

Hudson River (HUD) NERR Nutrient Metadata
January 1, 2023 – December 31, 2023
Latest Update: 06/03/2024

Note: This is a provisional metadata document; it has not been authenticated as of its download date. Contents of this document are subject to change throughout the QAQC process and it should not be considered a final record of data documentation until that process is complete. Contact the CDMO (cdmosupport@baruch.sc.edu) or reserve with any additional questions.

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

a) Reserve Contact:

Chris Mitchell, Research Coordinator

Email: Christopher.Mitchell@dec.ny.gov

Phone: 845-889-4745 x119

Fax: 845-889-4749

Christina Pacella, SWMP Technician

Email: Christina.Pacella@dec.ny.gov

Phone: 845-889-4745 x104

Fax: 845-889-4749

Address:

Hudson River NERR

Norrie Point Environmental Center

256 Norrie Point Way

PO Box 315

Staatsburg, NY 12580

2) Research objectives –

a) Monthly grab sampling program

The objective of this study is to monitor nutrient concentrations at three of the four component sites of the Hudson River National Estuarine Research Reserve (HRNERR; the Reserve). Grab samples are taken from four freshwater tidal locations; Ferry Landing (FL; Stockport Flats Component), Tivoli North Bay and Tivoli South Bay (TN and TS, respectively; Tivoli Component), and Norrie Point (NP; Headquarters Location). Grab samples are also collected at Bear Mountain (BM; Iona Island Component), which is located in the typical geographic location of the salt front where the salinity gradient varies yearly. YSI datasondes are deployed at all grab sampling sites and meteorological data are collected continuously at the Norrie Point and Tivoli Components, thus relationships can be established between nutrient levels, the aquatic environment, and meteorological conditions. A concerted effort is made to collect samples 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; however, it should be noted that logistical challenges such as inclement weather events and unfeasible tide cycles may result in the collection of samples during a flood tide.

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 South 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 YSI data logger locations in the Stockport, Tivoli Bays, and Iona Island components of the Reserve and one additional location at the Norrie Point headquarters of the Reserve. These sites include Ferry Landing, Tivoli North Bay, Tivoli South Bay, and Bear Mountain. Monthly sampling at Tivoli North and South Bays are conducted on the same day, typically during an ebb tide within and 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 handheld YSI multiparameter digital meter is used to measure temperature, salinity, specific conductivity, field pH, and dissolved oxygen (% and mg/L), and the values are recorded. Grab samples are placed on ice and returned to the laboratory. Within 24 hours, pH and alkalinity are measured and samples are filtered for seston (TSS) and chlorophyll A (CHLA)/phaeophytin (PHEA). The filtrate is collected and transferred to 60 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 1.8 mL of 1 N H₂SO₄ is added to samples that will be analyzed for ammonium, orthophosphate, and nitrate/nitrite. Filters for CHLA/PHEA analysis are placed in borosilicate vials and stored in a freezer at -4°C.

b) Diel sampling program

Monthly diel sampling is conducted 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 six inches from the datasonde. Water is collected 25 cm off the river bottom; approximate sampling depths are 0.5 meters at low tide and 2.5 meters at high tide.

Until November 2002, two sequential samples were collected once every 2 hours for 22 hours. After November 2002, the protocol changed to collect two sequential samples once every 2.5 hours for 27.5 hours. The first sample is always collected at slack low tide. Samples are collected in 1 L 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 3.6 mL of 10 N H₂SO₄ prior to deployment to preserve the sample for ammonium, orthophosphate, and nitrate/nitrite analyses. 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 60 mL Nalgene bottles that have been acid washed and rinsed as described previously. Non-acidified samples, the first in each collection sequence, are filtered for seston and CHLA/PHEA. The filtrate is collected and transferred to 60 mL Nalgene bottles that have been acid washed and rinsed as described previously. All filtered water samples are stored at 4°C until nutrient analyses are conducted. Filters used for CHLA/PHEA analysis are placed in borosilicate vials and stored in a freezer at -4°C.

4) Site location and character –

Site name	Ferry Landing (FL)
Latitude and longitude	42°21'14.36"N, 73°47'20.76"W
Tidal range (<i>meters</i>)	1.19 m
Salinity range (<i>psu</i>)	0 – 0.20 psu
Type and amount of freshwater input	An unnamed tributary is located approximately 0.7 miles south of the station drains approximately 5.56 square miles (sq. mi).

Water depth (<i>meters</i> , <i>MLW</i>)	<i>This information is pending – surveying activities are being conducted during the field season of 2024, and MLW will be updated on a site-by-site basis as it becomes available.</i>
Sonde distance from bottom (<i>meters</i>)	0.25 m
Bottom habitat or type	Soft silt and clay
Pollutants in area	None known; potential inputs include combined sewer overflows (CSOs)
Description of watershed	This station is situated along the eastern bank of the Hudson River and is affixed to a fishing pier. Land use within the immediate vicinity is comprised predominantly of vegetated wetland and forested areas with some residential development

Site name	Tivoli North Bay (TN)
Latitude and longitude	42° 02' 11.56464" N, 73° 55' 31.16645" W
Tidal range (<i>meters</i>)	1.19 m
Salinity range (<i>psu</i>)	0 – 0.20 psu
Type and amount of freshwater input	Stony Creek is the primary tributary which contributes freshwater input into this site; it drains approximately 22.2 sq. mi into TN.
Water depth (<i>meters</i> , <i>MLW</i>)	<i>This information is pending – surveying activities are being conducted during the field season of 2024, and MLW will be updated on a site-by-site basis as it becomes available.</i>
Sonde distance from bottom (<i>meters</i>)	0.50 m
Bottom habitat or type	Soft silt and clay
Pollutants in area	None known
Description of watershed	TN is a freshwater tidal marsh with emergent marsh vegetation dominated by narrowleaf cattail (<i>Typha angustifolia</i>). Located on the eastern side of the Hudson River, it is constrained to the west by a railroad. East of the site are wooded clay bluffs and forested uplands and fields, with some land utilized by Bard College facilities and properties

Site name	Tivoli South Bay (TS)
Latitude and longitude	42° 01' 37.336" N, 73° 55' 33.445" W
Tidal range (<i>meters</i>)	1.19 m
Salinity range (<i>psu</i>)	0 – 0.20 psu
Type and amount of freshwater input	The Sawkill is the primary tributary which contributes freshwater input into this site; it drains approximately 22 sq. mi into TS.
Water depth (<i>meters</i> , <i>MLW</i>)	<i>This information is pending – surveying activities are being conducted during the field season of 2024, and MLW will be updated on a site-by-site basis as it becomes available.</i>

Sonde distance from bottom (<i>meters</i>)	0.50 m
Bottom habitat or type	Soft silt and clay
Pollutants in area	None known
Description of watershed	TS is a freshwater tidal 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 water chestnut (<i>Trapa natans</i>). Similar to TN, the surrounding areas are characterized by wooded uplands and Bard College facilities and properties. This site is also abutted to the west by a railroad.

Site name	Bear Mountain (BM)
Latitude and longitude	41° 18' 51.0" N, 73° 59' 6.0" W
Tidal range (<i>meters</i>)	1.19 m
Salinity range (<i>psu</i>)	0.10 - 10
Type and amount of freshwater input	An unnamed stream located approximately 100 m west of the sonde station drains roughly 0.048 sq. mi into the Hudson River; this stream contributes a slight freshwater signature to the site.
Water depth (<i>meters</i> , MLW)	<i>This information is pending – surveying activities are being conducted during the field season of 2024, and MLW will be updated on a site-by-site basis as it becomes available.</i>
Sonde distance from bottom (<i>meters</i>)	0.50 m
Bottom habitat or type	Rocky substrate composed of cobbles and gravel
Pollutants in area	None known
Description of watershed	BM is situated approximately 700 m north of the Iona Island Marsh component site at River Mile (RM) 45. This is a tidal brackish wetland with emergent vegetation dominated by narrowleaf cattail and invasive common reed (<i>Phragmites australis</i>). A freshwater creek, Doodletown Brook, is the main tributary flowing into Iona Island Marsh. BM sits at the foot of Bear Mountain State Park, a mostly undeveloped, mountainous woodland. The Bear Mountain samples are frequently in the salt frontal boundary in the Hudson River. Salinity concentrations at this site are driven primarily by tidal and meteorological factors.

All Hudson River NERR historical nutrient/pigment monitoring stations:

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
FL	P	Ferry Landing	42°21'14.43" N 73°47'20.72"W	04/01/2022 - Current	NA	NA

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
TN	P	Tivoli North Bay	42° 2' 11.56 N, 73° 55' 31.17 W	07/01/1999 00:00 - Current	NA	NA
TS	P	Tivoli South Bay	42° 1' 37.34 N, 73° 55' 33.45 W	05/01/1995 00:00 - Current	NA	NA
NP	S	Norrie Point	41°49'54.0"N 73°56'31.0"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
BM	P	Bear Mountain	41°18'53.19" N 73°59'6.78"W	01/01/2020 00:00 - Current	NA	New site established for the 2020 sampling season. Replaced Saw Kill (SK) as primary station in 2019
SK	D	Sawkill	42° 1' 1.82 N, 73° 54' 53.86 W	05/01/1995 00:00 – 12/3/2019	The attachment point (dam) is scheduled for demolition	NA
SC	D	Stony Creek	42° 2' 46.68 N, 73° 54' 38.88 W	04/01/2002 00:00 – 12/31/2022	Site Profile has been significant altered due to slope failure, beaver activity, and anthropogenic changes and no longer is a viable location to deploy instruments.	NA

5) Coded variable definitions –

hudbmnut = Hudson River Reserve nutrient data for Bear Mountain

hudsknut = Hudson River Reserve nutrient data for Sawkill

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 (Secondary Station)

hudflnut = Hudson River Reserve nutrient data for Ferry Landing

monthly grab sample program = 1

diel grab sample program = 2

6) Data collection period –

a) Monthly sampling

Site	Date	Rep 1 Time	Rep 2 Time
BM	01/19/2023	12:12	12:13
BM	02/14/2023	11:38	11:39

Site	Date	Rep 1 Time	Rep 2 Time
BM	03/28/2023	11:01	11:02
BM	04/27/2023	11:09	11:10
BM	05/31/2023	12:22	12:23
BM	06/29/2023	10:15	10:16
BM	08/10/2023	12:45	12:46
BM	09/26/2023	12:31	12:32
BM	10/23/2023	11:16	11:17
BM	11/21/2023	11:46	11:47
BM	12/20/2023	11:13	11:14

Site	Date	Rep 1 Time	Rep 2 Time
NP	01/27/2023	10:58	10:59
NP	02/22/2023	09:42	09:43
NP	03/27/2023	11:19	11:20
NP	04/21/2023	07:55	07:56
NP	05/12/2023	13:24	13:25
NP	06/21/2023	09:40	09:41
NP	07/06/2023	07:50	07:51
NP	08/18/2023	08:38	08:39
NP	09/07/2023	13:36	13:37
NP	10/20/2023	08:11	08:12
NP	11/17/2023	11:15	11:16
NP	12/07/2023	14:12	14:13

Site	Date	Rep 1 Time	Rep 2 Time
FL	03/09/2023	10:40	10:41
FL	04/20/2023	09:40	09:41
FL	05/19/2023	10:02	10:03
FL	06/20/2023	10:45	10:46
FL	07/24/2023	12:09	12:10
FL	08/24/2023	12:31	12:32
FL	09/18/2023	12:50	12:51
FL	10/30/2023	10:05	10:06
FL	11/28/2023	10:34	10:35
FL	12/29/2023	10:28	10:29

Site	Date	Rep 1 Time	Rep 2 Time
TN	03/23/2023	09:30	09:31
TN	04/11/2023	10:55	10:56
TN	05/24/2023	10:52	10:53
TN	06/07/2023	10:46	10:47
TN	07/19/2023	09:23	09:24
TN	08/17/2023	09:47	09:48
TN	09/06/2023	12:05	12:06
TN	10/18/2023	09:40	09:41
TN	12/01/2023	10:18	10:19

Site	Date	Rep 1 Time	Rep 2 Time
TS	03/23/2023	08:40	08:41
TS	04/11/2023	11:42	11:43

Site	Date	Rep 1 Time	Rep 2 Time
TS	05/24/2023	10:32	10:33
TS	06/07/2023	11:38	11:39
TS	07/19/2023	09:40	09:41
TS	08/17/2023	10:15	10:16
TS	09/06/2023	11:31	11:32
TS	10/18/2023	09:57	09:58
TS	12/01/2023	10:02	10:03

b) Diel Sampling

Site	GRAB	Start Date	Start Time	End Date	End Time
TS	-	Not Deployed Due to Ice			
TS	-	Not Deployed Due to Ice			
TS	-	Not Deployed Due to Ice			
TS	-	04/11/2023	23:30	04/13/2023	03:00
TS	-	05/23/2023	23:30	05/25/2023	03:00
TS	-	06/06/2023	22:30	06/08/2023	02:00
TS	-	07/18/2023	21:00	07/20/2023	00:30
TS	-	08/15/2023	20:00	08/16/2023	23:30
TS	-	09/20/2023	00:00	09/21/2023	03:30
TS	-	10/17/2023	23:00	10/19/2023	02:30
TS	-	11/29/2023	21:30	12/01/2023	01:30
TS	-	Not Deployed Due to Ice			

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 2022.

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/nitrite, orthophosphate, chloride, sulfate), data files are transferred directly from analytical instruments to desktop computers. Reports are generated as Excel spreadsheets and verified by Reserve staff. Data are examined for completeness, consistency, and outliers. Suspect data are flagged, and if possible, samples are analyzed a second time.

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

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 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 asterisk “*”.

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:	*Orthophosphate	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
Plant Pigments:	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
Carbon:			
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	°C
	Specific Conductance	SCON_N	mS/cm
	Salinity	SALT_N	psu
	% 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 NO₃ 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, NO₃F
 Phosphorus species: PO₄F
 Other: CHLA_N, PHEA, Cl, SO₄, TSS

b) **Calculated parameters**

None

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. These values are reviewed and revised periodically.

***Beginning in 2022, HUDNERR began processing nutrient data in-house, and no longer utilizes the methodologies and MDLs provided by the Cary Institute of Ecosystem Studies Rachel L Carson Analytical Laboratory.**

Prior years MDLs and RLs are as follows:

Parameter	Variable	MDL	Reporting Limit	Dates in Use	Revisited
Ammonium	NH ₄ F	0.003 mg/L	0.02 mg/L as N	2009 – 2021	01/01/2021
Nitrate	NO ₃ F	0.005 mg/L	0.02 mg/L as N	1991 – 2021	01/01/2021
Orthophosphate	PO ₄	0.0006 mg/L	0.002 mg/L as P	2009 – 2021	01/01/2021
Chloride	CL	0.074 mg/L	0.02 mg/L	1991 – 2021	01/01/2021
Sulfate	SO ₄	0.055 mg/L	0.02 mg/L	1991 – 2021	01/01/2021

Cary Institute of Ecosystem Studies Rachel L Carson Analytical Laboratory Annual Method Detection Limit					
Test	NH ₄ -N	Cl	NO ₃	SO ₄	PO ₄ -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	Colormetric	IC	IC	IC	Colormetric
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
2019	0.0080	0.0250	0.040	0.0110	0.0013
2020	0.0080	0.0250	0.040	0.0110	0.0013
2021	0.003	0.074	0.005	0.055	0.006

Beginning with the 2022 Sample Year, HUDNERR utilizes MDLs established by the SEAL Analytical Detection Limit Studies.

Parameter	Variable	MDL	Dates in Use	Revisited
Ammonia	NH3F	0.003 mg/L	2022 - Current	01/01/2023
Nitrate + Nitrite	NO23F	0.002 mg/L	2022 - Current	01/01/2023
Orthophosphate	PO4	0.002 mg/L	2022 - Current	01/01/2023
Chlorophyll A	CHLA_N	0.02 ug/L	2004 – 2022	01/01/2023
Phaeophytin	PHEA_N	0.02 ug/L	2004 – 2022	01/01/2023
Total Suspend Solids	TSS	0.1 mg/L	1991 – 2022	01/01/2023
Chloride	CL	0.3 mg/L	2022 - Current	01/01/2023
Sulfate	SO4	0.09 mg/L	2022 - Current	01/01/2023

13) Laboratory methods –

a) Parameter: NH3F

AQ300 HUDNERR Laboratory Method: 148 - Ammonia

EPA Reference Method: EPA-148-D Rev 1

Method Reference: Methods for the Determination of Inorganic Substances in Environmental Samples, EPA 600/R 93/100, August 1993: Method 350.1, Revision 2.0

Method Descriptor: At alkaline pH, ammonia in the sample reacts with hypochlorite (HClO⁻), as previously liberated from dichloroisocyanurate. The chloramine formed then reacts with salicylate, at pH at least 12.6, in presence of nitroferrocyanide. During static incubation at 40°C, a blue-green indophenol dye forms, which is measured photometrically at 660nm.

Preservation Method: Samples are filtered with gf/f filters, and preserved with 1.8 mL of 1N H2SO4 and stored at 4°C. Samples are analyzed within 28 days

b) Parameter: NO23F

AQ300 HUDNERR Laboratory Method: 127 – NO_x (Nitrate + Nitrite)

EPA Reference Method: EPA-127-D Rev 2A

Method Reference: Methods for the Determination of Inorganic Substances in Environmental Samples, EPA 600/R 93/100, August 1993: Method 353.2, Revision 2.0.

Standard Methods for the Examination of Water and Wastewater, APHA/AWWA/WEF, method 4500 NO₃- F (2017 forward).

Method Descriptor: The sample is mixed with pH buffer and then transferred to a copperized cadmium coil, where nitrate is chemically reduced to nitrite. The chemically reduced sample is mixed with color reagent, prepared in dilute phosphoric acid. Original nitrite, plus nitrite from chemical reduction, reacts with sulfanilamide to form a diazonium compound. This species couples with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a reddish-purple azo dye that is measured photometrically at 520nm. Separate results for nitrite are obtained using AQ method EPA-115.

Preservation Method: Samples are filtered with gf/f filters and preserved with 1.8 mL of 1N H2SO4 and stored at 4°C. Samples are analyzed within 28 days.

c) Parameter: PO4F

AQ300 HUDNERR Laboratory Method: 118 – oPhosphate High

EPA Reference Method: EPA-118-D Rev 1

Method Reference: Methods for the Determination of Inorganic Substances in Environmental Samples, USEPA 600/R 93/100, August 1993: Method 365.1, Rev 2.0.

Standard Methods for the Examination of Water and Wastewater, APHA/AWWA/WEF, method 4500-P F (1999 forward).

Method Descriptor: Reaction with acidic molybdate in the presence of antimony forms an antimony phosphomolybdate complex. This complex is chemically reduced by ascorbic acid to an intensely blue complex: phosphomolybdenum blue. The absorbance of this complex is measured photometrically at 880nm.

Preservation Method: Samples are filtered with gf/f filters and preserved with 1.8 mL of 1N H₂SO₄ and stored at 4°C. Samples are analyzed within 48 hours.

d) **Parameter: ClF**

AQ300 HUDNERR Laboratory Method: 105 – Chloride

EPA Reference Method: EPA-105-D Rev 1A

Method Reference: Methods for Chemical Analysis of Waters and Wastes, US EPA 600/4-79-020, 1983: Method 325.2 Standards Methods for the Examination of Water and Wastewater, APHA/AWWA/WEF, method 4500-Cl-E (18th, 19th, 20th Ed.).

Method Descriptor: The thiocyanate ion (SCN⁻) is liberated from mercuric thiocyanate through sequestration of mercury by the chloride ion to form non-ionized mercuric chloride. In the presence of ferric ions, the liberated thiocyanate ions form a highly colored ferric thiocyanate. The absorbance of this complex is measured spectrophotometrically at 480nm.

Preservation Method: Samples are filtered with gf/f filters and stored at 4°C. Samples are analyzed within 28 days.

e) **Parameter: SO₄F**

AQ300 HUDNERR Laboratory Method: 165 – Chloride

EPA Reference Method: EPA-165-D Rev. 2A

Method Reference:

ASTM D516-11, *Standard Test Methods for Sulfate Ion in Water*, ASTM International, West Conshohocken, PA, 2011, www.astm.org.

Standard Methods for the Examination of Water and Wastewater, APHA/AWWA/WEF, 4500-SO₄-E (1997 forward).

ISO/DIS 15923-1, *Water Quality – Determination of selected parameters by a discrete analysis system – Part 1: Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate and silicate with photometric detection*.

Method Descriptor: Sulfate ion is converted to a barium suspension under controlled conditions. The resulting turbidity is determined using a filter photometer at 405 nm.

Preservation Method: Samples are filtered with gf/f filters and stored at 4°C. Samples are analyzed within 28 days.

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:

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

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

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

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 1 minute 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** – See below.

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:

<u>Nutrient</u>	<u>Standard Conc. Range</u> (mg/L)	<u>1% Dilution</u> (10mL in 1L)	<u>IES Results A</u> (mg/L)	<u>IES Results B</u> (mg/L)	<u>Pass/Fail</u>
NH ₄	0.65 - 19 mg/l	0.0065 - 0.19	0.14	0.11	Pass
NO ₃ (as N)	0.25 - 40 mg/l	0.0025 - 0.40	0.075	0.073	Pass
NO ₃ +	0.25 - 40 mg/l	0.0025 - 0.40	0.33	0.32	Pass
PO ₄	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
SO ₃	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
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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
<i>Tide stage</i>	
TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide
<i>Wave height</i>	
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
<i>Wind direction</i>	
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
<i>Wind speed</i>	
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 NERR 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.

Sample hold times for 2023: NERRS SOP allows nutrient samples to be held for up to 24 hours if held at 4°C with no preservation, for NH₄F and NO₃F up to 28 days if acidified and held at 4°C, and up to 28 days (CHLA for 30 days) if held at -20°C. Tier II parameters, with a few exceptions, are subject to the same sample hold times. In all cases, up to an additional 5 days is allowed for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect and coded CHB in the data set.

Data coded (CDR) Dilution

The following samples were diluted to achieve a measurement:

Chlorophyll

Station Code	Sample Date/Time	Monitoring Program	Rep	Dilution %
FL	06/20/2023 @ 10:45	1	A	25%
FL	06/20/2023 @ 10:46	1	B	25%
TN	05/25/2023 @ 10:52	1	A	50%
TN	05/25/2023 @ 10:53	1	B	50%
TS	05/25/2023 @ 10:32	1	A	50%
TS	05/25/2023 @ 10:33	1	B	50%
TS	05/23/2023 @ 23:30	2	Diel	50%
TS	05/24/2023 @ 02:00	2	Diel	50%
TS	05/24/2023 @ 04:30	2	Diel	50%
TS	05/24/2023 @ 09:30	2	Diel	50%
TS	05/24/2023 @ 14:30	2	Diel	50%
TS	05/24/2023 @ 17:00	2	Diel	50%
TS	05/24/2023 @ 22:00	2	Diel	50%
TS	05/25/2023 @ 03:30	2	Diel	50%
TS	05/25/2023 @ 03:00	2	Diel	50%

Data coded (CSM) See metadata

TS 07/19/2023 @ 14:30 – 22:00, Monitoring Program 2

These data are missing due to samples not being collected as scheduled. At some point between 12:00 and 14:30, the sample arm tube of the ISCO unit detached, resulting in a disruption of flow to the sample bottles.

The following tables describe the analysis dates for both Tier I and Tier II parameters for SWMP monthly and diel samples collected in 2023. Parameters with a 28-day hold time are included in Table A, and those with a 48-hour hold time are included in Table B.

Table A

Sample Descriptor	NH ₄ F	NO ₃ F	CLF	CHLA_N, PHEA	SO ₄ F
January 2023, SWMP Monthly	02/09/2023	02/10/2023	02/13/2023	02/10/2023	02/10/2023
February 2023, SWMP Monthly	03/03/2023	03/07/2023	03/18/2023	03/10/2023	03/10/2023
March 2023, SWMP Monthly	04/19/2023*	04/17/2023*	04/18/2023*	04/21/2023*	04/26/2023*
April 2023, SWMP Monthly	05/04/2023	05/05/2023	05/03/2023	05/16/2023*	04/28/2023
04/11-04/13, all diel samples	05/04/2023	04/14/2023	04/18/2023	05/16/2023*	04/28/2023

Sample Descriptor	NH4F	NO23F	CLF	CHLA_N, PHEA	SO4F
May 2023, SWMP Monthly	06/08/2023	06/02/2023	06/07/2023	06/15/2023*	06/01/2023
05/23-05/25, all diel samples	06/08/2023	06/02/2023	06/07/2023	06/15/2023*	06/01/2023
June 2023, SWMP Monthly	07/10/2023*	07/17/2023*	07/13/2023*	07/07/2023	07/11/2023*
06/06-06/08, all diel samples	07/10/2023*	07/17/2023*	07/13/2023*	07/07/2023	07/12/2023*
July 2023, SWMP Monthly	07/31/2023	07/27/2023	07/28/2023	08/08/2023*	07/28/2023
07/18 – 07/20, all diel samples	07/31/2023	07/27/2023	07/28/2023	08/08/2023	07/28/2023
August 2023, SWMP Monthly	08/25/2023	08/24/2023	08/24/2023	09/07/2023	08/25/2023
08/15 – 08/16, all diel samples	08/25/2023	08/24/2023	08/24/2023	09/07/2023	08/25/2023
September 2023 SWMP Monthly	10/03/2023	09/27/2023	09/29/2023	10/13/2023*	10/02/2023
09/20-09/21, all diel samples	10/03/2023	09/27/2023	09/29/2023	10/13/2023	10/02/2023
October 2023, SWMP Monthly	11/07/2023	11/06/2023	11/01/2023	11/22/2023*	11/01/2023
10/17-10/19, all diel samples	11/07/2023	11/06/2023	11/01/2023	11/22/2023*	11/01/2023
November 2023, SWMP Monthly	12/07/2023	12/04/2023	12/06/2023	12/22/2023*	12/06/2023
December 2023, SWMP Monthly	N/A	01/23/2024*	N/A	01/19/2024*	01/25/2023*

* Sample held longer than allowed by NERRS and/or Reserve method protocols.

** Due to freezing temperatures, the ISCO unit was not deployed during the months of November and December.

Table B – PO4 Analyses

Month	Site*	Analysis Date	Month	Site*	Analysis Date
January 2023	FL	No samples collected	July 2023	FL	07/24/2023
	TN	No samples collected		TN	07/19/2023
	TS	No samples collected		TS	07/19/2023
	NP	02/08/2023**		NP	07/10/2023
	BM	02/08/2023**		BM	N/A
	All diels	N/A***		All diels	07/20/2023
February 2023	FL	No samples collected	August 2023	FL	08/31/2023**
	TN	No samples collected		TN	08/31/2023**
	TS	No samples collected		TS	08/31/2023**
	NP	02/24/2023		NP	08/31/2023**
	BM	02/24/2023**		BM	08/31/2023**

Month	Site*	Analysis Date	Month	Site*	Analysis Date
	All diels	N/A***		All diels	08/31/2023**
March 2023	FL	03/10/2023	September 2023	FL	09/19/2023
	TN	03/24/2023		TN	09/07/2023
	TS	03/24/2023		TS	09/07/2023
	NP	03/29/2023		NP	09/07/2023
	BM	03/29/2023		BM	09/27/2023
	All diels	N/A***		All diels	09/22/2023
April 2023	FL	04/21/2023	October 2023	FL	10/31/2023
	TN	04/12/2023		TN	10/18/2023
	TS	04/12/2023		TS	10/18/2023
	NP	04/21/2023		NP	10/20/2023
	BM	04/28/2023		BM	10/24/2023
	All diels	04/12/2023, 04/14/2023		All diels	10/18/2023
May 2023	FL	05/19/2023	November 2023	FL	11/28/2023
	TN	05/26/2023		TN	No samples collected
	TS	05/26/2023		TS	No samples collected
	NP	05/12/2023		NP	11/17/2023
	BM	06/01/2023		BM	11/22/2023
	All diels	05/26/2023**		All diels	N/A***
June 2023	FL	06/21/2023	December 2023	FL	12/29/2023
	TN	06/12/2023**		TN	12/1/2023
	TS	06/12/2023**		TS	12/1/2023
	NP	06/21/2023		NP	12/8/2023
	BM	06/30/2023		BM	12/22/2023
	All diels	06/12/2023**		All diels	N/A***

* Includes both A and B reps for monthly samples

** Sample held longer than allowed by NERRS and/or Reserve method protocols.

*** Due to freezing temperatures, the ISCO unit was not deployed during the months of November and December.