## Delaware (DEL) NERR Nutrient Metadata

January 01, 2016 – December 31, 2016 Latest Update: September 26, 2017

## I. Data Set and Research Descriptors

# 1) Principal investigator(s) and contact persons –

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Michael G. Mensinger is responsible for the collection, implementation, and data management related to the DNERR nutrient program. Carol Pollard (VIMS) was responsible for sample processing, analyses, and data output from January – June 2016 and Mark Crane took over Carol's responsibilities in July of 2016 when the nutrient analyses contract was changed from VIMS to the DNREC Lab.

#### 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 six 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: Scotton Landing, Lebanon Landing, Division Street, Blackbird Landing, Beaver Branch (Secondary-SWMP site), and Taylor's Bridge (Secondary-SWMP site). All 6 sites are also equipped with water quality datasondes; water quality data for the primary sites are reported as part of SWMP and are also available at <a href="https://www.nerrsdata.org">www.nerrsdata.org</a>, water quality data for the secondary SWMP stations are currently considered non-SWMP and only available by contacting the Reserve directly. Please note that Secondary SWMP data in the nutrient/pigment dataset are treated exactly the same as Primary SWMP data.

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. One grab sample is collected from each station monthly, with triplicate (N=3) samples collected every other month at a randomly chosen station. 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 took place at the Virginia Institute for Marine Science (VIMS) from January – June 2016 and at the DNREC Lab from July – December 2016. The filtering methods differ between samples for Chla analysis and other nutrient parameter analysis. Chl-a processing included filtering a 100ml sample (January through August 8th) or a 50 mL sample (August 22 to current) through a 47mm Whatman GF/F filters using a vacuumpump and filter flask apparatus. The Whatman type GF/F filter is folded immediately after sample filtering, enclosed in tinfoil, placed in a sealed bag or glass jar, and placed in the freezer until it is sent off for analysis the following day (January – June 2016) or transported in an ice-filled cooler via car to the DNREC lab (July 2016 - current). 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. Once at the laboratory samples are held at -20°C (January – June 2016) and 4°C (July 2016 – current).

## 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 widemouth, 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 located upstream of Delaware Route 113. The river is 22.3 km long (mainstream linear dimension), has an average depth of 4 m MHW and width of 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) (Secondary SWMP) - 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) (Secondary SWMP) - 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

All Delaware NERR historical nutrient/pigment monitoring stations:

Station	SWMP	Station	Location	Active	Reason	Notes
Code	Status	Name		Dates	Decommissioned	
delblnut	Р	Blackbird Landing	39° 23' 19.54 N, 75° 38' 9.60 W	01/01/2002 - current	NA	NA
deldsnut	Р	Division Street	39° 9' 49.32 N, 75° 31' 8.76 W	01/01/2002 - current	NA	NA

dellInut	Р	Lebanon Landing	39° 6' 51.84 N, 75° 29' 57.12 W	01/01/2002 current	NA	NA
delsInut	Р	Scotton Landing	39° 5' 5.93 N, 75° 27' 38.09 W	01/01/2002 - current	NA	NA
delbbnut	S	Beaver Branch	39° 24' 8.64 N, 75° 37' 40.80 W	02/01/2002 - current	NA	NA
deltbnut	S	Taylor's Bridge	39° 24' 17.6 N, 75° 35' 58.4 W	01/01/2007 - current	NA	NA

#### 5) Coded 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 Taylors 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 triplicates sample are taken utilize a "1" for the first sample, a "2" for the second sample, and a "3" for the third sample. Diel samples are always labeled with a "1" since only one sample is taken at each 2.5 hour interval.

#### 6) Data collection period –

SWMP nutrient monitoring via grab samples and diel samples began in 2002 at Scotton Landing, Lebanon Landing, Division Street, Blackbird Landing, and Beaver Branch. Taylors Bridge was added as a nutrient and water quality monitoring station in 2008.

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

Site Start Date	Start Time	End Date	End Time
January Diel Sample	es Not Collecte	d Due to Ice	
SL 02/29/2016	09:00	03/01/2016	10:00
SL 03/30/2016	09:30	03/31/2016	10:30
SL 04/25/2016	08:00	04/26/2016	09:00
SL 05/16/2016	08:00	05/17/2016	09:00
SL 06/27/2016	08:00	06/28/2016	09:00
SL 07/11/2016	08:00	07/12/2016	09:00
SL 08/22/2016	07:30	08/23/2016	08:30
SL 09/12/2016	10:00	09/13/2016	11:00
SL 10/25/2016	11:00	10/26/2016	12:00
SL 11/02/2016	08:00	11/03/2016	09:00

SL 12/12/2016 08:30 12/13/2016	09:30
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Grab Sampling (A	,		
Site Start Date	Start Time	End Date	End Time
SL 01/04/2016	10:39	01/04/2016	10:39
SL 02/29/2016	08:34	02/29/2016	08:39
SL 03/28/2016	08:55	03/28/2016	08:55
SL 04/25/2016	07:28	04/25/2016	07:28
SL 05/02/2016	09:56	05/02/2016	09:56
SL 06/06/2016	07:29	06/06/2016	07:33
SL 07/25/2016	08:08	07/25/2016	08:08
SL 08/08/2016	07:58	08/08/2016	07:58
SL 09/20/2016	07:04	09/20/2016	07:04
SL 10/10/2016	10:06	10/10/2016	10:06
SL 11/30/2016	12:02	11/30/2016	12:02
SL 12/05/2016	08:32	12/05/2016	08:32
3L 12/03/2010	00.32	12/03/2010	00.32
Site Start Date	Start Time	End Date	End Time
LL 01/04/2016	10:49	01/04/2016	10:49
LL 02/29/2016	08:50	02/29/2016	08:50
LL 03/28/2016	09:06	03/28/2016	09:06
LL 04/25/2016	07:47	04/25/2016	07:51
LL 05/02/2016 LL 05/02/2016	10:08	05/02/2016	10:08
LL 06/06/2016 LL 06/06/2016	07:47	06/06/2016	07: 47
LL 07/25/2016	08:20	07/25/2016	08:20
LL 08/08/2016	08:12	08/08/2016	08:12
LL 09/20/2016	07:16	09/20/2016	07:16
LL 10/10/2016	10:18	10/10/2016	10:18
LL 11/30/2016	12:13	11/30/2016	12:13
LL 12/05/2016	08:46	12/05/2016	08:46
Site Start Date	Start Time	End Date	End Time
DS 01/04/2016	11:11	01/04/2016	11:11
DS 02/29/2016	09:16	02/29/2016	09:16
DS 03/28/2016	09:20	03/28/2016	09:20
DS 04/25/2016	08:06	04/25/2016	08:06
DS 05/02/2016	10:23	05/02/2016	10:23
DS 06/06/2016	08:04	06/06/2016	08:04
DS 07/25/2016	08:38	07/25/2016	08:38
DS 08/08/2016	08:28	08/08/2016	08:28
DS 09/20/2016 DS 09/20/2016	07:29	09/20/2016	07:29
DS 10/10/2016	10:35	10/10/2016	10:35
DS 11/30/2016	12:22	11/30/2016	12:22
DS 12/05/2016	09:02	12/05/2016	09:08
Site Start Date	Start Time	End Date	End Time
BL 01/04/2016	13:56	01/04/2016	13:56
BL 02/29/2016	10:43	02/29/2016	10:43
BL 03/28/2016	10:40	03/28/2016	10:40
BL 04/25/2016	09:39	04/25/2016	09:39
BL 05/02/2016	12:58	05/02/2016	12:58
BL 06/06/2016	10:15	06/06/2016	10:15
BL 07/25/2016	10:20	07/25/2016	10:20
BL 08/08/2016	10:27	08/08/2016	10:27
21 00/00/2010	10.41	00/00/2010	10.21

BL 09/20/2016	09:30	09/20/2016	09:30
BL 10/10/2016	13:14	10/10/2016	13:14
BL 11/30/2016	13:43	11/30/2016	13:43
BL 12/05/2016	11:22	12/05/2016	11:22
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Site Start Date	Start Time	End Date	End Time
BB 01/04/2016	14:04	01/04/2016	14:04
BB 02/29/2016	10:50	02/29/2016	10:50
BB 03/28/2016	10:47	03/28/2016	10:47
BB 04/25/2016	09:47	04/25/2016	09:47
BB 05/02/2016	13:05	05/02/2016	13:05
BB 06/06/2016	10:22	06/06/2016	10:22
BB 07/25/2016	10:29	07/25/2016	10:29
BB 08/08/2016	10:35	08/08/2016	10:39
BB 09/20/2016	09:39	09/20/2016	09:39
BB 10/10/2016	13:23	10/10/2016	13:23
BB 11/30/2016	13:50	11/30/2016	13:50
BB 12/05/2016	11:29	12/05/2016	11:29
Site Start Date	Start Time	End Date	End Time
TB 01/04/2016	14:10	01/04/2016	14:10
TB 02/29/2016	10:55	02/29/2016	10:55
TB 03/28/2016	10:55	03/28/2016	10:55
TB 04/25/2016	09:54	04/25/2016	09:54
TB 05/02/2016	13:13	05/02/2016	13:13
TB 06/06/2016	10:31	06/06/2016	10:31
TB 07/25/2016	10:37	07/25/2016	10:37
TB 08/08/2016	10:47	08/08/2016	10:47
TB 09/20/2016	09:47	09/20/2016	09:47
TB 10/10/2016	13:30	10/10/2016	13:36
TB 11/30/2016	13:59	11/30/2016	13:59
TB 12/05/2016	11:37	12/05/2016	11:37

#### 7) Associated researchers and projects-

The DNERR water quality monitoring program occurs at the corresponding nutrient sample sites. A Xylem/YSI EXO datasonde is deployed at each site measuring: dissolved oxygen, salinity, water temperature, water level, 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. Water quality data from the St. Jones River sites (Scotton Landing, Lebanon Landing, and Division Street), Blackbird Creek (Blackbird Landing), and meteorological data from the St. Jones station are available at <a href="www.nerrsdata.org">www.nerrsdata.org</a>. One additional St. Jones River water quality station (Aspen Landing), two additional Blackbird Creek water quality stations (Beaver Branch & Taylors Bridge), and Blackbird Creek meteorological data are available from Reserve staff. Contact Michael G. Mensinger at <a href="mike.mensinger@state.de.us">mike.mensinger@state.de.us</a> with data inquiries pertaining to these additional sites.

## 8) Distribution -

NOAA retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The NERRS retains the right to be fully credited for having collected and process the data. Following academic courtesy standards, the NERR

site where the data were collected should be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. 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.

#### Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2016.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page <a href="https://www.nerrsdata.org">www.nerrsdata.org</a>. Data are available in comma separated version format.

## II. Physical Structure Descriptors

## 9) 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 for review; and exports the resulting data file to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

Michael G. Mensinger is also responsible for all data entry and QA/QC procedures related to the Delaware NERR dataset. 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 category –

Required NOAA/NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisks "\*\*"

Data Category Parameter Variable Name Units of Measure

Phosphorus and Nitrogen:

\*Orthophosphate, Filtered PO4F mg/L as P \*Ammonium, Filtered NH4F mg/L as N

*Nitrita	e, Filtered	NO2F	mg/L as N
			0
*Nıtrat	e, Filtered	NO3F	mg/L as N
*Nitrite	e + Nitrate, Filtered	NO23F	mg/L as N
Dissolv	ved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:			_
*Chlore	ophyll a	CHLA_N	μg/L
Phaeop	phytin	PHEA	μg/L
Carbon:			-
Other Lab Parameters:			
Silicate	, Filtered	SiO4F	mg/L as SI

#### Notes:

- 1. Time is coded based on a 2400 clock and is referenced to Standard Time.
- 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 or calculated laboratory parameters –

## a) Parameters measured directly

Nitrogen species: NH4F, NO2F, NO23F

Phosphorus species: PO4F

Other: CHLA\_N, PHEA, SiO4F

b) Calculated parameters

NO3F 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. Tables 1 and 2 present the current MDL's for each lab; these values are reviewed and revised periodically.

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

Variable	Method Detection Limit	Dates in Use	Revisited
NH4F	0.0056 mg/L as N	01/01/2016 - 06/28/2016	
NO2F	0.0016 mg/L as N	01/01/2016 - 06/28/2016	
PO4F	0.0020 mg/L as P	01/01/2016 - 06/28/2016	
NO23F	0.0047 mg/L as N	01/01/2016 - 06/28/2016	
CHLA	0.50 ug/L	01/01/2016 - 06/28/2016	
PHEA	0.50 ug/L	01/01/2016 - 06/28/2016	
SiO4F	$0.0800~\mathrm{mg/L}$	01/01/2016 - 06/28/2016	

Table 2. DNREC Method Detection Limits (MDL) for measured water quality parameters.

Variable	Method Detection Limit	Dates in Use	Revisited
NH4F	0.005 mg/L as N	07/01/2016 - 12/31/2016	
NO2F	0.004 mg/L as N	07/01/2016 - 12/31/2016	
PO4F	0.004 mg/L as P	07/01/2016 - 12/31/2016	
NO23F	0.004 mg/L as N	07/01/2016 - 12/31/2016	
CHLA	0.50 ug/L	07/01/2016 - 12/31/2016	

PHEA	0.50 ug/L	07/01/2016 - 12/31/2016
SiO4F	0.1 mg/L	07/01/2016 - 12/31/2016

### 13) Laboratory methods -

Virginia Institute of Marine Sciences Laboratory (VIMS)

## 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  $40^{\circ}\text{C}$  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. <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: 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. <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. 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 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. <u>Methods for Chemical Analysis of Water and Wastewater</u>, 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. <u>Methods of Seawater Analysis</u>. 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.

Delaware Department of Natural Resources & Environmental Control – Division of Water Resources – Environmental Laboratory Section Laboratory

## i) Parameter: Orthophosphate

## Method References:

USEPA Method 365.1 Revision 2.0 Determination of Phosphorus by Semi-Automated Colorimetry. *Methods for Chemical Analysis of Water and Wastes*; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993 OI Analytical Low-Level Orthophosphate by Segmented Flow Analysis (SFA) Method Descriptor:

Instrumentation: OI Analytical Flow Solution IV with WinFLOW software

Ammonium molybdate and antimony potassium tartrate react in a sulfuric acid environment to form an antimony-phospho-molybdo complex, which is reduced to a blue colored complex by ascorbic acid. Reaction is heat catalyzed at 40°C and measured colorimetrically at 880nm. The range is 0.01-0.2mg/L.

## Preservation Method:

250ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. The liquid volume of the filtered sample is collected into a HDPE bottle, cooled to <6°C, and delivered to the ELS within 24 hours.

## ii) Parameter: Nitrite

#### Method References:

USEPA Method 353.2, Revision 2.0: Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Cadmium Reduction). *Methods for Chemical Analysis of Water and Wastes*; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993. OI Analytical Nitrite determination by Segmented Flow Analysis (SFA)

## Method Descriptor:

Instrumentation: OI Analytical Flow Solution IV with WinFLOW software

The nitrite is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride at pH 2.0 to 2.5 to form a reddish purple azo dye. The absorbance of the colored azo dye is quantitatively measured at 540 nm. The range is 0.008 to 0.500 mg/L. Higher concentrations may be quantified by diluting the sample.

### Preservation Method:

250ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. The liquid volume of the filtered sample is collected into a HDPE bottle, cooled to <6°C, and delivered to the ELS within 24 hours.

## iii) Parameter: Nitrate + Nitrite

#### Method References:

USEPA Method 353.2, and Method 353.2 LL (Low Level) Revision 2.0: Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Cadmium Reduction). *Methods for Chemical Analysis of Water and Wastes*; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993.

OI Analytical Nitrate/Nitrite determination by Segmented Flow Analysis (SFA)

## Method Descriptor:

Instrumentation: OI Analytical Flow Solution IV with WinFLOW software

Nitrate is reduced quantitatively to nitrite by cadmium metal. The nitrite formed; in addition to any nitrite originally present in the sample is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride at pH 2.0 to 2.5 to form a reddish purple azo dye. The absorbance of the colored azo dye is quantitatively measured at 540 nm. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step. The range is 0.108 to 0.500 mg/L. The Low Level range is 0.01 to 0.2 mg/L.

## Preservation Method:

250ml of a sample is filtered through 0.45um Millipore filters using a vaccum-pump and a filtering flask

apparatus. The liquid volume of the filtered sample is collected into a HDPEbottle, cooled to <6°C, delivered to the ELS within 24 hours.

#### iv) Parameter: Ammonia

#### Method References:

USEPA method 350.1 Revision 2.0: determination of Ammonia Nitrogen by Semi-Automated Colorimetry. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993 Method Descriptor:

Instrumentation: SEAL AA3 flow autoanalyzer.

The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is mixed into a solution of boric acid. 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 and measured colorimetrically. The range is 0.02 - 1.0 mg/L.

## Preservation Method:

250ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask apparatus. The liquid volume of the filtered sample is collected into a HDPEbottle, cooled to <6°C, and delivered to the ELS within 24 hours. The pH is adjusted to <2 with sulfuric acid.

## v) Parameter: Chlorophyll and Pheophytin

## Method References:

Trilogy Laboratory Fluorometer Operating Manual. Version 1.2. September 15, 2010. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

USEPA Method 445.0. In Vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence. Turner Designs Application Notes, Chlorophyll and Pheophytin March 24 2008. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

## Method Descriptor:

Instrumentation: Turner Designs Triology fluorometer.

Chlorophyll-containing phytoplankton in a measured volume of sample water is concentrated by filtering through a glass fiber filter. The pigments are extracted from the phytoplankton in a DMSO/Acetone solution because this solution has a greater extraction efficiency than Acetone alone. Conversion of chlorophyll to phaeophytin is carried out by acidification of the sample. Typically 50-100 mL of water is filtered. The concentration in the water sample is reported in units of µg/L. Range is 0.5 to 200µg/L 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 placed in a clean wide-mouth glass sample jar, protected from light exposure, cooled to <6°C and delivered to the ELS within 24 hours.

#### vi) Parameter: Silica

#### Method References:

Standard Methods for the Examination of Water and Wastewater, Method 4500-SiO2C-1997. Automated Method for Molybdate-Reactive Silica.

## Method Descriptor:

Instrumentation: SEAL AQ2 Discrete autoanalyzer.

This analysis is used for the determination of Reactive silica, often referred to as molybdate-reactive silica. It includes mainly monomeric and dimeric silica acids and silicate. Under acidic conditions molybdate-reactive silica combines with ammonium molybdate to form a yellow molybdo-silica acid complex. The absorbance of the final product is measured spectrophotometrically at 405 nm. The applicable range is 0.25 to 25 mg/L. Preservation Method:

250ml of a sample is filtered through 0.45um Millipore filters using a vacuum-pump and a filtering flask

apparatus. The liquid volume of the filtered sample is collected into a HDPE bottle, cooled to <6°C, and delivered to the ELS within 24 hours.

## 14) Field and Laboratory QAQC programs -

#### a) Precision:

- i) **Field Variability** True field replicates are taken at a single site every other month during grab sampling. The two replicates are successive grabs. Sample #1 is taken and the sampler emptied. The grab sampler is deployed once again to acquire XXXXXX-G2, and then again for replicate #3. 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 not available
- iii) Cross Calibration Exercises none

Information for DNREC Lab:

#### Nitrate-Nitrite & Nitrite

Quality Control Checks	Criteria	Frequency
Quantitative limit	0.005 mg/L	On SOP approval
Initial Calibration	$r \ge 0.995$	A valid initial calibration is required
	minimum 3 standards	for sample analysis initially and
	%D <u>≤</u>	verified every 6 months.
Continuing Calibration	%D ≤ 10%	With each analytical batch; at the
Verification/CCVI		beginning and end of the run and after every 10 samples.
Method Detection Limit	A MDL must be achieved	Once prior to the use of this
(MDL)	prior to the practice of this	procedure with semi-annual
	procedure.	verification.
Initial Demonstration of	Precision ≤ 10%	Each analyst prior to analyzing
Capability (IDOC)	Recovery (X) between 80-120%	(preparing) samples by this procedure.
Continuous Demonstration	Acceptable performance on a PE	Each analyst annually.
of Capability (DOC)	or blind sample.	
Laboratory Blank	< 0.005  mg/L	Each analytical batch
(Method Blank)		
Standard Reference	Percent Recovery between	Each analytical batch
Material / Quality Control	90-110% ±10%	_
Sample		
Duplicate	% RPD ≤ 30%.	Each analytical batch of 10 or less samples

## Orthophosphate

Quality Control Checks	Criteria	Frequency
Initial Calibration	$r \ge 0.995$	A valid initial calibration is required
		for sample analysis.

Continuing Calibration Verification	$\%D \le 25\%$ at the reporting limit $\%D \le 10\%$ for all other levels	Immediately following daily calibration, after every 10% of samples and at the end of the run.		
Initial Demonstration of Capability (IDOC)Initial Precision and Recovery (IPR)	Precision ≤ 10% Recovery (X) between 90- 110%	Each analyst prior to analyzing (preparing) samples by this procedure.		
Continuous Demonstration of Capability (DOC)Laboratory Blank (Method Blank)	Acceptable performance on a PE or blind sample.	Each analyst annually.		
Method Detection Limit (MDL)	Follow procedure in the Quality Manual.	Once prior to the use of this procedure and verified annually.		
Laboratory Blank (Method Blank)	< MDL	Each analytical batch of 20 or less samples.		
Matrix Spike (MS) and Matrix Spike Duplicate (MSD)	Recovery 90-110%	Each analytical batch of 10 or less samples.		
Duplicate (sample duplicate or matrix spike duplicate)	%RPD ≤ 20%.	Each analytical batch of 10 or less samples.		
Laboratory Control Sample (LCS)	Recovery 90-110%	Each analytical batch of 20 or less samples		

# Chlorophyll-a & Pheophytin

Quality Control Checks	Criteria F	requency
Initial Demonstration of Capability (IDOC)	Four aliquots of an environmental samp are extracted and analyzed. Average recovery 90-110% (compared to an experienced analyst extracting and analyzing four aliquots of the same samp %RSD \( \leq 20\%. \)	Each analyst upon completion of training.
On-going Demonstration of Capability (DOC)	Acceptable performance on a PE or blind sample. Recovery 75-125%.	Each analyst annually.
Method Blank	<u>≤</u> 0.2μg l <sup>-1</sup>	Analyze one extracted blank with each batch of 20 samples.
Duplicate	% RPD ≤ 20%	As required by project/customer
Laboratory Control Sample (LCS) and LCSD	% recovery = 80-120% % RPD \le 10%	Each analytical batch of 20 environmental samples.
Matrix Spike and Matrix Spike Duplicate	% Recovery = 75-125% %RPD \le 20%	As required by the Customer, contract or QAPP.
Calibration Verification	Calibration Verification % recovery = 90-110%	
Follow manufacturer recommendations Calibrate with high (~200 µg l <sup>-1</sup> ) seconda standard  Instrument Calibration Check calibration with low (~20 µg l <sup>-1</sup> ) secondary standard (criteria 100 ± 10%) % Recovery of Standards ≤ 10% of true value.		photomultiplier has been changed.  When QC no longer meets acceptance criteria, or when

## Silica

Quality Control Checks	Criteria	

Quality Control Checks	Criteria		
Initial Calibration	0.995 regression or better		
Continuing Calibration Verification (CCVB)	±20% - 80%-120%		
Method Detection Limit (MDL)	A MDL must be achieved prior to the		
	practice of this procedure.		
Initial Demonstration of Capability (IDOC)	Precision ≤ 10%		
	Recovery (X) between 80-120%		
Continuous Demonstration of Capability (DOC)	Acceptable performance on a PE or blind		
	sample.		
Matrix Spike and Matrix Spike Duplicate Recovery (MS &	$%$ RPD(s) $\leq 20 \%$		
MSD)	Recovery (X) between 80-120 %		
Laboratory Blank (Method Blank)	< 0.10  mg/L (< MDL)		
Laboratory Control Sample	This check standard is a commercial		
Laboratory Control Sample Duplicate	standard with a certified value and		
	acceptance limits. The standard will vary		
	each time it is purchased. Please refer the		
	current Certificate of Analysis.		

## 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

## 16) 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 error	·s
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
GSM	See metadata
0	
Sensor errors	
SBL SCB	Value below minimum limit of method detection
SCC	Calculated value could not be determined due to a below MDL component 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 Co	omments
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 comn	nents
CAB	Algal bloom
СНВ	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	1 (0.4004)
CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB COC	partly to broken (50-90%)
CFY	overcast (>90%)
CHY	foggy hazy
CCC	cloud (no percentage)
Precipitation	eroud (no percentage)
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 low tide TSL 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 metersWH4 1.0 to 1.3 meters 1.3 or greater meters WH5 Wind direction Ν 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 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 NWfrom 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/notes –

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. Notes for <CSM> "See Metadata Code" usage with grab sample data:
- 1. The Scotton Landing PO4, NH4, and NO2 values are missing from the 03/31/2016 (08:00 EST) diel sample due to a VIMS analytical laboratory error.
- 2. The Beaver Branch NH4 value (0.019 mg/L) from the 07/25/2016 (10:29 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 3. The Lebanon Landing NO2 value (0.007 mg/L) from the 08/08/2016 (08:12 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 4. The Blackbird Landing NH4 value (0.015 mg/L) from the 08/08/2016 (10:27 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 5. The Beaver Branch NH4 value (0.018 mg/L) from the 08/08/2016 (10:37 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 6. The Beaver Branch CHLA (862.00, 882.00, 884.00 ug/L) values from the three triplicate samples on 08/08/2016 (10:27, 10:35, and 10:37) were rejected due to their substantial deviation from the annual range despite all three samples being consistent.
- 7. The Division Street CHLA (23.30 ug/L) values from the 08/08/2016 (8:28 EST) grab sample is a qualified result. The samples were over diluted during analysis causing the results to fall below the dilution adjusted, estimated Method Detection Limit (MDL) and Limit of Quantitation (LOQ). The standard Laboratory protocol is to report results below the MDL as not detected.
- 8. The Scotton Landing NH4 (0.017 mg/L) value from the 08/22/2016 (20:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 9. The Scotton Landing NO2 (0.005, 0.004, 0.006, 0.007, and 0.006 mg/L) values from the 08/22/2016 (07:30, 10:00, 12:30, 15:00, 17:30, and 20:00 EST) diel samples and NO2 values (0.006, 0.005 and 0.005 ug/L) from the 08/23/2016 (01:00, 06:00 and 08:30 EST) diel samples are estimated since the concentrations are below the range for accurate quantitation (>MDL, but <LOQ).
- 10. The Scotton Landing CHLA (22.5 ug/L and 22.3 ug/L) values from the 08/22/2016 (12:30 EST) and 08/23/2016 (01:00 EST) diel samples are qualified results. The samples were over diluted during analysis causing the results to fall below the dilution adjusted, estimated Method Detection Limit (MDL) and Limit of Quantitation (LOQ). The standard Laboratory protocol is to report results below the MDL as not detected.
- 11. The Scotton Landing PHEA (20.5, 19.9, 20.8, 24.9, 20.9, 18.4, and 6.09 ug/L) values from the 08/22/2016 (12:30, 15:00, 17:30, and 22:30 EST) and 08/23/2016 (01:00, 06:00, and 08:30 EST) diel samples are qualified results. The samples were over diluted during analysis causing the results to fall below the dilution adjusted, estimated Method Detection Limit (MDL) and Limit of Quantitation (LOQ). The standard Laboratory protocol is to report results below the MDL as not detected.
- 12. The Scotton Landing PO4 (0.136 mg/L) value from the 09/12/2016 (10:00 EST) diel sample is likely overestimated due to the matrix effect.
- 13. The Scotton Landing NH4 (0.018 mg/L) value from the 09/12/2016 (20:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 14. The Scotton Landing NO23 (0.102 mg/L) value from the 09/13/2016 (01:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

- 15. The Blackbird Landing NH4 (0.017 mg/L) value from the 09/20/2016 (09:30 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 16. The Blackbird Landing NO23 (0.004 mg/L) value from the 09/20/2016 (09:30 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 17. The Blackbird Landing NO2 (0.006 mg/L) value from the 10/10/2016 (13:14 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 18. The Beaver Branch NO2 (0.005 mg/L) value from the 10/10/2016 (13:23 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 19. The Taylors Bridge NO2 (0.004, 0.005, and 0.005 mg/L) values from the 10/10/2016 (13:30, 13:33, and 13:36 EST) grab samples are estimated since the concentrations are below the range for accurate quantitation (>MDL, but <LOQ).
- 20. The Scotton Landing NO23 (0.548 mg/L) value from the 11/30/2016 (12:02 EST) grab sample is likely overestimated due to the matrix effect.
- 21. The Taylors Bridge NO2 (0.004 mg/L) value from the 11/30/2016 (13:59 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 22. The Division Street NO2 (0.004 mg/L) value from the 12/05/2016 (09:02 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 23. The Blackbird Landing NH4 (0.014 mg/L) value from the 12/05/2016 (11:22 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 24. The Blackbird Landing NO2 (0.005 mg/L) value from the 12/05/2016 (09:02 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
- 25. The Taylors Bridge NO2 (0.004 mg/L) value from the 12/05/2016 (09:02 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).
  - Major rain/storm events (near or exceeding 25.4 mm (1 inch) of rainfall) during 2016 took place on the following dates (data originates from the Delaware NERR St. Jones meteorological station):

February 16, 2016	(31.5 mm)
May 06, 2016	(24.6 mm)
May 29, 2016	(46.2 mm)
June 25, 2016	(41.1 mm)
July 05, 2016	(35.8  mm)
July 18, 2016	(25.9 mm)
July 28, 2016	(31.5 mm)
August 01, 2016	(49.5 mm)
August 21, 2016	(34.8 mm)
September 19, 2016	(71.6 mm)
September 30, 2016	(29.2 mm)
October 09, 2016	(40.6  mm)
December 05, 2016	(25.9 mm)

c. Sample/Parameter Hold Time Table (contains sample collection and sample analysis date or date/time where applicable):

	Date Analyzed					
Sample Descriptor	PO4F	NH4F	NO2F	NO23F	CHLA_N, PHEA	SiO4F
1/4/2016, all grab samples	1/13/2016	1/13/2016	1/13/2016	1/13/2016	1/12/2016	1/21/2016
2/29/2016, all grab samples	3/24/2016	3/24/2016	3/24/2016	3/24/2016	3/21/2016	4/1/2016
2/29-3/1/2016, all diel samples	3/24/2016	3/24/2016	3/24/2016	3/24/2016	3/21/2016	4/1/2016
3/28/2016, all grab samples	4/22/2016	4/22/2016	4/22/2016	4/22/2016	4/27/2016	5/4/2016
3/30-3/31/2016, all diel samples	4/22/2016	4/22/2016	4/22/2016	4/22/2016	4/18/2016	5/4/2016
4/25/2016, all grab samples	5/20/2016	5/20/2016	5/20/2016	5/20/2016	5/11/2016	5/23/2016
4/25-4/26/2016, all diel samples	5/20/2016	5/20/2016	5/20/2016	5/20/2016	5/17/2016	5/23/2016
5/2/2016, all grab samples	5/20/2016	5/20/2016	5/20/2016	5/20/2016	5/24/2016	5/23/2016
5/16-17/2016, all diel samples	6/8/2016	6/8/2016	6/8/2016	6/8/2016	6/1/2016	6/10/2016
6/6/2016, all grab samples	7/1/2016	7/1/2016	7/1/2016	7/1/2016	6/30/2016	7/1/2016
6/27-28/2016, all diel samples	7/1/2016	7/1/2016	7/1/2016	7/1/2016	7/12/2016	7/1/2016
7/11/2016 8:00 diel sample	7/12/2016	7/15/2016	7/12/2016	7/12/2016	8/4/2016	8/4/2016
7/11/2016 10:30, 13:00, 20:30, 23:00; 7/12/2016 1:30 and 9:00 diel samples	7/12/2016	7/13/2016	7/12/2016	7/12/2016	8/4/2016	8/4/2016
7/11/2016 15:30, 18:00; 7/12/2016 4:00, 6:30 diel samples	7/12/2016	7/13/2016	7/12/2016	7/13/2016	8/4/2016	8/4/2016
7/25/2016, all grab samples	7/26/2016	7/26/2016	7/26/2016	7/26/2016	8/4/2016	8/4/2016
8/8/2016, all grab samples	8/9/2016	8/9/2016	8/9/2016	8/9/2016	8/10/2016	8/29/2016
8/22-23/2016, all diel samples	8/24/2016	8/25/2016	8/25/2016	8/25/2016	8/31/2016	8/29/2016
9/12/2016 10:00 diel sample	9/13/2016	9/24/2016	9/13/2016	9/13/2016	9/28/2016	10/7/2016
9/12/2016 12:30, 15:00; 9/13/2016 1:00, 3:30, 11:00 diel samples	9/13/2016	9/14/2016	9/13/2016	9/13/2016	9/28/2016	10/7/2016
9/12/2016 17:30, 20:00, 22:30; 9/13/2016 6:00, 8:30 diel samples	9/13/2016	9/14/2016	9/13/2016	9/14/2016	9/28/2016	10/7/2016
9/20/2016, all grab samples	9/21/2016	9/21/2016	9/21/2016	9/21/2016	9/28/2016	10/7/2016
10/10/2016, all grab samples	10/11/2016	10/11/2016	10/11/2016	10/11/2016	10/27/2016	11/1/2016
10/25-26/2016, all diel samples	10/27/2016	10/27/2016	10/27/2016	10/27/2016	11/2/2016	11/1/2016
11/2-3/2016, all diel samples	11/3/2016	11/4/2016	11/3/2016	11/3/2016	11/10/2016	11/14/2016
11/30/2016, all grab samples but DS	12/1/2016	12/2/2016	12/1/2016	12/1/2016	12/1/2016	12/13/2016
11/30/2016, DS grab at 9:05	12/1/2016	12/2/2016	12/1/2016	12/7/2016*	12/1/2016	12/13/2016
12/5/2016, all grab samples	12/6/2016	12/7/2016	12/6/2016	12/6/2016	12/9/2016	12/22/2016
12/12/2016 8:30, 11:00, 13:30, 16:00,						
18:30, 21:00, 23:30; 12/13/2016 2:00, 4:30,	12/13/2016	12/16/2016	12/13/2016	12/13/2016	12/15/2016	12/13/2016
9:30 diel samples						
12/13/2016 7:00 diel sample	12/14/2016	12/16/2016	12/13/2016	12/13/2016	12/15/2016	12/13/2016

<sup>\*</sup>sample held longer than allowed by NERRS protocols