Delaware (DEL) National Estuarine Research Reserve Nutrient Metadata (January 2005-December 2005) 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 0.45m 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 0.45m 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 slacklow 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 watersheddraining 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.

End Time

1030

End Date

01/04/2005

6) Data collection period –

Site Start Date

SL 01/03/2005

LL 09/21/2005

LL 10/31/2005

0733

0337

09/21/2005

10/31/2005

0736

0340

Diel Sampling (All times in EST)

Start Time

0930

SL 01/03/2003	0930	01/04/2003	1030
SL 02/23/2005	0400	02/24/2005	0500
SL 03/15/2005	0800	03/16/2005	0900
SL 04/05/2005	1300	04/06/2005	1400
SL 05/25/2005	0800	05/26/2005	0900
SL 06/15/2005	1030	06/16/2005	1130
SL 07/20/2005	0630	07/21/2005	0730
SL 08/16/2005	0130	08/17/2005	0230
SL 09/12/2005	1100	09/13/2005	1200
SL 10/24/2005	0830	10/25/2005	0930
SL 11/28/2005	1200	11/29/2005	1300
SL 12/28/2005	0900	12/29/2005	1000
Grab Sampling (All times in ES	<u>T)</u>	
Site Start Date	Start Time	End Date	End Time
SL 01/11/2005	0647	01/11/2005	0650
SL 02/15/2005	0826	02/15/2005	0829
SL 03/29/2005	0811	03/29/2005	0813
SL 04/27/2005	0618	04/27/2005	0621
SL 05/31/2005	0928	05/31/2005	0931
SL 06/28/2005	0738	06/28/2005	0744
SL 07/26/2005	0724	07/26/2005	0727
SL 08/04/2005	0647	08/04/2005	0650
SL 09/21/2005	0715	09/21/2005	0718
SL 10/31/2005	0321	10/31/2005	0324
SL 11/08/2005	0839	11/08/2005	0842
SL 12/20/2005	0832	12/20/2005	0834
Site Start Date	Start Time	End Date	End Time
LL 01/11/2005	0704	01/11/2005	0706
LL 02/15/2005	0843	02/15/2005	0845
LL 03/29/2005	0827	03/29/2005	0830
LL 04/27/2005	0634	04/27/2005	0637
LL 05/31/2005	0947	05/31/2005	0950
LL 06/28/2005	0812	06/28/2005	0815
LL 07/26/2005	0744	07/26/2005	0747
LL 08/04/2005	0706	08/04/2005	0709
22 00/01/2000	0700	00/01/2005	0707

LL 11/08/2005 LL 12/20/2005	0853 0850	11/08/2005 12/20/2005	0856 0853
Site Start Date	Start Time	End Date	End Time
DS 01/11/2005	0719	01/11/2005	0722
DS 02/15/2005	0900	02/15/2005	0904
DS 03/29/2005	0845	03/29/2005	0848
DS 04/27/2005 DS 05/31/2005	0654	04/27/2005	0657
	1008 0831	05/31/2005 06/28/2005	1010
DS 06/28/2005 DS 07/26/2005	0806	06/28/2005	0834
DS 07/20/2003 DS 08/04/2005	0729	08/04/2005	0809 0732
DS 09/21/2005	0751	09/21/2005	0754
DS 10/31/2005	0356	10/31/2005	0401
DS 10/31/2003 DS 11/08/2005	0911	11/08/2005	0913
DS 12/20/2005	0911	12/20/2005	0913
DS 12/20/2003	0711	12/20/2003	0713
Site Start Date	Start Time	End Date	End Time
BL 01/11/2005	0753	01/11/2005	0757
BL 02/15/2005	0946	02/15/2005	0949
BL 03/29/2005	0932	03/29/2005	0934
BL 04/27/2005	0733	04/27/2005	0735
BL 05/31/2005	1050	05/31/2005	1053
BL 06/28/2005	0918	06/28/2005	0926
BL 07/26/2005	0857	07/26/2005	0901
BL 08/04/2005	0815	08/04/2005	0819
BL 09/21/2005	0838	09/21/2005	0842
BL 10/31/2005	0435	10/31/2005	0437
BL 11/08/2005	0945	11/08/2005	0948
BL 12/20/2005	0952	12/20/2005	0955
Site Start Date	Start Time	End Date	End Time
BB 01/11/2005	0802	01/11/2005	0805
BB 02/15/2005	0956	02/15/2005	0958
BB 03/29/2005	0942	03/29/2005	0944
BB 04/27/2005	0741	04/27/2005	0744
BB 05/31/2005	1058	05/31/2005	1100
BB 06/28/2005	0936	06/28/2005	0941
BB 07/26/2005	0909	07/26/2005	0912
BB 08/04/2005	0829	08/04/2005	0832
BB 09/21/2005	0850	09/21/2005	0854
BB 10/31/2005	0446	10/31/2005	0449
BB 11/08/2005	0956	11/08/2005	0959
BB 12/20/2005	1003	12/20/2005	1006

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 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	2002-2005
Nitrite	NO2F	0.0002 mg/L as N	2002-2005
Orthophosphate	PO4F	0.0006 mg/L as P	2002-2005
Nitrite + Nitrate,	filtered NO23F	0.0008 mg/L as N	2002-2005
Chlorophyll a	CHLA	0.5000	2002-2005
Phaeophytin	PHEA	0.5000	2002-2005
Silicate	SiO4F	0.008 mg/L	2003-2005

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 catalizyed 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 0.45um 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 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.

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.

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: <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.

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. 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. <u>Methods for Chemical Analysis of Water and Wastes</u>, 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 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. <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. 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
C	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 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.

		Historic	
Flag/code	If also C	Letter Code	Historic Code Definition
<1>[SUL]		Α	Value above upper limit of method detection
<-4>[SBL]	<-4>[SOB]	В	Value below method detection limit
no need to flag/code unless combined		С	Calculated value
<-3>[GQD]	<>[COR]	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]	M	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	Sgnificant 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

- a) The silicate (SiO4F) value from the January 04, 2005 (10:30 EST) diel sample set is not available because this value was not reported by the analytical lab.
- b) Rainfall for 2005:

January Precipitation Totals (mm)

<u>Januar</u>	y r recipitation rotals (iiii
05	1.5
06	1.5
08	10.4
11	3.3
12	0.3
14	43.4
20	0.5
26	5.3
30	1.3
31	5.3

Monthly Total (mm): 72.8

February Precipitation Totals (mm)

04	0.3	
10	2.8	
14	15	
16	0.8	
20	1.5	
21	9.1	
22	0.8	
23	0.3	
24	0.3	
25	4.1	
28	7.6	

Monthly Total (mm): 42.6

March Precipitation Totals (mm)

1 5.1 8 19.3

11	1.3
20	5.
23	32.5
25	0.3
27	1.5
28	16.0
29	0.5

Monthly Total (mm): 81.6

April Precipitation Totals (mm)

2.3 43.9 2 4 0.5 7 5.8 8 34.8 23 4.8 24 0.5 27 6.6 13.5 30

Monthly Total (mm): 112.7

May Precipitation Totals (mm)

1 10.4 2 0.3 0.3 3 6 4.1 7 0.5 14 1.3 15 0.3 20 83.3 21 0.3 22 0.3 23 0.5 24 0.3 25 10.2 30 0.5

Monthly Total (mm): 112.6

June Precipitation Totals (mm)

3 26.2 4 0.5 6 17.5 7 2.5 8 2 9 1.8 16 1.8 22 21.3

- 23 0.3
- 27 24.1
- 29 9.1

Monthly Total (mm): 107.1

July Precipitation Totals (mm)

- 1 0.3 5 9.7
- 6 2.8
- 7 2.5
- 8 36.3
- 14 6.4
- 2.8 16
- 17 24.9
- 25 5.8
- 26 0.3
- 27 17.3
- 29 18.8
- 30 7.6

Monthly Total (mm): 135.5

August Precipitation Totals (mm)

- 14.7 5
- 6 3.3
- 7 3.0
- 8 41.4
- 9 5.6
- 10 0.3
- 16 56.4
- 17 1.0
- 19 2.3
- 27 3.8
- 1.3 28
- 30 6.4

Monthly Total (mm): 139.5

September Precipitation Totals (mm)

No Precipitation Recorded

Monthly Total (mm): 0

October Precipitation Totals (mm)

- 1.5
- 6 1.0
- 7 17.5
- 8 55.9
- 9 0.3
- 10 2.5

```
11
       28.2
12
       2.3
13
        16.3
14
       0.3
21
       8.4
22
24
       29.7
       29.0
25
       18.3
26
       0.3
```

Monthly Total (mm): 211.5

November Precipitation Totals (mm) 10 4.3

10 4.3 17 0.5 21 31.8 22 32.8 24 0.5 29 16.3 30 3.0

Monthly Total (mm): 89.2

December Precipitation Totals (mm)

13.0 4 6 1.0 9 19.6 10 0.5 15 19.1 16 10.2 25 11.9 26 0.5 29 13.5 31 0.5

Monthly Total (mm): 89.8

2005 Annual Total (mm): 1194.9