References:

Virginia Institute of Marine Science Analytical Service Center.

SKALAR Method 467

Method Descriptor:

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

An adaptation of the diazotization method. Under acidic conditions, nitrite ion reacts with sulfanilamide to yield a diazo compound which couples with

N-1-napthylethylenediamine dihydrochloride to form a soluble dye which is measured colorimetrically at 540nm. The range is 0.001 to 0.050 mg/L.

Preservation Method:

100ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47mm GF/C filter may be used to filter the sample prior to filtering through the 0.45um Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day.

iii) Parameter: Nitrate + Nitrite

Method References:

Virginia Institute of Marine Science Analytical Service Center.

SKALAR Method: Nitrate + Nitrite/ Total Dissolved Nitrogen Catnr. 461-353.2 issue 120293/MH/93128060.

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.

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.

Method Descriptor:

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

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 $\text{NO}_3^- + \text{NO}_2^-$ concentration. The color development chemistry is the same as that used in Nitrite. Range is 0 -1.2 mg/L.

Preservation Method:

100ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47mm GF/C filter may be used to filter the sample prior to filtering through the 0.45um Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day.

iv) Parameter: Ammonia

Method References:

Virginia Institute of Marine Science Analytical Service Center.

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.

Method Descriptor:

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

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. The range is 0.01 - 2.0 mg/L.

Preservation Method:

100ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47mm GF/C filter may be used to filter the sample prior to filtering through the 0.45um Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day.

v) Parameter: Chlorophyll and Pheophytin

Method References:

Virginia Institute of Marine Science Analytical Service Center.

Strickland, J.D.H., and Parsons, 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 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.

Method Descriptor:

Instrumentation: Milton Roy Spectronic 1201 spectrophotometer or Turner Designs TD-700 fluorometer. The two methods for determining Chlorophyll a given here are with 1) a scanning spectrophotometer and 2) a Turner Design fluorometer. 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 1-3mLs of 90% acetone are 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 a spectrophotometer or fluorometer. If the samples can not be read within that time period, storage in the freezer at -20°C for a few days is acceptable. If pheophytin measurements are desired, the sample is acidified and read again.

Preservation Method:

A 100ml sample is filtered through a 47mm Whatman GF/F filters using a vacuum-pump and filter flask apparatus. The Whatman type GF/F filter is folded immediately after sample filtering, enclosed in tinfoil, placed in a sealed bag, and placed in the freezer until it is sent off for analysis the following day.

vi) **Parameter: Silicate**

Method References:

Virginia Institute of Marine Science Analytical Service Center.

Technicon Industrial Systems Method: Silica. 1973. Technicon Auto-analyzer II Industrial Method No. 186-72W, Silicates in Water and Seawater.

U.S. EPA. 1982. Methods for Chemical Analysis of Water and Wastewater, 18th edition. Method 4500-Si F. Automated Method for Molybdate-Reactive Silica. pp. 4-122 through 4-123.

Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. Methods of Seawater Analysis. Verlag Chemie, Federal Republic of Germany. pp. 175-180.

Method Descriptor:

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.

The determination of soluble silica is based on the reduction

Preservation Method:

100ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47mm GF/C filter may be used to filter the sample prior to filtering through the 0.45um Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the refrigerator until shipment time arrives the following day. Samples may be kept up to 28 days.

14) Reporting of Missing Data and 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 (significant for Delaware: >1.0cm occurred within 72 hours of sampling)
U	Lab analysis from unpreserved sample
S	Data suspect, see metadata for further details

15) **QA/QC Programs** – [This section describes field variability, laboratory variability, the use of inter-organizational splits, sample spikes, standards and cross calibration exercises.]

a) **Precision:**

- i) **Field Variability** – True field replicates are taken at each site during grab sampling. The one replicate is a successive grab. Sample XXXXXX-G1 is taken and the sampler emptied. The grab sampler is deployed once again to acquire XXXXXX-G2.
- 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 analyzed a matrix spike once for every ten samples.
- ii) **Standard Reference Material Analysis** –information unavailable
- iii) **Cross Calibration Exercises** – none

16) **Other Remarks** –

On 5/16/2025 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.

Flag/code	If also C	Historic Letter Code	Historic Code Definition
<1> [SUL]		A	Value above upper limit of method detection
<4> [SBL]	<4> [SCB]	B	Value below method detection limit
<i>no need to flag/code unless combined</i>		C	Calculated value
<3> [GCD]	<3> [GCR]	D	Data deleted or calculated value could not be determined due to deleted data, see metadata for details
<1> (CHB)		H	Sample held beyond specified holding time
<0> (CSM) unless other flag		K	Check metadata for further details
<2> [GDM]	<2> [GOM]	M	Data missing, sample never collected or calculated value could not be determined due to missing data
<3> [SNV] and <1> [SOC] for components (CRS) or F_Record (CRS)		N	Negative calculated value
<0> (CJS)		P	Significant precipitation (reserve defined, see metadata for further details)
<1> (CSM)		U	Lab analysis from unpreserved sample
		S	Data suspect, see metadata for further details

a) The chlorophyll a (CHLA) and phaeophytin (PHEA) values from the March 03, 2006 (07:21 EST) Lebanon Landing grab sample (G-2) are not available. These values were not reported by the analytical lab due to cloudiness in the acetone extract.

b) The fifth (14:30 EST) and sixth (17:00 EST) samples from the April 26/27, 2006 diel data were not collected by the Isco sampler due to possible and probable intake tube blockage. As such, no data is present for these two sample times.

c) The nitrite (NO₂) value (0.1350) from the sixth (22:30 EST) diel sample on October 31, 2006 is extremely high compared to the other NO₂ values from this data set. The data was retained, but is viewed as highly suspect.

d) The chlorophyll a (CHLA) values (92.48 and 94.15) from the Beaver Branch grab samples collected on June 1, 2006 (09:17 and 09:21 EST) are much higher than expected. The data were retained, but considered potentially anomalous.

e) Rainfall for 2006:

January Precipitation Totals (mm)

Monthly Total (mm): 84.2

February Precipitation Totals (mm)

Monthly Total (mm): 36.9

March Precipitation Totals (mm)

Monthly Total (mm): 5.7

April Precipitation Totals (mm)

Monthly Total (mm): 0.9

May Precipitation Totals (mm)

Monthly Total (mm): 5.6

June Precipitation Totals (mm)

Monthly Total (mm): 204.7

July Precipitation Totals (mm)

Monthly Total (mm): 140.6

August Precipitation Totals (mm)

Monthly Total (mm): 6.5

September Precipitation Totals (mm)

Monthly Total (mm): 126.1

October Precipitation Totals (mm)

Monthly Total (mm): 129.9

November Precipitation Totals (mm)

Monthly Total (mm): 154.3

December Precipitation Totals (mm)

Monthly Total (mm): 39.9

2006 Annual Total (mm): 935.3