Delaware (DEL) NERR Nutrient Metadata
January 01, 2019 – December 31, 2019
Latest Update: September 29, 2023

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 DEL NERR nutrient program. Kathy Knowles is responsible for sample processing, analyses, and data output for 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 www.nerrsdata.org, 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 DEL NERR 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 DNREC Lab from January – December 2019. The filtering methods differ between samples for Chla analysis and other nutrient parameter analysis. Chl-a processing included filtering 50 ml samples through 47 mm Whatman GF/F filter using a vacuum-pump and filter flask apparatus. The Whatman type GF/F is immediately placed in a glass jar, and transported in an ice-filled cooler via car to the DNREC lab upon completion of sample processing. Sample processing for other parameters includes filtering 225 ml of a sample through 0.45 µm Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47 mm GF/C filter may be used to filter the sample prior to filtering through the 0.45 µm Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and transported to the DNREC lab the same day once sample processing is complete. 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 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° 23' 19.5196" N
Longitude 75° 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 28 ppt.
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 4 m MHW and the width is 50 m. At the sampling site, the depth is 0.6 m 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 km^2 (22810 ha) and Division Street's drainage area is 81.2 km^2 (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 1.5 m MHW, and an average width of 37 m. At the sampling site, the depth is 1.4 m 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 km^2 (9060 ha) and Beaver Branch's drainage area is 4.8 km^2 (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° 24' 08.6" N
Longitude 75° 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 km^2 (9060 ha) and Taylor's Bridge's drainage area is 63.6 km^2 (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° 24' 17.8" N
Longitude 75° 35' 58.1" W

All Delaware NERR historical nutrient/pigment monitoring stations:

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

delllnut	P	Lebanon Landing	39° 6' 51.84 N, 75° 29' 57.12 W	01/01/2002 - current	NA	NA
delslnut	P	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.

<u>Diel Sampling (All times in EST)</u>

Site	Start Date	Start Time	End Date	End Time
SL	01/07/2019	05:00	01/08/2019	06:00
SL	02/25/2019	08:00	02/26/2019	09:00
SL	03/25/2019	07:30	03/26/2019	08:30
SL	04/22/2019	06:30	04/23/2019	07:30
SL	05/20/2019	06:30	05/21/2019	07:30
SL	06/19/2019	05:30	06/20/2019	06:30
SL	07/15/2019	04:30	07/16/2019	05:30
SL	08/19/2009	06:30	08/20/2019	07:30
SL	09/03/2019	07:30	09/04/2019	08:30
SL	10/16/2019	05:00	10/17/2019	06:00
SL	11/18/2019	08:30	11/19/2019	09:30
SL	12/02/2019	08:00	12/03/2019	09:00

<u>Grab Sampling (All times in EST)</u>

Site	Start Date	Start Time	End Date	End Time
SL	01/28/2019	09:38	01/28/2019	09:38
SL	02/25/2019	07:49	02/25/2019	07:49
SL	03/05/2019	04:02	03/05/2019	04:02
SL	04/08/2019	07:17	04/08/2019	07:17
SL	05/30/2019	03:11	05/30/2019	03:11
SL	06/03/2019	04:48	06/03/2019	04:48
SL	07/01/2019	04:44	07/01/2019	04:44
SL	08/19/2019	06:22	08/19/2019	06:22
SL	09/17/2019	06:25	09/17/2019	06:25
SL	10/28/2019	06:14	10/28/2019	06:20
SL	11/18/2019	07:51	11/18/2019	07:51
SL	12/16/2019	07:26	12/16/2019	07:26

Site	Start Date	Start Time	End Date	End Time
LL	01/28/2019	09:50	01/28/2019	09:50
LL	02/25/2019	08:06	02/25/2019	08:06
LL	03/05/2019	04:18	03/05/2019	04:18
LL	04/08/2019	07:33	04/08/2019	07:37
LL	05/30/2019	03:43	05/30/2019	03:43
LL	06/03/2019	05:01	06/03/2019	05:01
LL	07/01/2019	05:09	07/01/2019	05:09
LL	08/19/2019	06:40	08/19/2019	06:44
LL	09/17/2019	06:37	09/17/2019	06:37
LL	10/28/2019	06:31	10/28/2019	06:31
LL	11/18/2019	08:02	11/18/2019	08:02
LL	12/16/2019	07:38	12/16/2019	07:38

Site	Start Date	Start Time	End Date	End Time
DS	01/28/2019	10:04	01/28/2019	10:04
DS	02/25/2019	08:21	02/25/2019	08:21
DS	03/05/2019	04:41	03/05/2019	04:41
DS	04/08/2019	07:52	04/08/2019	07:52
DS	05/30/2019	04:34	05/30/2019	04:34
DS	06/03/2019	05:13	06/03/2019	05:13
DS	07/01/2019	05:26	07/01/2019	05:26
DS	08/19/2019	07:02	08/19/2019	07:02
DS	09/17/2019	06:52	09/17/2019	06:52
DS	10/28/2019	06:48	10/28/2019	06:48
DS	11/18/2019	08:18	11/18/2019	08:18
DS	12/16/2019	07:55	12/16/2019	07:55

Site	Start Date	Start Time	End Date	End Time
BL	01/28/2019	11:29	01/28/2019	11:29
BL	02/25/2019	10:13	02/25/2019	10:17
BL	03/05/2019	06:10	03/05/2019	06:10
BL	04/08/2019	09:16	04/08/2019	09:16
BL	05/30/2019	05:02	05/30/2019	05:02
BL	06/03/2019	06:35	06/03.2019	06:41
BL	07/01/2019	06:44	07/01/2019	06:44
BL	08/19/2019	08:12	08/19/2019	08:12
BL	09/17/2019	08:22	09/17/2019	08:22

Site	Start Date	Start Time	End Date	End Time
BL	10/28/2019	07:52	10/28/2019	07:52
BL	11/18/2019	09:52	11/18/2019	09:52
BL	12/16/2019	09:13	12/16/2019	09:13

Site	Start Date	Start Time	End Date	End Time
BB	01/28/2019	11:41	01/28/2019	11:41
BB	02/25/2019	10:25	02/25/2019	10:25
BB	03/05/2019	06:28	03/05/2019	06:28
BB	04/08/2019	09:23	04/08/2019	09:23
BB	05/30/2019	05:10	05/30/2019	05:10
BB	06/03/2019	06:46	06/03/2019	06:46
BB	07/01/2019	06:51	07/01/2019	06:51
BB	08/19/2019	08:20	08/19/2019	08:20
BB	09/17/2019	08:28	09/17/2019	08:28
BB	10/28/2019	08:03	10/28/2019	08:03
BB	11/18/2019	10:01	11/18/2019	10:01
BB	12/16/2019	09:21	12/16/2019	09:21

Site	Start Date	Start Time	End Date	End Time
TB	01/28/2019	11:50	01/28/2019	11:50
TB	02/25/2019	10:32	02/25/2019	10:32
TB	03/05/2019	06:38	03/05/2019	06:38
TB	04/08/2019	09:29	04/08/2019	09:29
TB	05/30/2019	05:18	05/30/2019	05:18
TB	06/03/2019	06:55	06/03/2019	06:55
TB	07/01/2019	07:05	07/01/2019	07:05
TB	08/19/2019	08:28	08/19/2019	08:28
TB	09/17/2019	08:36	09/17/2019	08:36
TB	10/28/2019	08:13	10/28/2019	08:13
TB	11/18/2019	10:07	11/18/2019	10:07
TB	12/16/2019	09:31	12/16/2019	09:36

7) Associated researchers and projects–

The DELNERR 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 www.nerrsdata.org. 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 mike.mensinger@delaware.gov 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 processed 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 2020.

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 DNREC 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 asterisk "*".

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
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	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. DNREC Method Detection Limits (MDL) for measured water quality parameters.

Variable	Method Detection Limit	Dates in Use	Revisited
NH4F	0.010 mg/L as N	01/01/2019 – 12/31/2019	04/12/2019
NO2F	0.004 mg/L as N	01/01/2019 – 12/31/2019	12/17/2018
PO4F	0.004 mg/L as P	01/01/2019 – 12/31/2019	01/17/2019
NO23F	0.010 mg/L as N	01/01/2019 – 12/31/2019	01/16/2019
CHLA	0.50 µg/L	01/01/2019 – 12/31/2019	08/26/2016
PHEA	0.50 µg/L	01/01/2019 – 12/31/2019	08/26/2016
SiO4F	0.2 mg/L	01/01/2019 – 12/31/2019	04/01/2019

13) Laboratory methods –

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 880 nm. The range is 0.01-0.2 mg/L.

Preservation Method:
250 ml of a sample is filtered through 0.45 µm 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:
250 ml of a sample is filtered through 0.45 µm 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:
250 ml of a sample is filtered through 0.45 µm 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, 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:
250 ml of a sample is filtered through 0.45 μm 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. 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 200 μg/L
Preservation Method:
A 100 ml sample is filtered through a 47 mm Whatman GF/F filter using a vacuum-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:
250 ml of a sample is filtered through 0.45 μm 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** – see charts below

iii) **Inter-organizational splits** – none

b) **Accuracy:**
i) **Sample spikes** – see charts below.
ii) **Standard reference material analysis –**see charts below
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 ≥ 0.995 minimum 3 standards %D ≤	A valid initial calibration is required for sample analysis initially and verified every 6 months.
Continuing Calibration Verification/CCVI	%D ≤ 10%	With each analytical batch; at the beginning and end of the run and after every 10 samples.
Method Detection Limit (MDL)	A MDL must be achieved prior to the practice of this procedure.	Once prior to the use of this procedure with semi-annual verification.
Initial Demonstration of Capability (IDOC)	Precision ≤ 10% Recovery (X) between 80-120%	Each analyst prior to analyzing (preparing) samples by this procedure.
Continuous Demonstration of Capability (DOC)	Acceptable performance on a PE or blind sample.	Each analyst annually.
Laboratory Blank (Method Blank)	< 0.005 mg/L	Each analytical batch
Standard Reference Material / Quality Control Sample	Percent Recovery between 90-110% ±10%	Each analytical batch
Duplicate	% RPD ≤ 30%.	Each analytical batch of 10 or less samples

Orthophosphate

Quality Control Checks	Criteria	Frequency
Initial Calibration	r ≥ 0.995	A valid initial calibration is required for sample analysis.
Continuing Calibration Verification	%D ≤ 25% at the reporting limit %D ≤ 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 $\leq$ 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	Frequency
Initial Demonstration of Capability (IDOC)	Four aliquots of an environmental sample are extracted and analyzed. Average recovery 90-110% (compared to an experienced analyst extracting and analyzing four aliquots of the same sample). %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	$\leq$0.2 µg l^{-1}	Analyze one extracted blank with each batch of 20 samples.
Duplicate	% RPD $\leq$ 20%	As required by project/customer
Laboratory Control Sample (LCS) and LCSD	% recovery = 80-120% % RPD $\leq$ 10%	Each analytical batch of 20 environmental samples.
Matrix Spike and Matrix Spike Duplicate	% Recovery = 75-125% %RPD $\leq$ 20%	As required by the Customer, contract or QAPP.
Calibration Verification	% recovery = 90-110%	Analysis of solid standards (high and low) at the start of each analytical run.
Instrument Calibration	Follow manufacturer recommendations. Calibrate with high (~200 µg l^{-1}) secondary standard Check calibration with low (~20 µg l^{-1}) secondary standard (criteria 100 $\pm$ 10%) % Recovery of Standards $\leq$ 10% of true value.	Whenever lamp, filter or photomultiplier has been changed. When QC no longer meets acceptance criteria, or when instrument maintenance is required.

Silica

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 $\leq$ 10% Recovery (X) between 80-120%

Quality Control Checks	Criteria
Continuous Demonstration of Capability (DOC)	Acceptable performance on a PE or blind sample.
Matrix Spike and Matrix Spike Duplicate Recovery (MS & MSD)	%RPD(s) $\leq$ 20 % Recovery (X) between 80-120 %
Laboratory Blank (Method Blank)	< 0.10 mg/L (< MDL)
Laboratory Control Sample Laboratory Control Sample Duplicate	This check standard is a commercial 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 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
GSM See metadata

Sensor errors

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

Parameter Comments

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

Record comments

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

Cloud cover

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

Precipitation

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

Tide stage

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

Wave height

WH0	0 to <0.1 meters
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.6 meters
WH3	0.6 to > 1.0 meters

WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters
Wind direction	
N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest
Wind speed	
WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) Other remarks/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 nutrient data:

1. The Scotton Landing NO2F value (0.012 mg/L) from the 01/07/2019 (05:00 EST) diel sample is likely overestimated due to the matrix effect.

2. The Scotton Landing SiO4F value (12 mg/L) from the 01/07/2019 (05:00 EST) diel sample is likely overestimated due to the matrix effect.

3. The Scotton Landing NO2F value (0.006 mg/L) from the 01/07/2019 (12:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

4. The Scotton Landing NO2F value (0.007 mg/L) from the 01/07/2019 (15:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

5. The Scotton Landing NO2F value (0.016 mg/L) from the 01/28/2019 (09:38 EST) grab sample is likely underestimated due to the matrix effect.

6. The Blackbird Landing NO2F value (0.004 mg/L) from the 01/28/2019 (11:29 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

7. The Lebanon Landing NO2F value (0.007 mg/L) from the 02/25/2019 (08:06 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

8. The Division Street NO2F value (0.006 mg/L) from the 02/25/2019 (08:21 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

9. The Blackbird Landing NO2F value (0.004 mg/L) from the 02/25/2019 (10:13 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

10. The Blackbird Landing NO2F value (0.004 mg/L) from the 02/25/2019 (10:15 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

11. The Blackbird Landing NO2F value (0.004 mg/L) from the 02/25/2019 (10:17 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

12. The Scotton Landing NO2F value (0.007 mg/L) from the 02/25/2019 (08:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

13. The Scotton Landing NO2F value (0.007 mg/L) from the 03/05/2019 (04:02 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

14. The Lebanon Landing NO2F value (0.006 mg/L) from the 03/05/2019 (04:18 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

15. The Division Street NO2F value (0.006 mg/L) from the 03/05/2019 (04:41 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

16. The Taylors Bridge NO2F value (0.006 mg/L) from the 03/05/2019 (06:38 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

17. The Scotton Landing PO4F value (0.009 mg/L) from the 03/25/2019 (15:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

18. The Scotton Landing PO4F value (0.008 mg/L) from the 03/26/2019 (01:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

19. The Scotton Landing PO4F value (0.009 mg/L) from the 03/26/2019 (03:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

20. The Division Street NO2F value (0.059 mg/L) from the 04/08/2019 (07:52 EST) grab sample is suspect due to deviation from the annual trend.

21. The Blackbird Landing NH4F value (0.013 mg/L) from the 04/08/2019 (09:16 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

22. The Scotton Landing PO4F value (0.008 mg/L) from the 04/22/2019 (06:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

23. The Scotton Landing PO4F value (0.009 mg/L) from the 04/22/2019 (09:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

24. The Scotton Landing PO4F value (0.007 mg/L) from the 04/22/2019 (11:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

25. The Scotton Landing PO4F value (0.004 mg/L) from the 04/22/2019 (14:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

26. The Scotton Landing PO4F value (0.008 mg/L) from the 04/22/2019 (16:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

27. The Scotton Landing PO4F value (0.004 mg/L) from the 04/22/2019 (19:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

28. The Scotton Landing PO4F value (0.005 mg/L) from the 04/22/2019 (21:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

29. The Scotton Landing PO4F value (0.008 mg/L) from the 04/23/2019 (00:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

30. The Scotton Landing PO4F value (0.004 mg/L) from the 04/23/2019 (02:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

31. The Scotton Landing NO2F value (0.005 mg/L) from the 04/23/2019 (02:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

32. The Scotton Landing PO4F value (0.008 mg/L) from the 04/23/2019 (05:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

33. The Scotton Landing NO2F value (0.005 mg/L) from the 04/23/2019 (05:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

34. The Scotton Landing PO4F value (0.009 mg/L) from the 04/23/2019 (07:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

35. The Scotton Landing NO2F value (0.004 mg/L) from the 05/21/2019 (00:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

36. The Scotton Landing PO4F value (0.006 mg/L) from the 05/21/2019 (02:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

37. The Scotton Landing NO2F value (0.006 mg/L) from the 05/21/2019 (02:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

38. The Blackbird Landing NH4F value (0.378 mg/L) from the 05/30/2019 (05:02 EST) grab sample is suspect due to its deviation from the annual trend. It is more than double the next highest value (0.163 mg/L on 12/16/2019) recorded at this site during 2019. A similar elevated value was also seen at Beaver Branch within this set of grab samples, so runoff related to minor storm events may explain these values.

39. The Beaver Branch NH4F value (0.300 mg/L) from the 05/30/2019 (05:10 EST) grab sample is suspect due to its deviation from the annual trend. A similar elevated value was also seen at Blackbird Landing within this set of grab samples, so runoff related to minor storm events may explain these values, however the Beaver Branch value does not deviate as much from the annual trend as Blackbird Landing's value.

40. The Division Street NO2F value (0.007 mg/L) from the 06/03/2019 (05:13 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

41. The Taylors Bridge NO2F value (0.006 mg/L) from the 06/03/2019 (06:55 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

42. The Scotton Landing PO4F value (0.008 mg/L) from the 06/19/2019 (23:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

43. The Scotton Landing PO4F value (0.007 mg/L) from the 06/20/2019 (01:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

44. The Division Street NO2F value (0.005 mg/L) from the 07/01/2019 (05:26 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

45. The Taylors Bridge NO2F value (0.007 mg/L) from the 07/01/2019 (07:05 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

46. The Scotton Landing PO4F value (0.008 mg/L) from the 07/15/2019 (22:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

47. The Scotton Landing NO2F value (0.006 mg/L) from the 07/15/2019 (22:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

48. The Scotton Landing NO2F value (0.006 mg/L) from the 07/16/2019 (00:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

49. The Scotton Landing NH4F value (0.124 mg/L) from the 08/19/2018 (06:22 EST) grab sample is likely underestimated due to the matrix effect.

50. The Scotton Landing NO2F value (0.004 mg/L) from the 08/19/2019 (06:22 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

51. The Lebanon Landing PO4F value (0.009 mg/L) from the 08/19/2019 (06:42 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

52. The Division Street NH4F value (0.420 mg/L) from the 08/19/2019 (07:02 EST) grab sample is suspect due to its deviation from the annual trend.

53. The Beaver Branch PO4F value (0.008 mg/L) from the 08/19/2019 (08:20 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

54. The Taylors Bridge NO2F value (0.006 mg/L) from the 08/19/2019 (08:28 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

55. The Scotton Landing NH4F value (0.274 mg/L) from the 08/19/2019 (06:30 EST) diel sample is suspect due to its deviation from the other values from this diel sample set.

56. The Scotton Landing NO2F value (0.007 mg/L) from the 08/19/2019 (06:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

57. The Scotton Landing NO23F value (0.010 mg/L) from the 08/19/2019 (16:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

58. The Scotton Landing NH4F value (0.010 mg/L) from the 08/19/2019 (19:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

59. The Scotton Landing NH4F value (0.016 mg/L) from the 09/03/2019 (07:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

60. The Scotton Landing NO23F value (0.015 mg/L) from the 09/03/2019 (07:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

61. The Scotton Landing NH4F value (0.010 mg/L) from the 09/03/2019 (10:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

62. The Scotton Landing NO2F value (<0.004 mg/L) from the 09/03/2019 (12:30 EST) diel sample is likely overestimated due to the matrix effect.

63. The Scotton Landing NO23F value (0.012 mg/L) from the 09/03/2019 (15:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

64. The Scotton Landing NO2F value (0.067 mg/L) from the 09/03/2019 (17:30 EST) diel sample was rejected. All other NO2F values from this diel sample set were 0.004 mg/L, so this value was considerably higher. It is also higher than the NO23F (0.023 mg/L) and resulted in the calculation of a negative NO3 value.

65. The Scotton Landing NH4F value (0.019 mg/L) from the 09/03/2019 (20:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

66. The Scotton Landing NH4F value (0.016 mg/L) from the 09/04/2019 (08:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

67. The Blackbird Landing NH4F value (0.011 mg/L) from the 09/17/2019 (08:22 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

68. The Beaver Branch PO4F value (0.008 mg/L) from the 09/17/2019 (08:28 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

69. The Taylors Bridge NH4F value (0.018 mg/L) from the 09/17/2019 (08:36 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

70. The Scotton Landing PO4F value (0.102 mg/L) from the 10/16/2019 (05:00 EST) diel sample is suspect due to its deviation from the annual and monthly trend.

71. The Scotton Landing NO23F value (0.180 mg/L) from the 10/16/2019 (10:00 EST) diel sample is likely overestimated due to the matrix effect.

72. The Scotton Landing NO2F value (0.006 mg/L) from the 10/16/2019 (22:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

73. The Scotton Landing NO2F value (0.004 mg/L) from the 10/17/2019 (01:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

74. The Scotton Landing PO4F value (0.006 mg/L) from the 10/17/2019 (03:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

75. The Scotton Landing NO2F value (0.005 mg/L) from the 10/17/2019 (03:30 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

76. The Scotton Landing PO4F value (0.005 mg/L) from the 10/17/2019 (06:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

77. The Scotton Landing NO2F value (0.006 mg/L) from the 10/17/2019 (06:00 EST) diel sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

78. The Lebanon Landing PO4F value (0.005 mg/L) from the 10/28/2019 (06:31 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

79. The Blackbird Landing PO4F value (0.008 mg/L) from the 10/28/2019 (07:52 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

80. The Blackbird Landing NH4F value (0.016 mg/L) from the 10/28/2019 (07:52 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

81. The Blackbird Landing NO2F value (0.005 mg/L) from the 10/28/2019 (07:52 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

82. The Taylors Bridge NO2F value (0.007 mg/L) from the 10/28/2019 (08:13 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

83. The Division Street PO4F value (0.005 mg/L) from the 11/18/2019 (08:18 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

84. The Division Street NO23F value (0.257 mg/L) from the 11/18/2019 (08:18 EST) diel sample is likely overestimated due to the matrix effect.

85. The Blackbird Landing NH4F value (0.017 mg/L) from the 11/18/2019 (09:52 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

86. The Beaver Branch PO4F value (0.007 mg/L) from the 11/18/2019 (10:01 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

87. The Scotton Landing NO2F value (0.023 mg/L) from the 11/18/2019 (21:00 EST) diel sample is likely overestimated due to the matrix effect.

88. The Lebanon Landing NO2F value (0.013 mg/L) from the 12/16/2019 (07:38 EST) grab sample is likely overestimated due to the matrix effect.

89. The Blackbird Landing NO2F value (0.007 mg/L) from the 12/16/2019 (09:13 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

90. The Beaver Branch NO2F value (0.005 mg/L) from the 12/16/2019 (09:21 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

91. The Taylors Bridge POF value (0.006 mg/L) from the 12/16/2019 (09:31 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

92. The Taylors Bridge PO4F value (0.006 mg/L) from the 12/16/2019 (09:33 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

93. The Taylors Bridge NO2F value (0.004 mg/L) from the 12/16/2019 (09:33 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

94. The Taylors Bridge PO4F value (0.006 mg/L) from the 12/16/2019 (09:36 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

95. The Taylors Bridge NO2F value (0.004 mg/L) from the 12/16/2019 (09:36 EST) grab sample is estimated since the concentration is below the range for accurate quantitation (>MDL, but <LOQ).

b) Major rain/storm events (at or exceeding 25.4 mm (1 inch) of rainfall) during 2019 took place on the following dates (data originates from the Delaware NERR St. Jones meteorological station):

February 12, 2019	(27.4 mm)
March 03, 2019	(26.4 mm)
April 15, 2019	(28.4 mm)
April 26, 2019	(27.7 mm)
May 26, 2019	(40.4 mm)
June 10, 2018	(57.4 mm)
June 13, 2019	(40.9 mm)
June 29, 2019	(54.6 mm)
October 16, 2019	(35.6 mm)
October 20, 2019	(41.7 mm)
December 09, 2019	(25.7 mm)

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

Sample Descriptor	Date Analyzed					
	PO4F	NH4F	NO2F	NO23F	CHLA_n, PHEA	SiO4F
01/07-01/08/2019, all diel samples	01/09/2019	01/14/2019	01/08/2019	01/08/2019	01/25/2019	01/29/2019
01/28/2019, all grab samples	01/29/2019	01/31/2019	01/29/2019	01/29/2019	02/12/2019	01/29/2019
02/25/2019, all grab samples	02/25/2019	02/28/2019	02/25/2019	02/25/2019	03/06/2019	02/27/2019
02/25-02/26/2019, all diel samples	02/27/2019	02/28/2019	02/27/2019	02/27/2019	03/06/2019	02/27/2019
03/05/2019, grab samples at 04:02, 04:18, 04:41, 06:10	03/05/2019	03/06/2019	03/06/2019	03/06/2019	03/06/2019	03/18/2019
03/05/2019, grab samples at 06:28, 06:38	03/05/2019	03/06/2019	03/06/2019	03/06/2019	03/06/2019	03/26/2019
03/25-03-26/2019, all diel samples	03/05/2019	04/08/2019	03/26/2019	03/26/2019	04/09/2019	03/28/2019
04/08/2019, all grab samples	04/09/2019	04/12/2019	04/09/2019	04/09/2019	04/09/2019	04/26/2019
04/22-04-23/2019, all diel samples	04/23/2019	05/02/2019	04/23/2019	04/23/2019	05/07/2019	04/26/2019
5/20-05/21/2019, all diel samples	05/21/2019	05/22/2019	05/21/2019	05/21/2019	06/04/2019	06/10/2019
05/30/2019, all grab samples	05/30/2019	05/30/2019	05/30/2019	05/30/2019	06/04/2019	06/10/2019
06/03/2019, all grab samples	06/04/2019	06/05/2019	06/04/2019	06/04/2019	06/04/2019	06/10/2019
6/19-06/20/2019, all diel samples	06/20/2019	06/24/2019	06/20/2019	06/20/2019	07/08/2019	07/11/2019
07/01/2018, all grab samples	07/02/2019	07/02/2019	07/01/2019	07/01/2019	07/08/2019	07/11/2019
07/15-07/16/2019, all diel samples	07/16/2019	08/06/2019	07/17/2019	07/17/2019	07/22/2019	07/29/2019
08/19/2019, all grab samples	08/20/2019	08/30/2019	08/20/2019	08/20/2019	08/23/2019	08/21/2019
8/19-08/20/2019, all diel samples	08/20/2019	08/30/2019	08/20/2019	08/20/2019	08/23/2019	08/21/2019
9/03-09/04/2019, all diel samples	09/04/2019	09/13/2019	09/04/2019	09/05/2019	09/19/2019	10/17/2019*
09/17/2019, all grab samples	09/17/2019	09/27/2019	09/17/2019	09/17/2019	09/19/2019	09/30/2019
10/16-10/17/2019, all diel samples	10/17/2019	10/18/2019	10/17/2019	10/17/2019	10/30/2019	10/17/2019
10/28/2019, all grab samples	10/29/2019	10/30/2019	10/29/2019	10/29/2019	10/30/2019	11/22/2019
11/18/2018, all grab samples	11/19/2019	11/21/2019	11/19/2019	11/19/2019	11/21/2019	11/22/2019
11/18-11/19/2018, all diel samples	11/19/2019	11/21/2019	11/19/2019	11/19/2019	11/21/2019	11/22/2019
12/02-12/03/2019, all diel samples	12/03/2019	12/06/2019	12/03/2019	12/03/2019	12/18/2019	12/20/2019
12/16/2019, all grab samples	12/17/2019	12/20/2019	12/17/2019	12/17/2019	12/18/2019	12/20/2019

* sample held longer than allowed by NERRS protocols