Delaware (DEL) NERR Nutrient Metadata
January 01, 2009 - December 31, 2009
Latest Update: April 8, 2013

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

a) Reserve Contacts:

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c) Other Contacts and Programs: None

Michael G. Mensinger is responsible for the collection, implementation, and data management related to the DNERR nutrient program. Carol Pollard (VIMS) is responsible for sample processing, analyses, and data output.

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 six sampling sites, three located in the St. Jones component and three 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 St. Jones watershed drainage area is 228.1 km2 (22810 ha) and Scotton Landing's drainage area is 196.2 km2 (19620 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 Blackbird watershed drainage area is 90.6 km2 (9060 ha) and Blackbird Landing's drainage area is 48.3 km2 (4830 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 St. Jones watershed drainage area is 228.1 km2 (22810 ha) and Lebanon Landing's drainage area is 171.6 km2 (17160 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 St. Jones watershed drainage area is 228.1 km2 (22810 ha) and Division Street’s drainage area is 81.2 km2 (8120 ha). 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 Blackbird watershed drainage area is 90.6 km2 (9060 ha) and Beaver Branch’s drainage area is 4.8 km2 (480 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

6) Taylor’s Bridge (TB) - is located in the upper Blackbird Creek. . The sampling site is situated on the east side of Taylor’s Bridge on Route 9**.** 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 Blackbird watershed drainage area is 90.6 km2 (9060 ha) and Taylor’s Bridge’s drainage area is 63.6 km2 (6360 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 Range: 0.1-10.2 ppt
Tidal Range: Spring Mean (m) – 1.31
Neap Mean (m)-0.91
Position: Latitude 39 degree 24' 17.8" N
Longitude 75 degree 35' 58.1" 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
deltbnut = Delaware Reserve nutrient data for Taylor's Bridge

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 triplicate samples are taken utilize a "1" for the first sample and a "2" for the second sample, etc. 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	Not performed due to ice			
SL	02/18/2009	1230	02/19/2009	1330
SL	03/16/2009	0730	03/17/2009	0830
SL	04/01/2009	0815	04/01/2009	0915
SL	05/28/2009	0900	05/29/2009	1000
SL	06/24/2009	0600	06/25/2009	0700
SL	07/23/2009	0730	07/24/2009	0830
SL	08/25/2009	0830	08/26/2009	0930
SL	09/22/2009	0800	09/23/2009	0900
SL	10/20/2009	0800	10/21/2009	0900
SL	11/23/2009	1030	11/24/2009	1130
SL	12/08/2009	0900	12/09/2009	1000

Grab Sampling (All times in EST)

Site	Start Date	Start Time	End Date	End Time
SL	01/14/2009	0847	01/14/2009	0847
SL	02/25/2009	1405	02/25/2009	1405
SL	03/06/2009	1028	03/06/2009	1028
SL	04/20/2009	1142	04/20/2009	1142
SL	05/12/2009	0747	05/12/2009	0747
SL	06/12/2009	0732	06/12/2009	0732
SL	07/10/2009	0718	07/10/2009	0718
SL	08/10/2009	0728	08/10/2009	0728
SL	09/09/2009	0736	09/09/2009	0736
SL	10/06/2009	0703	10/06/2009	0703
SL	11/23/2009	0930	11/23/2009	0935
SL	12/07/2009	0824	12/07/2009	0824

Site	Start Date	Start Time	End Date	End Time
LL	01/14/2009	0857	01/14/2009	0901
LL	02/25/2009	1421	02/25/2009	1421
LL	03/06/2009	1040	03/06/2009	1040

LL	04/20/2009	1157	04/20/2009	1157
LL	05/12/2009	0759	05/12/2009	0759
LL	06/12/2009	0742	06/12/2009	0742
LL	07/10/2009	0728	07/10/2009	0728
LL	08/10/2009	0739	08/10/2009	0739
LL	09/09/2009	0747	09/09/2009	0747
LL	10/06/2009	0716	10/06/2009	0716
LL	11/23/2009	0950	11/23/2009	0950
LL	12/07/2009	0834	12/07/2009	0834

Site	Start Date	Start Time	End Date	End Time
DS	01/14/2009	0917	01/14/2009	0917
DS	02/25/2009	1442	02/25/2009	1442
DS	03/06/2009	1102	03/06/2009	1102
DS	04/20/2009	1221	04/20/2009	1221
DS	05/12/2009	0816	05/12/2009	0816
DS	06/12/2009	0757	06/12/2009	0757
DS	07/10/2009	0743	07/10/2009	0743
DS	08/10/2009	0756	08/10/2009	0756
DS	09/09/2009	0804	09/09/2009	0808
DS	10/06/2009	0731	10/06/2009	0731
DS	11/23/2009	1048	11/23/2009	1048
DS	12/07/2009	0848	12/07/2009	0848

Site	Start Date	Start Time	End Date	End Time
BL	01/14/2009	0942	01/14/2009	0942
BL	02/25/2009	1526	02/25/2009	1526
BL	03/06/2009	1153	03/06/2009	1158
BL	04/20/2009	1302	04/20/2009	1302
BL	05/12/2009	0846	05/12/2009	0856
BL	06/12/2009	0825	06/12/2009	0825
BL	07/10/2009	0816	07/10/2009	0816
BL	08/10/2009	0823	08/10/2009	0823
BL	09/09/2009	0836	09/09/2009	0836
BL	10/06/2009	0800	10/06/2009	0800
BL	11/23/2009	1116	11/23/2009	1116
BL	12/07/2009	0914	12/07/2009	0914

Site	Start Date	Start Time	End Date	End Time
BB	01/14/2009	0953	01/14/2009	0953
BB	02/25/2009	1535	02/25/2009	1535
BB	03/06/2009	1208	03/06/2009	1208
BB	04/20/2009	1310	04/20/2009	1310
BB	05/12/2009	0917	05/12/2009	0917
BB	06/12/2009	0831	06/12/2009	0831
BB	07/10/2009	0822	07/10/2009	0825
BB	08/10/2009	0830	08/10/2009	0830
BB	09/09/2009	0844	09/09/2009	0844
BB	10/06/2009	0809	10/06/2009	0809
BB	11/23/2009	1121	11/23/2009	1121
BB	12/07/2009	0920	12/07/2009	0920

Site	Start Date	Start Time	End Date	End Time

TB 01/14/2009	1002	01/14/2009	1002
TB 02/25/2009	1544	02/25/2009	1544
TB 03/06/2009	1218	03/06/2009	1218
TB 04/20/2009	1321	04/20/2009	1321
TB 05/12/2009	0908	05/12/2009	0908
TB 06/12/2009	0840	06/12/2009	0840
TB 07/10/2009	0832	07/10/2009	0832
TB 08/10/2009	0836	08/10/2009	0836
TB 09/09/2009	0850	09/09/2009	0850
TB 10/06/2009	0816	10/06/2009	0816
TB 11/23/2009	1132	11/23/2009	1132
TB 12/07/2009	0926	12/07/2009	0926

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 and nutrient 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.

II. Physical Structure Descriptors:

9) Entry verification –

Entry verification:
Nutrient data are entered into a Microsoft Excel worksheet and processed using the NutrientQAQC Excel macro. The NutrientQAQC macro sets up the data worksheet,

metadata worksheets, and MDL worksheet; adds chosen parameters and facilitates data entry; allows the user to set the number of significant figures to be reported for each parameter and rounds using banker's rounding rules; allows the user to input MDL values and then automatically flags/codes measured values below MDL and inserts the MDL ; calculates parameters chosen by the user and automatically flags/codes for component values below MDL, negative calculated values, and missing data; allows the user to apply QAQC flags and codes to the data; produces summary statistics; graphs selected parameters

Michael G. Mensinger is responsible for these tasks as well as 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	0.0054 mg/L as N	01/01/2009 – 12/31/2009
Nitrite	NO2F	0.0002 mg/L as N	01/01/2009 – 12/31/2009
Orthophosphate	PO4F	0.0015mg/L as P	01/01/2009 – 12/31/2009
Nitrite + Nitrate	NO23F	0.0010 mg/L as N	01/01/2009 – 12/31/2009
Chlorophyll a	CHLA	0.50	01/01/2009 – 12/31/2009
Phaeophytin	PHEA	0.50	01/01/2009 – 12/31/2009
Silica	SiO4F	0.0080 mg/L	01/01/2009 – 12/31/2009

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 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.

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. 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 37ºC 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.
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 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 4ºC, 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 -20ºC 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) **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** – Triplicate samples are collected at a single site every other month during grab sampling. The triplicates are successive grabs. Sample #1 is taken and the sampler emptied. The grab sampler is deployed once again to acquire XXXXXX-G2, etc. During months when replicates are not taken, a single sample is collected from each site.

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

15) **QAQC flag definitions**

QAQC flag definitions:

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

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

16) **QAQC code definitions** – This section details the secondary QAQC Code definitions used in combination with the flags above.

QAQC code definitions:

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

General errors

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

Sensor errors

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

Parameter Comments

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

Record comments

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

Cloud cover

CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)
CFY	foggy
CHY	hazy
CCC	cloud (no percentage)

Precipitation

PNP	none
PDR	drizzle
PLR	light rain
PHR	heavy rain
PSQ	squally
PFQ	frozen precipitation (sleet/snow/freezing rain)
PSR	mixed rain and snow

Tide stage

TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide

Wave height

WH0	0 to <0.1 meters
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.6 meters
WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest

Wind speed

WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) **Other Remarks –**

Other remarks:

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of NO23F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the Reserve submitting the data.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2007-2010 were also flagged/coded, but either reported as the measured value or a blank cell. Any 2007-2011 nutrient/pigment data downloaded from the CDMO prior to November of 2011 will reflect this difference.

a) The January 2009 diel samples were not collected due to freezing/ice conditions.

b) Notes for <CSM> "See Metadata Code" usage with grab sample data:

The PHEA concentration (64.53) from SL0209-G1 associated with the February grab samples (02/25/2009, 14:05 EST) is outside the annual trend and considered suspect.

The CHLA concentration (76.92) from LL0809-G1 associated with the August grab samples (08/10/2009, 07:39 EST) is outside the annual trend and considered suspect.

The PHEA concentration (41.00) from LL0809-G1 associated with the August grab samples (08/10/2009, 07:39 EST) is outside the annual trend and considered suspect.

c) Major rain/storm events (exceeding 25.4 mm (1 inch) of rainfall in a single day) during 2009 took place on the following dates (data originates from the Delaware NERR St. Jones meteorological station):

April 14, 2009	(26.670 mm)
April 15, 2009	(33.782 mm)
May 26, 2009	(29.718 mm)
June 03, 2009	(31.242 mm)
June 05, 2009	(42.418 mm)
August 22, 2009	(88.900 mm)
September 10, 2009	(30.988 mm)
September 11, 2009	(68.072 mm)
September 27. 2009	(35.814 mm)
October 27, 2009	(30.480 mm)
October 28, 2009	(45.720 mm)

November 12, 2009	(54.356 mm)
December 09, 2009	(61.722 mm)