# Delaware (DEL) National Estuarine Research Reserve Site Nutrient Metadata (February 2003-December 2003) 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. 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. 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 0.45mm 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 0.45mm 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.

# Nutrient/Chla Monitoring Program Flag Column Code:

- A = Value above upper limit of detection
- B = Value below method detection limit
- C = Calculated value
- D= Deleted data
- H = Sample held beyond specific holding time
- K = Check metadata for further information
- M = Data missing, sample never collected or calculated value could not be determined due to missing data
- P = Significant rainfall, >1.0cm occurred within 72 hours of sampling
- U= Lab analysis from unpreserved sample
- S = Data suspect, see metadata for further details

# 6) Data collection period –

# **Diel Sampling (All times in EST)**

Site Start Date	Start Time	End Date	End Time	
SL No January diel sample taken due to ice				
SL No February diel sample taken due to ice				
SL 03/25/2003	0830	03/26/2003	0930	
SL 04/22/2003	0830	04/23/2003	0930	
SL 05/27/2003	1300	05/28/2003	1400	
SL 06/02/2003	0800	06/03/2003	0900	
SL 07/08/2003	1130	07/09/2003	1230	
SL 08/07/2003	1100	08/08/2003	1200	
SL 09/09/2003	0500	09/10/2003	0600	
SL 10/07/2003	0300	10/08/2003	0400	
SL 11/04/2003	0030	11/05/2003	0130	
SL 12/09/2003	0930	12/10/2003	0530	

# **Grab Sampling (All times in EST)**

Gi ab Sampling (A			D 0.TT
Site Start Date	Rep 1 Time	Start Date	Rep 2 Time
SL No January gr			
SL 02/13/2003	1048	02/13/2003	1053
SL 03/11/2003	0953	03/11/2003	0957
SL 04/30/2003	0611	04/30/2003	0615
SL 05/29/2003	0713	05/29/2003	0716
SL 06/10/2003	0945	06/10/2003	0948
SL 07/24/2003	0717	07/24/2003	0720
SL 08/25/2003	0403	08/25/2003	0407
SL 09/26/2003	0431	09/26/2003	0434
SL 10/28/2003	0559	10/28/2003	0603
SL 11/25/2003	0501	11/25/2003	0505
SL 12/17/2003	1028	12/17/2003	1030
Site Start Date	Rep 1 Time	Start Date	Rep 2 Time
LL No January gr			
LL 02/13/2003	1109	02/13/2003	1113
LL 03/11/2003	1023	03/11/2003	1026
LL 04/30/2003	0634	04/30/2003	0639
LL 05/29/2003	0732	05/29/2003	0735
LL 06/10/2003	1001	06/10/2003	1003
LL 07/24/2003	0744	07/24/2003	0749
LL 08/25/2003	0421	08/25/2003	0425
LL 09/26/2003	0448	09/26/2003	0452
LL 10/28/2003	0617	10/28/2003	0620
LL 11/25/2003	0522	11/25/2003	0526
LL 12/17/2003	1048	12/17/2003	1050
Site Start Date	Rep 1 Time	Start Date	Rep 2 Time
DS No January gr			
DS 02/13/2003	1133	02/13/2003	1138
DS 03/11/2003	1045	03/11/2003	1048
DS 04/30/2003	0658	04/30/2003	0704
DS 05/29/2003	0749	05/29/2003	0752
DS 06/10/2003	1025	06/10/2003	1028

0805	07/24/2003	0810
0437	08/25/2003	0440
0506	09/26/2003	0510
0635	10/28/2003	0639
0540	11/25/2003	0545
1105	12/17/2003	1108
Rep 1 Time	Start Date	Rep 2 Time
ab samples taker	n due to ice cond	litions
1224	02/13/2003	1229
1130	03/11/2003	1132
0736	04/30/2003	0738
0837	05/29/2003	0841
1108	06/10/2003	1110
0900	07/24/2003	0906
0511	08/25/2003	0514
0541	09/26/2003	0545
0705	10/28/2003	0708
0616	11/25/2003	0619
1221	12/17/2003	1224
Rep 1 Time	Start Date	Rep 2 Time
	02/13/2003	1250
		1141
0744	04/30/2003	0749
0846	05/29/2003	0850
1118	06/10/2003	1120
0914		0920
		0529
		0555
0713	10/28/2003	0717
les taken due to		
1233	12/17/2003	1235
	0437 0506 0635 0540 1105 Rep 1 Time rab samples taken 1224 1130 0736 0837 1108 0900 0511 0541 0705 0616 1221 Rep 1 Time rab samples taken 1245 1138 0744 0846 1118 0914 0526 0549 0713 les taken due to	0437 08/25/2003 0506 09/26/2003 0635 10/28/2003 0540 11/25/2003 1105 12/17/2003 Rep 1 Time Start Date rab samples taken due to ice condition of the condit

# 7) Associated researchers and projects –

The DNERR water quality monitoring program occurs at the corresponding nutrient sample sites. AYSI 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 <a href="http://cdmo.baruch.sc.edu/">http://cdmo.baruch.sc.edu/</a>. 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. Both directly measured and calculated values were entered into this document by Michael G. Mensinger. Michael G. Mensinger is also responsible for a visual QA/QC to make sure 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	of Measure
i) Phosphorus:	*Orthophosphate	PO4F	mg/L as P
ii) Nitrogen:	*Nitrite + Nitrate, Filtered  *Nitrite, Filtered  *Nitrate, Filtered  *Ammonium, Filtered  *Dissolved Inorganic Nitrogen	NO23F NO2F NO3F NH4F DIN	mg/L as N mg/L as N mg/L as N mg/L as N mg/L as N
iii) Plant Pigments:	*Chlorophyll a *Phaeophytin	CHLA_N PHEA	μg/L μg/L
iv) Other Lab Paran	neters: 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 NO23 or NO2 or 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	2002-2003
Nitrite	NO2F	0.0002 mg/L as N	2002-2003
Orthophosphate	PO4F	0.0006 mg/L as P	2002-2003
Nitrite + Nitrate, filtere	ed NO23F	0.0008 mg/L as N	2002-2003
Chlorophyll a	CHLA	0.5000	2002-2003
Phaeophytin	PHEA	0.5000	2002-2003
Silicate	SiO4F	0.008  mg/L	2003

# 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:

<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.

# 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 catalized 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 vaccum-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 0.45mm 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 sulfanilimide 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 vaccum-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.

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. 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-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  $NO_3^- + NO_2^-$  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 vaccum-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.

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 vaccum-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 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.

<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.

#### Method Descriptor:

Instrumentation: Milton Roy Spectronic 1201 spectrophometer 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 vaccum-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 vaccum-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	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

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 none
- iii) Inter-organizational splits samples were not split or analyzed by two different labs
- b) Accuracy:
- i) Sample Spikes –information unavailable

- ii) Standard Reference Material Analysis -information unavailable
- iii) Cross Calibration Exercises DNERR did not participate in cross calibration exercises.

#### 16) Other Remarks-

On 07/19/2024 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]	<>[GOR]	D	Data deleted or calculated value could not be determined due to deleted data, see metadata for details
<1>(OHB)		Н	Sample held beyond specified holding time
<0>(CSM) unless other flag		K	Check metadata for further details
<-2>[GDM]	<-2>[GOM]	М	Data missing, sample never collected or calculated value could not be determined due to missing data
<-3>[SNV] and <1>[SOC] for components		N	Negative calculated value
(CRE) or F_Record (CRE)		Р	Significant precipitation (reserve defined, see metadata for further details)
<0>(OUS)		U	Lab analysis from unpreserved sample
<1>(CSM)		S	Data suspect, see metadata for further details

- a) September 2003 marked the decision to include Silicate (SiO4F) in the list of analyzed parameters, thus the first data set for this parameter is the diel sample set on September 09-10, 2003.
- b) No Beaver Branch data are available for the grab samples taken in November 2003 (25<sup>th</sup>). The grab sampler broke making sample acquisition impossible.
- c) No data are available for the first two December 2003 diel samples (0430 EST & 0700 EST) due to equipment failure. The sampler indicated "no liquid detected" caused by suspected freezing near the strainer or in the intake hose.

# d) Rainfall for 2003:

# January Precipitation Totals (mm)

01 12.700

02 2.032

03	8.128
05	.254
06	1.270
08	1.270
29	1.524
30	.254
31	.508

Monthly Total (mm): 27.94

# February Precipitation Totals (mm)

<u>Februa</u>	ary Precipitation 10
01	9.906
04	8.382
07	1.524
09	7.620
10	3.048
15	1.524
18	.254
19	14.224
20	.762
21	7.874
22	39.116
23	6.858
27	1.270
28	7.112

Monthly Total (mm): 109.474

# March Precipitation Totals (mm)

2 9.906 3 .254 5 5.588 6 10.922 13 1.270 16 9.398 17 12.192

15.748 20 4.318 21 22 .254 26 6.604 28 1.778 29 13.208 30 4.572

Monthly Total (mm): 96.012

# April Precipitation Totals (mm)

- 1.016 20.828
- 9 26.670
- 10 3.556
- 29.972 11
- 6.096 12
- 18 8.636 1.524
- 21 22
- .508 25 4.318
- 26 2.286

Monthly Total (mm): 105.41

# May Precipitation Totals (mm)

- 10.160
- 5 .508
- 6 1.016
- 4.318
- .762
- 3.810
- 1.778 10
- 11 .762
- 48.768 16
- 18 .508

8.382 21 22 1.778 23 9.144 .508 24 25 20.066 26 32.004 27 2.032 28 5.588 29 1.016 31 4.318

Monthly Total (mm): 157.226

#### June Precipitation Totals (mm) 8.636 4 11.938 9.398 55.372 9 .508 11 6.350 12 7.874 16.764 13 17 10.160 18 24.384 19 10.414 20 35.814 21 19.304 3.048 27

Monthly Total (mm): 219.964

# July Precipitation Totals (mm) 1 .762 2 22.606 3 41.910 5 1.016

```
4.572
6
9
      11.684
10
      8.636
12
      1.778
13
      7.112
14
      15.240
18
      .254
22
      8.636
23
      2.540
24
      4.572
28
      23.114
29
      6.350
30
      .762
```

Monthly Total (mm): 161.544

# August Precipitation Totals (mm) .508

3 2.794 5.080 5 35.560 6 7.874 16.764 7 9 .254 10 6.350 12 5.842 13 .254 16 15.494 17 3.302

.508

1.270 26

22

29 5.842

30 6.604

Monthly Total (mm): 114.3

# September Precipitation Totals (mm)

.508 2 3 6.858 8.128 .254

11.430

12 10.414 6.858

13 14 .762

15 1.778 18 21.590

19 4.318

23 28.448

25 .254

27 9.652

28 .762

Monthly Total (mm): 112.014

# October Precipitation Totals (mm)

9 .254

.254 11

1.270 12

14 15.494

15 2.032

17 1.524

22 3.302

25 .254

26 1.524

27 24.638

28 7.366

29 25.908

.254 31

Monthly Total (mm): 84.074

#### November Precipitation Totals (mm) 0.254 22.86 5 6 27.178 12 18.034 .254 13 18 .254 19 33.528 20 5.334 23 0.254 24 3.556

Monthly Total (mm): 125.73

14.224

28

# December Precipitation Totals (mm)

29.21 0.508 1.524 8 1.27 10 3.048 31.496 11 26.67 15 18 8.636 25 33.782 30 0.508 31 1.778

Monthly Total (mm): 138.43

2003 Annual Total (mm): 1452.118