Delaware (DEL) NERR Nutrient Metadata
January 01, 2007 - December 31, 2007
Latest Update: November 15, 2011

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

a) Reserve Contacts:

Robert Scarborough (P.I)
Dept. of Natural Resources & Environmental Control
Division of Soil & Water Conservation
Delaware Coastal Programs/ National Estuarine Research Reserve Program
818 Kitts Hummock Road
Dover, Delaware 19901
Phone: 302-739-3436
e-mail: bob.scarborough@state.de.us

Michael G. Mensinger
Dept. of Natural Resources & Environmental Control
Division of Soil & Water Conservation
Delaware Coastal Programs/National Estuarine Research Reserve Program
818 Kitts Hummock Road
Dover, Delaware 19901
Phone: 302-739-3436
e-mail: mike.mensinger@state.de.us

b) Laboratory Contact:

Carol Pollard
Rt. 1208 Greate Road
Nutrient Analytical Laboratory
Virginia Institute of Marine Science
Gloucester Point, Virginia 23062
Phone: 804-684-7213
e-mail: pollard@VIMS.edu

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 3 sites in the Blackbird watershed. These sites coincide with the six datasonde sites: Scotton Landing, Lebanon Landing, Division Street, Blackbird Landing, Taylor's Bridge (non-SWMP water quality site) 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 were collected in January. In February a new sampling regime was implemented with triplicates collected at a randomly chosen station and single samples collected at the other 5 sites. Grab samples were 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 duplicate or 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	01/29/2007	0830	01/30/2007	0930
SL	02/21/2007	0930	02/22/2007	1030
SL	03/26/2007	0600	03/27/2007	0700
SL	04/17/2007	0830	04/18/2007	0930
SL	05/21/2007	0800	05/24/2007	0900
SL	06/20/2007	0800	06/21/2007	0900
SL	07/23/2007	0800	07/24/2007	0900
SL	08/22/2007	0800	08/23/2007	0900
SL	09/26/2007	1100	09/27/2007	1200
SL	10/15/2007	0800	10/16/2007	0900
SL	11/28/2007	0900	11/29/2007	1000
SL	12/11/2007	0830	12/12/2007	0930

Grab Sampling (All times in EST)

Site	Start Date	Start Time	End Date	End Time
SL	01/16/2007	0833	01/16/2007	0835
SL	02/27/2007	0827	02/27/2007	0833
SL	03/12/2007	0715	03/12/2007	0715
SL	04/03/2007	0731	04/03/2007	0731
SL	05/18/2007	0730	05/18/2007	0730
SL	06/01/2007	0810	06/01/2007	0810
SL	07/13/2007	0737	07/13/2007	0737
SL	08/08/2007	0733	08/08/2007	0733
SL	09/12/2007	1224	09/12/2007	1228
SL	10/30/2007	1141	10/30/2007	1141
SL	11/13/2007	1248	11/13/2007	1248
SL	12/04/2007	1307	12/04/2007	1307

Site	Start Date	Start Time	End Date	End Time
LL	01/16/2007	0852	01/16/2007	0856
LL	02/27/2007	0850	02/27/2007	0850
LL	03/12/2007	0746	03/12/2007	0746
LL	04/03/2007	0746	04/03/2007	0753
LL	05/18/2007	0744	05/18/2007	0744
LL	06/01/2007	0750	06/01/2007	0755
LL	07/13/2007	0751	07/13/2007	0751
LL	08/08/2007	0747	08/08/2007	0747
LL	09/12/2007	1244	09/12/2007	1244
LL	10/30/2007	1153	10/30/2007	1153
LL	11/13/2007	1303	11/13/2007	1303
LL	12/04/2007	1321	12/04/2007	1321

Site	Start Date	Start Time	End Date	End Time
DS	01/16/2007	0914	01/16/2007	0916
DS	02/27/2007	0907	02/27/2007	0907
DS	03/12/2007	0802	03/12/2007	0806
DS	04/03/2007	0811	04/03/2007	0811
DS	05/18/2007	0805	05/18/2007	0805
DS	06/01/2007	0733	06/01/2007	0733
DS	07/13/2007	0808	07/13/2007	0808
DS	08/08/2007	0806	08/08/2007	0806
DS	09/12/2007	1251	09/12/2007	1251
DS	10/30/2007	1213	10/30/2007	1213
DS	11/13/2007	1326	11/13/2007	1326
DS	12/04/2007	1340	12/04/2007	1340

Site	Start Date	Start Time	End Date	End Time
BL	01/16/2007	0947	01/16/2007	0951
BL	02/27/2007	0938	02/27/2007	0938
BL	03/12/2007	0851	03/12/2007	0851
BL	04/03/2007	0843	04/03/2007	0843
BL	05/18/2007	0840	05/18/2007	0840
BL	06/01/2007	0847	06/01/2007	0847
BL	07/13/2007	0841	07/13/2007	0841
BL	08/08/2007	0837	08/08/2007	0837

BL	09/12/2007	1404	09/12/2007	1404
BL	10/30/2007	1251	10/30/2007	1255
BL	11/13/2007	1358	11/13/2007	1358
BL	12/04/2007	1413	12/04/2007	1413

Site	Start Date	Start Time	End Date	End Time
BB	01/16/2007	1003	01/16/2007	1006
BB	02/27/2007	0949	02/27/2007	0949
BB	03/12/2007	0841	03/12/2007	0841
BB	04/03/2007	0854	04/03/2007	0854
BB	05/18/2007	0852	05/18/2007	0852
BB	06/01/2007	0858	06/01/2007	0858
BB	07/13/2007	0849	07/13/2007	0849
BB	08/08/2007	0843	08/08/2007	0849
BB	09/12/2007	1356	09/12/2007	1356
BB	10/30/2007	1306	10/30/2007	1306
BB	11/13/2007	1410	11/13/2007	1414
BB	12/04/2007	1421	12/04/2007	1425

Site	Start Date	Start Time	End Date	End Time
TB	01/16/2007	1019	01/16/2007	1021
TB	02/27/2007	1000	02/27/2007	1000
TB	03/12/2007	0903	03/12/2007	0903
TB	04/03/2007	0909	04/03/2007	0909
TB	05/18/2007	0902	05/18/2007	0907
TB	06/01/2007	0908	06/01/2007	0908
TB	07/13/2007	0859	07/13/2007	0904
TB	08/08/2007	0901	08/08/2007	0901
TB	09/12/2007	1344	09/12/2007	1344
TB	10/30/2007	1316	10/30/2007	1316
TB	11/13/2007	1424	11/13/2007	1424
TB	12/04/2007	sample not collected		

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** –

Excel data files containing measured values received from the VIMS Analytical Laboratory are used to create a yearly Excel file. 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; 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 automatically flags and codes values below MDL; calculates parameters chosen by the user and automatically flags for component values below MDL and negative values; allows the user to apply QAQC flags and codes to the data; graphs selected parameters for review; append files; and export the resulting data files to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

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	0.0015 mg/L as N	2002-2007
Nitrite	NO2F	0.0002 mg/L as N	2002-2007
Orthophosphate	PO4F	0.0006 mg/L as P	2002-2007
Nitrite + Nitrate, filtered	NO23F	0.0008 mg/L as N	2002-2007
Chlorophyll a	CHLA	0.5000	2002-2007
Phaeophytin	PHEA	0.5000	2002-2007
Silica	SiO4F	0.008 mg/L	2003-2007

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.
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 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.
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** – True field replicates were taken at each site during January grab sampling. Triplicates were taken at a randomly selected station beginning in February. Replicates or triplicates are a successive grab. Sample XXXXXX-G1 is taken and the sampler emptied. The grab sampler is deployed once again to acquire XXXXXX-G2, etc.

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 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

*The -4 Outside Low Sensor Range flag was added to the 2007 dataset in August of 2011. See the Other Remarks section for more details.

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

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	Value calculated with a value that is below the MDL
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 –**

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 with -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.

*The 2007 dataset was updated on August of 2011 to include the -4 Outside Low Sensor Range flag. The 2007 data published prior to that time used the -3 Rejected data flag with the SBL and SCB QAQC codes to indicate that data were below the minimum detection limit. These flag code combinations were all replaced with the -4 SBL or SCB update as mandated by the Data Management Committee.

a) Triplicate samples at a randomly generated site were not collected in January. Triplicate collection at a randomly chosen site commenced in February. Single sample collection at five of the six sites also started in February.

b) The sixth (21:00 EST), seventh (23:30 EST), eighth (02:00 EST), ninth (04:30 EST), and tenth (07:00 EST) samples from the January 29/30, 2007 diel data set were not collected by the Isco sampler due to probable intake tube blockage caused by freezing temperatures. As such, no data is present for these five sample times.

c) The seventh (00:30 EST), eighth (03:00 EST) and ninth (05:30 EST) samples from the February 21/22, 2007 diel data set were not collected by the Isco sampler due to probable intake tube blockage caused by freezing temperatures. As such, no data is present for these three sample times.

d) The December grab sample for Taylor's Bridge was not collected due to equipment failure at the site during collection.

e) CHLA & PHEA values from SL0607-T11 associated with the June diel samples (06/21-22/2007) are missing. The test tubes were broken at VIMS during analysis.

f) CHLA & PHEA values from SL0907-T5 associated with the September diel samples (09/26-27/2007) are missing due to insufficient water collection by the Isco sampler for this sample bottle.

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

NO23 values from LL0207-G1, DS0207-G1, BL0207-G1, BB0207-G1, and TB0207-G2 associated with the February grab samples (02/27/2007) were calculated using a 2nd order calibration curve since the concentrations are out of linear range.

NO23 values from SL0307-G1, LL0307-G1, D03207-G1, DS0307-G2, DS0307-G3, BL0307-G1, BB0307-G1, and TB0307-G2 associated with the March grab samples (03/12/2007) were calculated using a 2nd order calibration curve since the concentrations are out of linear range.

NO23 values from LL0407-G1, LL0407-G2, LL0407-G3, BL0407-G1, and TB0407-G1 associated with the April grab samples (04/03/2007) are greater than the highest standard concentration.

CHLA and PHEA values from TB0407-G1 associated with the April grab samples (04/03/2007) both have reported concentrations less than the lowest calibration standard concentration.

The PO4 value from SL0507-G1 associated with the May grab samples (05/18/2007) has a reported concentration less than the lowest calibration standard concentration.

The SiO4 value from DS0507-G1 associated with the May grab samples (05/18/2007) has a reported concentration less than the lowest calibration standard concentration.

SiO4 values from LL0607-G1, LL0607-G2, and LL0607-G3 associated with the June grab samples (06/01/2007) have reported concentrations less than the lowest calibration standard concentration.

NH4 values from LL0707-G1 and DS0707-G1 associated with the July grab samples (07/13/2007) are greater than the highest standard concentration.

The SiO4 value from DS0707-G1 associated with the July grab samples (07/13/2007) is greater than the highest standard concentration.

CHLA and PHEA values from LL0707-G1, BL0707-G1, BB0707-G1, and TB0707-G3 associated with the July grab samples (07/13/2007) originate from samples that were analyzed at a dilution.

CHLA and PHEA values from DS0807-G1, BL0807-G1, BB0807-G1, BB0807-G2, and BB0807-G3 associated with the August grab samples (08/08/2007) originate from samples that were analyzed at a dilution.

The SiO4 value from DS0907-G1 associated with the September grab samples (09/12/2007) is greater than the highest standard concentration.

CHLA and PHEA values from DS0907-G1, BL0907-G1, and BB0907-G1 associated with the September grab samples (09/12/2007) originate from samples that were analyzed at a dilution.

CHLA and PHEA values from LL1007-G1, DS1007-G1, BL1007-G1, BL10007-G2, BL1007-G3, and BB1007-G1 associated with the October grab samples (10/30/2007) originate from samples that were analyzed at a dilution.

The NO23 value from TB1107-G1 associated with the November grab samples (11/13/2007) is greater than the highest calibration standard concentration.

CHLA and PHEA values from DS1107-G1, BL1107-G1, BB1107-G1, BB1107-G2, and BB1107-G3 associated with the November grab samples (11/13/2007) originate from samples that were analyzed at a dilution.

CHLA and PHEA values from LL1207-G1 and DS1207-G1 associated with the November grab samples (12/04/2007) originate from samples that were analyzed at a dilution.

The SiO4 values from LL1207-G1, DS1207-G1, and BL1207-G1 associated with the December grab samples (12/04/2007) are greater than the highest calibration standard concentration.

h) Notes for <CSM> “See Metadata Code” usage with diel sample data:

The NO23 values from SL0207-T1 through T11 associated with the February diel samples (02/21-22/2007) were calculated using a 2nd order calibration curve since the concentrations were out of linear range.

The NO23 values from SL0307-T3, SL0307-T4, SL0307-T7, and SL0307-T9 associated with the March diel samples (03/26-27/2007) are greater than the highest calibration standard concentration.

CHLA & PHEA values from SL0707-T1, T4, T5, and T6 associated with the July diel samples (07/23-24/2007) originate from samples analyzed at a dilution.

CHLA & PHEA values from SL0807-T5 associated with the August diel samples (08/22-23/2007) originate from samples analyzed at a dilution.

CHLA & PHEA values from SL0907-T2, T4, and T11 associated with the September diel samples (09/26-27/2007) originate from samples analyzed at a dilution.

CHLA & PHEA values from SL1007-T10 and T11 associated with the October diel samples (10/15-16/2007) originate from samples analyzed at a dilution.

CHLA & PHEA values from SL1107-T2 and T3 associated with the November diel samples (11/28-29/2007) originate from samples analyzed at a dilution.

The NH4 value from SL1207-T10 associated with the December diel samples (12/11-12/2007) is greater than the highest calibration standard concentration.

e) Rainfall for 2007:

January Precipitation Totals (mm)

Monthly Total (mm): 90.424

February Precipitation Totals (mm)

Monthly Total (mm): 71.374

March Precipitation Totals (mm)

Monthly Total (mm): 83.820

April Precipitation Totals (mm)

Monthly Total (mm): 142.748

May Precipitation Totals (mm)

Monthly Total (mm): 32.766

June Precipitation Totals (mm)

Monthly Total (mm): 99.314

July Precipitation Totals (mm)

Monthly Total (mm): 23.114

August Precipitation Totals (mm)

Monthly Total (mm): 61.976

September Precipitation Totals (mm)

Monthly Total (mm): 76.454

October Precipitation Totals (mm)

Monthly Total (mm): 142.748

November Precipitation Totals (mm)

Monthly Total (mm): 43.688

December Precipitation Totals (mm)

Monthly Total (mm): 118.618

2007 Annual Total (mm): 987.044