Hudson River (HUD) NERR Nutrient Metadata
January 1, 2018 – December 31, 2018
Latest Update: September 7, 2022

I. Data Set and Research Descriptors

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2) Research objectives –

a) Monthly Grab Sampling Program

The objective of this study is to monitor nutrient concentrations at the Tivoli Bays component of the Hudson River National Estuarine Research Reserve. Grab samples are taken from two freshwater tidal wetlands, Tivoli North Bay and Tivoli South Bay, and their primary upland tributaries, Stony Creek and Saw Kill Creek respectively. YSI datasondes are deployed at all grab sampling sites and meteorological data are collected continuously, thus relationships can be established between nutrient levels, the aquatic environment and meteorological conditions. The tributaries are sampled above the area of tidal influence, allowing for determination of nutrient inputs to the Tivoli Bays via stream flow. This is important because it has previously been determined that urban and residential land use practices are markedly influencing the water chemistry of the tributaries, especially Saw Kill Creek. Since residential coverage continues to increase, we hope that the intensive monitoring of the surface waters in this watershed will identify trends caused by this rapid development. Tivoli North and South Bays are sampled on an ebb tide, which accounts for nutrient inputs to the wetlands via stream flow and tidal exchange, and includes the influence of intertidal areas on nutrient levels. In addition, ebb tide sampling allows for determination of nutrient inputs to the Hudson River Estuary via the Tivoli Bays.

b) Diel Sampling Program
Monthly diel sampling is conducted at Tivoli South Bay. Diel sampling highlights the relative importance of tidal forcing on nutrient levels within Tivoli North Bay through the inclusion of two complete tidal cycles (a lunar day). Sampling on a flood tide allows for isolation of nutrient inputs via tidal exchange. As with grab sampling, diel sampling on an ebb tide accounts for nutrient inputs via tidal exchange and stream flow and includes the influence of intertidal areas on nutrient levels. The combination of grab and diel sampling data will provide a better understanding of the relative importance of each water source in terms of nutrient delivery to Tivoli South Bay. In addition, these data will help us develop a better understanding of the effects of the intertidal area on nutrient dynamics

3) Research methods –

a) Monthly grab sampling program

Monthly grab samples are collected near the four YSI data logger locations within the Tivoli Bays component of the Hudson River National Estuarine Research Reserve. These sites include Tivoli South Bay, Tivoli North Bay, Saw Kill Creek, and Stony Creek. Monthly sampling at the two bays and the two creeks is conducted on the same day, during an ebb tide within three hours of slack low-water. Efforts are made to avoid precipitation events within 48 hours of sampling. Two replicate samples are collected sequentially at each site using 1 L amber Nalgene bottles. Prior to sample collection, bottles are acid washed with 10% HCL and rinsed with distilled-deionized water. At each site, bottles are rinsed three times with ambient water just before sample collection. All sampling sites are highly mixed and samples are collected at only one depth, approximately 15 cm below the surface. At the time of sample collection, a YSI Professional Plus meter is used to measure temperature, salinity, specific conductivity and dissolved oxygen (% and mg/L), and the values are recorded. Air temperature is recorded using a handheld Kestrel unit. Cloud cover, precipitation, wind speed and tide stage conditions are also noted. Grab samples are placed on ice and returned to the laboratory. Within 24 hours, pH (rep 1) and alkalinity (available directly from the Reserve) are measured and samples are filtered and analyzed for seston (TSS) and filtered for chlorophyll A (CHLA) and phaeophytin. The filtrate is collected and transferred to 125 ml Nalgene bottles that have been acid washed, rinsed with distilled-deionized water, and rinsed three times with the filtrate. Filtered samples are stored at -4°C until nutrient analysis and 1 ml of 1 N H_2SO_4 is added to samples that will be analyzed for ammonium. They are delivered to the analytical lab within a few days to a week and held there at -20°C until analysis. Filters for CHLA and PHEA analysis are placed in borosilicate vials and stored in a freezer at -4°C until they are analyzed in-house.

b) Diel sampling program

Monthly diel sampling occurred at Tivoli South Bay near the YSI datasonde location. An ISCO 6712 Portable Sampler equipped with a 25 ft siphoning tube is used for sample collection. The siphoning tube is deployed approximately one meter from the datasonde and water is collected 20 cm off the bottom, approximate sampling depths are 0.5 meters at low tide and 2.5 meters at high tide. Two sequential samples (a second immediately after the first) were collected once every 2 hours for 22 hours until November 2002, when collection of the two sequential samples changed to once every 2.5 hours for 27.5 hours. Cloud cover, precipitation, wind speed, and tide stage conditions are noted for at least one sample; air temperature dissolved oxygen concentration is recorded for the same sample using a YSI handheld unit. The first sample is always collected at slack low tide. Samples are collected in 1 liter clear Nalgene bottles that are acid washed with 10% HCL and rinsed with distilled-deionized water prior to deployment of the ISCO. The second sample bottle in each sequence receives 2 ml of 10 N H_2SO_4 prior to deployment in order to preserve the sample for ammonium analysis. The inside of the ISCO is packed with ice to keep the samples cool until the instrument is retrieved. Samples are processed on the day of retrieval. Acidified samples, the second in each collection sequence, are filtered and the filtrate is collected and transferred to 125 ml Nalgene bottles that have been acid washed and rinsed as described previously. Non-acidified samples, the first in each collection sequence, are filtered and analyzed for seston and filtered for CHLA and PHEA. The filtrate is collected and transferred to 125 ml Nalgene bottles that have been acid washed and rinsed as described previously. All filtered water samples are stored at -4°C until nutrient analysis is conducted. They are delivered to the analytical lab within a few days to a week and held there at -20°C until analysis. Filters used for CHLA analysis are placed in borosilicate vials and stored in a freezer at -4°C until they are analyzed in-house.

4) Site location and character –

The Hudson River National Estuarine Research Reserve (HUDNERR) is a multi-component site totaling approximately 5,000 acres. Each component of the reserve is referenced by River Mile (RM) of the Hudson River in New York State proceeding north from the southern tip of Manhattan (RM 0). The reserve includes the following four component sites: Piermont Marsh, Rockland County (RM 24)(41° 02' 30"N 73° 54' 15"W), Iona Island, Rockland County (RM 45)(41° 18' 15"N 73° 58' 45"W), Tivoli Bays, Dutchess County (RM 98)(42° 02' 15"N 73° 55' 10"W), and Stockport Flats, Columbia County (RM 124)(42° 02' 30"N 73° 46' 00"W). The four component sites include open water, tidal wetland, and adjacent upland buffer habitats and are representative of the diverse plant and animal communities that occupy the salinity gradient within the Hudson River Estuary. Development within the watersheds of the four component sites ranges from predominantly urban/suburban to forested/agricultural.

The highlighted component for this study is the Tivoli Bays in Annandale, NY. This component includes four monitored sites: Tivoli South Bay, Tivoli North Bay, Saw Kill Creek, and Stony Creek. All four monitored sites are freshwater (0.0 psu salinity).

Tivoli South Bay (latitude 42° 01' 37.336" N, longitude 73° 55' 33.445" W) is a tidal freshwater wetland with intertidal mudflats exposed at low tide. During the growing season (June – September), the subtidal area of Tivoli South Bay is dominated by the invasive floating macrophyte *Trapa natans*. Tivoli South Bay has a tidal range of 1.19 meters and a soft, silt/clay bottom type. The depth at the sampling location ranges from 0.5 to 2.5 meters. The non-tidal freshwater input to Tivoli South Bay includes that of a large upland tributary and a few small perennial streams.

Tivoli North Bay (latitude 42° 02' 11.56464" N, longitude 73° 55' 31.16645" W) is a freshwater tidal marsh with emergent marsh vegetation dominated by the cattail *Typha angustifolia*. Tivoli North Bay has a tidal range of 1.19 meters, a soft, silt/clay bottom type, and a depth range from 0.5 to 3.0 meters at the sampling location. The non-tidal freshwater input to Tivoli North Bay includes that of a large upland tributary and a few small perennial streams.

Saw Kill Creek (latitude 42° 01' 01.543" N, longitude 73° 54' 53.589" W) is the main tributary flowing into Tivoli South Bay. The Saw Kill Creek watershed is 26.6 square miles and land use within the watershed includes forested (51.1%), agricultural (25.8%), and urban (16.5%) areas. Characteristics of Saw Kill Creek at the sampling location include a rocky bottom type, a depth range of 0.5 to 2.0 meters, and discharge that can range from $2x10^{-5}$ to 1.2 m^3/sec.

Stony Creek (latitude 42° 02' 45.556" N, longitude 73° 54' 40.237" W) is the main tributary flowing into Tivoli North Bay. The Stony Creek watershed is approximately 23 square miles and is dominated by agricultural land use. Characteristics of Stony Creek at the sampling location include a solid rock bottom and a depth range of 0.5 to 1.5 meters. Stony Creek discharge is currently being determined. Both Stony Creek and Saw Kill Creek are non-tidal and freshwater input to the tributaries consists of smaller creeks in the watershed.

Norrie Point (latitude 41° 49' 54.75" N, longitude 73° 56' 33.32" W) is sampling location on the Eastern shore of the Hudson River. It sits outside of any tidal marshes and captures flow primarily from the main-stem river. Characteristics of this location are a silty bottom adjacent to manmade pier structure. The typical tidal range at this location is 1.2 Meters and a depth of 3-4 meters. The site is exhibits slight influence from a cove which is dominated by the invasive floating macrophyte *Trapa natans*. . Any non-tidal influence, is likely from seasonal creeks or output of a small tributary (Enderkill Creek) 0.5 km north of the sampling location.

The entire tidal Hudson River south of the Troy Dam is affected by polychlorinated biphenyls (PCBs), and Tivoli North and South Bays have low sedimentary concentrations of PCBs. Nutrient inputs to the Tivoli Bays via the non-tidal tributaries are the main concern in terms of pollutants. High concentrations of nitrate and phosphate have previously been documented in both Saw Kill Creek and Stony Creek. Saw Kill Creek appears to be strongly influenced by residential land use practices. This highlights the importance of continued monitoring and identification of non-point sources of pollution at these sites.

All Hudson River NERR historical nutrient/pigment monitoring stations:

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
TS	P	Tivoli Bay South	42° 1' 37.34 N, 73° 55' 33.45 W	05/01/1995 00:00 – current	NA	NA
TN	P	Tivoli Bay North	42° 2' 11.56 N, 73° 55' 31.17 W	07/01/1999 00:00 – current	NA	NA
SK	P	Saw Kill	42° 1' 1.82 N, 73° 54' 53.86 W	05/01/1995 00:00 – current	NA	NA
SC	P	Stony Creek	42° 2' 46.68 N, 73° 54' 38.88 W	04/01/2002 00:00 – current	NA	NA
NP	S	Norrie Point	41° 49' 54.75"N 73° 56' 33.32"W	(06/27/2008) *01/01/2018 00:00 - Current	NA	*Secondary SWMP status confirmed as of 01/01/2018, prior data may be available per request

5) Coded variable definitions –

hudsknut = Hudson River Reserve nutrient data for Saw Kill Creek
hudscnut = Hudson River Reserve nutrient data for Stony Creek
hudtnnut = Hudson River Reserve nutrient data for Tivoli North Bay
hudtsnut = Hudson River Reserve nutrient data for Tivoli South Bay
hudnpnut = Hudson River Reserve nutrient data for Norrie Point

Monitoring program codes:
1=Monthly grab sampling
2=Diel sampling

6) Data collection period –

Monthly grab samples have been collected at the four monitored sites of the Tivoli Bays since 06/17/1991. Diel sampling at Tivoli South Bay began in June 2002. The exact dates and times for the 2018 Nutrient Data collection period are listed below. Data collection is hampered during the winter months (December-March) because snow and ice often prohibit safe access to the sites.

Site	Date	Rep 1 Time	Rep 2 Time
SC	4/18/18	10:10	10:11
SC	5/17/18	10:29	10:30
SC	6/7/18	11:27	11:28
SC	7/31/18	11:36	11:37
SC	8/29/18	10:40	10:41
SC	9/12/18	10:24	10:25
SC	10/25/18	09:07	09:08
SC	11/29/18	11:00	11:01

Site	Date	Rep 1 Time	Rep 2 Time
SK	4/18/18	10:30	10:31
SK	5/17/18	10:55	10:56
SK	6/7/18	11:47	11:48
SK	7/31/18	11:10	11:11
SK	8/29/18	10:56	10:57
SK	9/12/18	10:07	10:08
SK	10/25/18	09:24	09:25
SK	11/29/18	11:17	11:18

Site	Date	Rep 1 Time	Rep 2 Time
TN	4/18/18	08:45	08:46
TN	5/17/18	09:50	09:51
TN	6/7/18	14:51	14:52
TN	7/31/18	10:22	10:23
TN	8/29/18	09:43	09:44
TN	9/12/18	09:27	09:28
TN	10/25/18	07:53	07:54
TN	11/29/18	11:48	11:49

Site	Date	Rep 1 Time	Rep 2 Time
TS	4/18/18	09:23	09:24
TS	5/17/18	09:50	09:51
TS	6/7/18	14:51	14:52

TS	7/31/18	10:22	10:23
TS	8/29/18	09:43	09:44
TS	9/12/18	09:27	09:28
TS	10/25/18	07:53	07:54
TS	11/29/18	12:05	12:06

Site	Date	Rep 1 Time	Rep 2 Time
NP	**4/30/2018**	07:15	07:16
NP	**5/30/2018**	07:47	07:48
NP	**6/29/2018**	08:10	08:11
NP	**7/20/2018**	12:42	12:43
NP	**8/17/2018**	11:45	11:46
NP	**9/27/2018**	8:20	8:21
NP	10/11/2018	8:15	8:16
NP	11/26/2018	9:15	9:16

b) Diel Sampling

Site	GRAB	Start Date	Start Time	End Date	End Time
TS	No*	No January diel sample taken due to ice			
TS	No*	No February diel sample taken due to ice			
TS	No*	No March diel sample taken due to ice			
TS	No*	4/17/18	20:30	4/19/18	00:00
TS	No*	5/16/18	20:30	5/18/18	00:00
TS	No*	6/6/18	13:30	6/7/18	17:00
TS	No*	7/30/18	22:00	8/1/18	01:30
TS	No*	8/28/18	21:30	8/30/18	01:00
TS	No*	9/11/18	21:00	9/13/18	00:30
TS	No*	10/24/18	20:00	10/25/18	23:30
TS	No*	11/29/18	00:00	11/30/18	03:30
TS	No*	No December diel sample taken due to ice			

*Effort is made to coincide monthly sampling with the Diel sampling to obtain a grab sample at the middle portion of the 27.5 hour cycle. In certain situations those samples could not be obtained. In this occasion, a TSDGrab sample is obtained independent of the monthly sample and processed accordingly.

7) Associated researchers and projects–

As part of the SWMP long-term monitoring program, HUD NERR also monitors 15-minute meteorological and water quality data which may be correlated with this nutrient/pigment dataset. These data are available at www.nerrsdata.org.

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 2019.

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 www.nerrsdata.org. Data are available in comma separated version format.

II. Physical Structure Descriptors

9) Entry verification –

Following sample analysis (ammonium, nitrate, orthophosphate, chloride, sulfate), data files are transferred directly from analytical instruments to desktop computers. Reports are generated as Excel spreadsheets and verified by the head of the CIES analytical laboratory. Data are examined for completeness, consistency and outliers. Suspect data are flagged, data are reviewed at CIES, and if possible, samples are analyzed a second time. The Excel spreadsheets are then sent to Hudson River Research Reserve staff.

For chlorophyll a and phaeophytin data, raw fluorescence data are entered by hand into spreadsheets that have been set up to perform necessary calculations. Entered data are checked twice for errors and calculated values are examined for completeness, consistency and outliers.

Laboratory data are then assigned an ID and imported into an Access database. Field data are entered directly into Access with a corresponding sample ID. The field and laboratory data for the four sites described here are then queried out of Access, imported into Excel, reformatted and pre-processed. In addition, since 2009 laboratory values are reported as PO4 mg/L as P, NHf in mg/L as N, and NO3 mg/L. The following calculation is used to convert NO3 to mg/L as N:

$$N = NO3 \times 0.2259$$

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.

The research coordinator, assistant, and SWMP technician are responsible for QA/QC of the data.

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	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
Other Lab Parameters:			
	Chloride, Filtered	Cl	mg/L
	Sulfate, Filtered	SO4	mg/L
	Total Suspended Solids	TSS	mg/L
Field Parameters			
	Water Temperature	WTEM_N	ºC
	Specific Conductance	SCON_N	mS/cm
	Salinity	SALT_N	ppt
	% Dissolved Oxygen Saturation	DO_S_N	%
	Dissolved Oxygen	DO_N	mg/L
	pH	PH_N	SU
	Air Temperature	ATEM_N	°C

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. HUD NERR has always measured only NO3.

11) Measured or calculated laboratory parameters –

a) **Parameters measured directly**

Nitrogen species:	NH4F, NO3F
Phosphorus species:	PO4F
Other:	CHLA_N, PHEA, Cl, SO4, TSS

b) **Calculated parameters**

None

12) Limits of detection –

A method detection limit (MDL), the lowest concentration of a parameter an analytical procedure can reliably detect, has been established by the CIES Analytical Laboratory for each parameter. The MDL is determined as three times the standard deviation of a minimum of 10 replicates of a single low concentration sample. These values are reviewed and revised periodically.

A Reporting Limit is also determined for each parameter as the greater of either ten times the standard deviation of a minimum of 10 replicates of a single low concentration sample, or the value of the lowest concentration calibration standard. The CIES Analytical Laboratory does not report measured data below the Reporting Limit. As a result, all data flagged and coded as "below minimum limit of method detection" for the NERRS dataset, are more specifically below the established reporting limit.

The current MDL and Reporting Limits are listed below. These values are reviewed and revised periodically.

Parameter	Variable	MDL	Reporting Limit	Dates in Use	Revisited
Ammonium	NH4F	0.0041 mg/L	0.02 mg/L as N	2009 – 2018	01/01/18
Nitrate	NO3F	0.0041 mg/L	0.02 mg/L as N	1991 – 2018	01/01/18
Orthophosphate	PO4	0.0007 mg/L	0.002 mg/L as P	2009 – 2018	01/01/18
Chlorophyll A	CHLA_N	0.02 µg/L	0.02 µg /L	2004 – 2018	01/01/18
Phaeophytin	PHEA_N	0.02 µg /L	0.02 µg /L	2004 – 2018	01/01/18
Total Suspend Solids	TSS	0.1 mg/L	0.1 mg/L	1991 – 2018	01/01/18
Chloride	CL	0.0250 mg/L	0.02 mg/L	1991 – 2018	01/01/18
Sulfate	SO4	0.0102 mg/L	0.02 mg/L	1991 – 2018	01/01/18

Cary Institute of Ecosystem Studies Rachel L Carson Analytical Laboratory Annual Method Detection Limits					
Test	NH4-N	Cl	NO3	SO4	PO4-P
Results_Units	mg/L	mg/L	mg/L	mg/L	mg/L
Reporting_Limit	0.02	0.02	0.02	0.02	0.002
Method	Colorimetric	IC	IC	IC	Colorimetric
2011	0.003	0.008	0.006	0.006	0.0005
2012	0.002	0.002	0.001	0.004	0.0004
2013	0.004	0.004	0.002	0.008	0.002
2014	0.004	0.004	0.002	0.008	0.002
2015	0.003	0.0020	0.0010	0.0010	0.0017
2016	0.0088	0.0098	0.0029	0.0074	0.0015
2017	0.0026	0.0038	0.0026	0.0041	0.0012
2018	0.0041	0.0250	0.0041	0.0102	0.0007

13) Laboratory methods –

a) Parameter: TSS

Method reference: Standard Methods for Examination of Water and Wastewater, # 2540D.

Method Descriptor: Well-mixed samples are filtered through a combusted, weighed glass fiber filter and the residue on the filter (suspended solids) is dried to a constant weight. The concentration of TSS (mg/L) is calculated by subtracting the original weight of the filter from the weight of the filter + suspended solids and dividing by the total volume filtered.

Preservation method: N/A

b) Parameter: NH4F

Method Reference: Lachat Quikchem8000 Flow Injection Analyzer using Lachat method 10-107-06-1-J

Method Descriptor: Ammonium reacts with alkaline phenol, and sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonium concentration in the sample.

Preservation Method: Samples are filtered using 47 mm GF/F filters within 24 h of collection and 1 ml of 1 N H_2SO_4 is added to the filtrate. Samples are stored at -20°C for up to one month prior to analysis.

c) Parameter: NO3F

Method Reference: Small, H., Stevens, T.S. and Bauman, W.C. 1975. Anal. Chem. 47:1801-1809.

Method Descriptor: A small volume of sample is injected into an ion-exchange column and eluted with a flowing stream of carbonate-bicarbonate. The sample is pumped through two different ion exchange columns, a suppressor device, and into a conductivity detector. Ions from the sample are separated into discrete bands due to different retention times, and the ions are compared to known standards.

Preservation Method: Samples are filtered using 47mm GF/F filters within 24 h of collection. Samples are stored at -20°C for up to one month prior to analysis.

d) Parameter: PO4F

Method Reference: Lachat Quickchem8000 Flow Injection Analyzer using Lachat method 10-115-01-1-M with modifications to eliminate silica interference, Phosphomolybdate method.

Method Descriptor: The orthophosphate ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample. Note that the stock Lachat Color Reagent was modified to decrease the level of silica interference. It was found that a decrease in pH of this reagent would decrease the level of silica interference (Jarvie et al 2002). However, a decrease in pH also creates a decrease in color development. Therefore a series of experiments were conducted to determine the optimal level of sulfuric acid concentration within the color reagent. The optimal sulfuric acid concentration that was determined is 1.98 N.

Preservation Method: Samples are filtered with 47mm GF/F filters within 24 h of collection. Samples are stored at -20°C for up to one month prior to analysis.

e) Parameter: CHLA_N and PHEA_N

Method references:
Holm-Hansen, O. and B. Riemann. 1978. Chlorophyll a determination: improvements in methodology. Oikos 30: 438-447.
Wetzel, R.G. and G.E. Likens. 1991. Limnological Analysis, 2nd ed. Springer-Verlag, New York: 168-169.

Method Descriptor: CHLA and PHEA are measured fluorometrically. Standards with known CHLA concentrations in 90% acetone are used to determine a relationship between CHLA and fluorescence (F). The standards are then acidified with 0.1 N HCL to determine the fluorescence ratio (t) of CHLA and PHEA for pure chlorophyll. Sample filters are extracted using basic methanol (5 ml) and the fluorescence is recorded (Rb). The samples are then acidified with 0.1 N HCL and the fluorescence is recorded (Ra). The following equations are used to determine CHLA and PHEA concentrations in samples:

$$\text{CHLA (ug/L)} = F*(t/t-1)*(Rb-Ra)*(v/V)$$
$$\text{PHEA (ug/L)} = F*(t/t-1)*(tRa-Rb)*(v/V)$$

Where v is the volume used for extraction (ml) and V is the volume filtered (ml).

Preservation method: Filters are stored in borosilicate vials in the dark at -4°C. Extraction solvent is not added until 24 h prior to fluorometry.

f) Parameter: Chloride (Cl)

Chloride ions present in water are analyzed using Standard Method 4110 – Determination of Anions by Ion Chromatography. We use a 4 mm-bore Dionex ICS 2000 ion chromatograph equipped with an EG50 eluent generator, AS18 analytical column, AG14 guard column, ASRS suppressor and 25 µL sample injection loop.

Method references: Standard Methods for the Examination of Water and Wastewater, 21st edition, 2005, American Public Health Association, Washington, D.C., pgs 4.3 – 4.5

Preservation Method: Samples are filtered using 47 mm GF/F filters within 24 h of collection. Samples are stored at -20°C for up to one month prior to analysis.

g) Parameter: Sulfate (SO4)

Sulfate ions present in water are analyzed using Standard Method 4110 – Determination of Anions by Ion Chromatography. We use a 4 mm-bore Dionex ICS 2000 ion chromatograph equipped with an EG50 eluent generator, AS18 analytical column, AG14 guard column, ASRS suppressor and 25 µL sample injection loop.

Method references: Standard Methods for the Examination of Water and Wastewater, 21st edition, 2005, American Public Health Association, Washington, D.C., pg 4.3 – 4.5

Preservation Method: Samples are filtered using 25 mm GF/F filters within 24 h of collection. Samples are stored at -20°C for up to one month prior to analysis.

14) Field and Laboratory QAQC programs –

a) **Precision**
   i) **Field variability** – All samples are collected successively. The replicates are taken at the same location, approximately 2 minutes apart.

   ii) **Laboratory variability** – There is no variability performed during laboratory analysis. All samples are processed using the same extraction methodology and procedure.
   iii) **Inter-organizational splits** – NA

b) **Accuracy**
   i) **Sample spikes** – NA
   ii) **Standard reference material analysis –** see below.
   iii) **Cross calibration exercises** - *NA*

Internal Standard Reference Material Analysis

A blind standard test was performed in December 2010 for NH4, NO3, NO3(as N), and PO4. A 1% dilution of a standard was utilized to perform said analysis. A duplicate of Standard A was also submitted as standard "B". The analyzed standard samples yielded the following results:

Nutrient	Standard Conc. Range (mg/L)	1% Dilution (10 mL in 1 L)	IES Results A (mg/L)	IES Results B (mg/L)	Pass/Fail
NH4	0.65-19 mg/l	0.0065-0.19	0.14	0.11	Pass
NO3-(as N)	0.25-40 mg/l	0.0025-0.40	0.075	0.073	Pass
NO3+	0.25-40 mg/l	0.0025-0.40	0.33	0.32	Pass

PO4	0.5-5.5 mg/l	0.005-0.055	0.032	0.029	Pass
Cl	N/A	N/A	2.52	2.62	N/A
SO3	N/A	N/A	4.4	1.05	N/A

All analyzed results were reported to be within acceptable range for the dilution. Both CL and SO3 were also analyzed; however, no concentration range was provided by the standard manufacturer for comparison.

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.

Data coded <CDR> Dilution

The following samples had to be diluted to achieve a measurement.
Dilutions as follows:

Chlorophyll Samples:

Station Code	DateTimeStamp	Rep	Dilution %
TS	06/07/18 14:30	Diel	50%

Data coded (CSM) See Metadata

TS diel samples at 4/17/2018 20:30 and 5/17/2018 14:00 were elevated compared to the rest of the year. Spring melt-off may have contributed to a higher NH4 abundance at the sample location, which often occurs earlier in the season from year to year.

Sample hold times

Nutrient samples are held at -20°C, CHLA and PHEA filters at -4°C. NERRS SOP allows nutrient samples to be held for up to 28 days at -20°C, plus allows for up to 5 days for collecting, processing, and shipping samples. Since CHLA and PHEA filters are not held at -20°C, they are only allowed to be held 24 hours in addition to the 5 days allowed for collecting and processing. Samples held beyond that time period are flagged suspect and coded CHB. Note that TSS samples are always analyzed immediately after collection in-house.

Sample Descriptor	PO4F	NH4F	NO3F	Cl	CHLA_N, PHEA	SO4
04/18/2018, all grab samples	05/18/2018	05/15/2018	05/18/2018	05/18/2018	06/13/2018*	05/18/2018
04/30/18 NP	05/18/2018	NA	05/18/2018	05/18/2018	06/13/2018*	5/18/2018
04/17-04/18, all diel samples	05/17/2018	05/15/2018	05/18/2018	05/18/2018	06/13/2018*	05/18/2018
05/17/18, all grab samples	06/05/2018	06/06/2018	06/06/2018	06/06/2018	06/13/2018*	06/06/2018
05/30/18 NP	06/05/2018	NA	6/6/2018	06/06/2018	06/13/2018*	06/06/2018
05/16-05/18/18, all diel samples	06/05/2018	06/06/2018	06/06/2018	06/06/2018	06/13/2018*	06/06/2018
06/07/18, all grab samples	07/13/2018*	07/12/2018*	07/16/2018*	07/16/2018*	7/10/2018*	07/16/2018*
06/29/18 NP	07/13/2018	NA	7/16/2018	07/16/2018	7/10/2018*	07/16/2018
06/06-06/07/2018, all diel samples	07/13/2018*	07/12/2018*	07/16/2018*	07/16/2018*	7/10/2018*	07/16/2018*
07/31/2018, all grab samples	8/14/2018	08/16/2018	08/14/2018	08/14/2018	10/05/2018*	08/14/2018
07/20/2018 NP	08/14/2018	NA	8/14/2018	08/14/2018	10/05/2018*	08/14/2018
07/30 – 07/31/18, all diel samples	08/14/2018	08/15/2018	08/14/2018	08/14/2018	10/05/2018*	08/14/2018
08/29/2018, all grab samples	09/13/2018	09/14/2018	09/14/2018	09/14/2018	11/07/2018*	09/14/2018
08/17/2018 NP	09/13/2018	NA	8/14/2018	09/14/2018	11/07/2018*	09/14/2018
08/28-08/29/2018, all diel samples	09/13/2018	09/14/2018	09/14/2018	09/14/2018	11/07/2018*	09/14/2018
09/12/2018, all grab samples	10/10/2018	10/11/2018	10/12/2018	10/12/2018	11/07/2018*	10/12/2018
09/27/2018 NP	10/10/2018	NA	10/12/2018	10/12/2018	11/07/2018*	10/12/2018
09/11-09/13/2018, all diel samples	10/10/2018	10/11/2018	10/12/2018	10/12/2018	11/07/2018*	10/12/2018
10/25/2018, all grab samples	11/27/2018	11/28/2018	11/27/2018	11/27/2018	02/20/2019*	11/27/2018
10/11/2018 NP	11/27/2018	NA	11/27/2018	11/27/2018	02/20/2019*	11/27/2018
10/24-10/25/2018, all diel samples	11/27/2018**	11/28/2018*	11/27/2018**	11/27/2018**	02/20/2019*	11/27/2018**
11/29/2018, all grab samples	12/17/2018	12/18/2018	12/18/2018	12/18/2018	02/20/2019*	12/18/2018

11/26/18 NP	12/17/2018	NA	12/18/2018	12/18/2018	02/20/2019*	12/18/2018
11/29-11/30/2018, all diel samples	12/17/2018	12/18/2018	12/18/2018	12/18/2018	02/20/2019*	12/18/2018

*sample held longer than allowed by NERRS protocols
**only the 10/24/2018 samples (not 10/25 samples) held longer than allowed for nutrient analyses.

References

Jarvie, Helen & Withers, J. & Neal, Caitlin. (2002). Review of robust measurement of phosphorus in river water: Sampling, storage, fractionation and sensitivity. Hydrology and Earth System Sciences. 6. 10.5194/hess-6-113-2002.