**Hudson River (HUD)** **NERR Nutrient Metadata**

**January 1, 2022 – December 31, 2022**

**Latest Update:** June 14, 2023

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](mailto:cdmosupport@baruch.sc.edu)) or reserve with any additional questions.

**I. Data Set and Research Descriptors**

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

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**2) Research objectives** –

1. 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.

1. 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** –

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.

1. Diel Sampling

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 –**

The HRNERR 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)(41o02'30"N 73o54'15"W), Iona Island, Rockland County (RM 45)(41o18'15"N 73o58'45"W), Tivoli Bays, Dutchess County (RM 98)(42o02'15"N 73o55'10"W), and Stockport Flats, Columbia County (RM 124)(42o02'30"N 73o46'00"W). The Reserve also operates a station at its headquarters at Norrie Point, Dutchess County (RM 92) (41°49'54.0"N 73°56'31.0"W). The 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.

**Historic Primary Sites**

The primary tributaries to the Tivoli Bays are Stony Creek and Saw Kill Creek, respectively. High concentrations of nitrate and phosphate have previously been documented in both watercourses. Nutrient concentrations in the Saw Kill Creek appear to be strongly influenced by adjacent residential land use practices. Water quality monitoring stations were operated at both streams to evaluate and identify non-point sources of nutrient inputs at these sites; however, they are currently inactive. Descriptions of both sites are provided below.

**Stony Creek (latitude 42° 02' 45.556" N, longitude 73° 54' 40.237" W; 2002-2022)**

Stony Creek is the main tributary flowing into Tivoli North Bay, contributing non-tidal and freshwater inputs. 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. Tributaries to Stony Creek consist of smaller creeks and streams within its watershed.

**Saw Kill (latitude 42° 1' 1.82 N, longitude 73° 54' 53.86 W; 1995-2019)**

The Saw Kill is the primary tributary flowing into Tivoli South Bay. With a watershed comprising approximately 26.6 square miles, land use within consists primarily of forested, agricultural, and urban areas. The substrate of the creek at the sampling location is characterized by rock and gravel, with a water depth ranging from 0.5 to 2.0 meters and discharge ranging from 2x10-5 to 1.2 m3/sec.

**Current Sites**

Ferry Landing (latitude 42°21'14.36"N, 73°47'20.76"W) is located within a freshwater tidal portion of the Hudson River at RM 125. It has a tidal range of 1.19 m, with a soft, silty/clay bottom, and a depth range of 0.5 to 2.5 m at the sampling location. The sampling location is adjacent to a fishing pier located on the northern end of the Stockport Flats component site of the Reserve.

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 narrowleaf cattail (*Typha angustifolia*)*.* Tivoli North Bay has a tidal range of 1.19 m, a soft, silt/clay substrate, and a depth range from 0.5 to 2.5 m at the sampling location. The non-tidal freshwater inputs to Tivoli North Bay include a large upland tributary (Stony Creek; see above) and a few small perennial streams.

Tivoli South Bay (latitude 42° 01' 37.336" N, longitude 73° 55' 33.445" W) 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 (*Trapa natans*). Tivoli South Bay has a tidal range of 1.19 m and a soft, silt/clay substrate. The depth at the sampling location ranges from 0.5 to 2.5 m. The non-tidal freshwater inputs to Tivoli South Bay include a large upland tributary (Saw Kill; see above) and a few small perennial streams.

Bear Mountain (latitude 41° 18' 51.0” N, longitude 73° 59' 6.0" W) is situated approximately 700 m north of the Iona Island Marsh component site at RM 45. This is a tidal brackish wetland with emergent vegetation dominated by narrowleaf cattailand invasive common reed (*Phragmites australis*)*.* A freshwater creek, Doodletown Brook, is the main tributary flowing into Iona Island Marsh. Bear Mountain 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. This sampling location sees salinity ranges from 0.1 to 10 psu annually, which is driven by meteorological and tidal factors. The tidal range at this site is 1.0 to 1.5 m. An unnamed freshwater spring 100 m to the west contributes a slight freshwater signature to this sampling site.

**Known Pollutants**

The entirety of the tidal portion of the Hudson River (i.e., south of the Troy Dam) is affected by historic polychlorinated biphenyls (PCBs). As a result, Tivoli North and South Bays have low sedimentary concentrations of these PCBs.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Station Code** | **SWMP Status** | **Station Name** | **Location** | **Active Dates** | **Reason Decommissioned** | **Notes** |
| BM | P | Bear Mountain | 41° 18' 51.0” N,  73° 59' 6.0” W | 01/01/2020 - Current | NA | NA |
| TS | P | Tivoli Bay South | 42° 1' 37.34 N, 73° 55' 33.45 W | 05/01/1995 –Current | NA | NA |
| TN | P | Tivoli Bay North | 42° 2' 11.56 N, 73° 55' 31.17 W | 07/01/1999 –Current | NA | NA |
| SK | D | Saw Kill | 42° 1' 1.82 N, 73° 54' 53.86 W | 05/01/1995 – 12/31/2019 | Site to be altered due to removal of dam | NA |
| SC | D | Stony Creek | 42° 2' 46.68 N, 73° 54' 38.88 W | 04/01/2002 –12/31/2021 | Location is no longer viable for sampling | NA |
| NP | S | Norrie Point | 41°49'54.0"N 73°56'31.0"W | (06/27/2008)  \*01/01/2018 - Current | NA | \*Secondary SWMP status confirmed as of 01/01/2018, prior data may be available per request |
| FL | S | Ferry Landing | 42°21'14.36"N  73°47'20.76"W | (04/01/2021)  \*04/01/2022 – Current) | NA | \*Secondary SWMP status confirmed as of 04/01/2022, prior data may be available on request |

**5) Coded variable definitions** –

hudbmnut = Hudson River Reserve nutrient data for Bear Mountain

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 (Secondary Station)

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 2022 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.

a) Monthly sampling

| **Site** | **Date** | **Rep 1 Time** | **Rep 2 Time** |
| --- | --- | --- | --- |
| BM | 4/11/2022 | 12:22 | 12:23 |
| BM | 5/24/2022 | 10:38 | 10:39 |
| BM | 6/22/2022 | 10:05 | 10:06 |
| BM | 7/25/2022 | 10:48 | 10:49 |
| BM | 8/18/2022 | 09:37 | 09:38 |
| BM | 9/19/2022 | 10:05 | 10:06 |
| BM | 10/20/2022 | 11:20 | 11:21 |
| BM | 11/22/2022 | 12:46 | 12:47 |
| BM | 12/20/2022 | 13:22 | 13:23 |

|  |  |  |  |
| --- | --- | --- | --- |
| **Site** | **Date** | **Rep 1 Time** | **Rep 2 Time** |
| NP | 04/04/2022 | 09:12 | 09:13 |
| NP | 05/20/2022 | 09:36 | 09:37 |
| NP | 06/21/2022 | 13:32 | 13:33 |
| NP | 07/21/2022 | 12:46 | 12:47 |
| NP | 08/30/2022 | 09:09 | 09:10 |
| NP | 09/27/2022 | 08:25 | 08:26 |
| NP | 10/25/2022 | 07:33 | 07:34 |
| NP | 11/28/2022 | 09:36 | 09:37 |
| NP | 12/27/2022 | 11:06 | 11:07 |

|  |  |  |  |
| --- | --- | --- | --- |
| **Site** | **Date** | **Rep 1 Time** | **Rep 2 Time** |
| FL | 04/05/2022 | 11:40 | 11:41 |
| FL | 05/19/2022 | 12:15 | 12:16 |
| FL | 6/30/2022 | 12:00 | 12:01 |
| FL | 07/19/2022 | 13:32 | 13:33 |
| FL | 08/25/2022 | 10:51 | 10:52 |
| FL | 09/27/2022 | 08:23 | 08:24 |
| FL | 10/24/2022 | 08:36 | 08:37 |
| FL | 11/30/2022 | 15:14 | 15:15 |
| FL | 12/28/2022 | 11:39 | 11:40 |

| **Site** | **Date** | **Rep 1 Time** | **Rep 2 Time** |
| --- | --- | --- | --- |
| TN | 04/06/2022 | 10:47 | 10:48 |
| TN | 06/01/2022 | 09:48 | 09:49 |
| TN | 06/16/2022 | 09:49 | 09:50 |
| TN | 07/15/2022 | 09:17 | 09:18 |
| TN | 08/03/2022 | 10:10 | 10:11 |
| TN | 09/13/2022 | 09:31 | 09:32 |
| TN | 10/12/2022 | 09:45 | 09:46 |
| TN | 11/15/2022 | 12:00 | 12:01 |
| TN | 12/14/2022 | 11:42 | 11:43 |

| **Site** | **Date** | **Rep 1 Time** | **Rep 2 Time** |
| --- | --- | --- | --- |
| TS | 04/06/2022 | 11:34 | 11:35 |
| TS | 06/01/2022 | 10:16 | 10:17 |
| TS | 06/16/2022 | 09:26 | 09:27 |
| TS | 07/15/2022 | 10:08 | 10:09 |
| TS | 08/03/2022 | 10:32 | 10:33 |
| TS | 09/13/2022 | 09:50 | 09:51 |
| TS | 10/12/2022 | 10:27 | 10:28 |
| TS | 11/15/2022 | 11:34 | 11:35 |
| TS | 12/14/2022 | 12:09 | 12:10 |

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 |  | 04/05/2022 | 23:00 | 04/07/2022 | 02:30 |
| TS |  | 05/31/2022 | 21:00 | 06/02/2022 | 00:30 |
| TS |  | 06/14/2022 | 20:00 | 06/15/2022 | 23:30 |
| TS |  | 07/13/2022 | 20:00 | 07/14/2022 | 23:30 |
| TS |  | 08/03/2022 | 00:00 | 08/04/2022 | 03:30 |
| TS |  | 09/12/2022 | 22:00 | 09/14/2022 | 01:30 |
| TS |  | 10/11/2022 | 21:45 | 10/13/2022 | 01:15 |
| TS |  | 11/15/2022 | 00:15 | 11/16/2022 | 03:45 |
| TS |  | Not Deployed Due to Ice | | | |

**7) Associated researchers and projects–**

As part of the SWMP long-term monitoring program, HUDNERR 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](http://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](http://cfcdmo.baruch.sc.edu/). 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, 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 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 ºC

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 oC

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** –

1. **Parameters measured directly**

Nitrogen species: NH4F, NO23F

Phosphorus species: PO4F

Other: CHLA\_N, PHEA, Cl, SO4, TSS

1. **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 Hudson River Research Reserve Laboratory. MDLs are established by Parameter according to the methodologies set forth by the equipment manufacturer. 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 | NH4F | 0.003 mg/L | 0.02 mg/L as N | 2009 – 2021 | 01/01/2021 |
| Nitrate | NO3F | 0.005 mg/L | 0.02 mg/L as N | 1991 – 2021 | 01/01/2021 |
| Orthophosphate | PO4 | 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 |
| Sulphate | SO4 | 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 | 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 | 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 | 01/01/2022 |
| Nitrate + Nitrite | NO23F | 0.002 mg/L | 2022 - Current | 01/01/2022 |
| Orthophosphate | PO4 | 0.002 mg/L | 2022 - Current | 01/01/2022 |
| Chlorophyll A | CHLA\_N | 0.02 ug/L | 2004 – 2022 | 01/01/2022 |
| Phaeophytin | PHEA\_N | 0.02 ug/L | 2004 – 2022 | 01/01/2022 |
| Total Suspend Solids | TSS | 0.1 mg/L | 1991 – 2022 | 01/01/2022 |
| Chloride | CL | 0.3 mg/L | 2022 - Current | 01/01/2022 |
| Sulphate | SO4 | 0.09 mg/L | 2022 - Current | 01/01/2022 |

**13) Laboratory methods** –

* 1. **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 nitroferricyanide. 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

* 1. **Parameter: NO23F**

**AQ300 HUDNERR Laboratory Method**: 127 – NOx (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

* 1. **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 phospho-molybdate 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

* 1. **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

* 1. **Parameter: SO4F**

**AQ300 HUDNERR Laboratory Method**: 105 – 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-SO42- 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 fluormetrically. 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:

CHLA (ug/L) = F\*(t/t-1) \*(Rb-Ra) \*(v/V)

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).

**14) Field and Laboratory QAQC programs** –

* 1. **Precision**
     1. **Field variability** – All samples are collected successively. The replicates are taken at the same location, approximately 1 minute apart.
     2. **Laboratory variability** – There is no variability performed during laboratory analysis. All samples are processed using the same extraction methodology and procedure.
     3. **Inter-organizational splits** – NA
  2. **Accuracy**
     1. **Sample spikes** – NA
     2. **Standard reference material analysis –** See below.
     3. **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:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Nutrient | Standard Conc. Range | 1% Dilution | IES Results A | IES Results B | Pass/Fail |
|  | (mg/L) | (10mL in 1L) | (mg/L) | (mg/L) |  |
| 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 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 in which below MDL values were 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 were diluted to achieve a measurement.

**Chlorophyll**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Station Code** | **Sample Date/Time** | **Monitoring Program** | **Rep** | **Dilution %** |
| FL | 06/30/2022 @ 12:00 | 1 | A | 25% |
| FL | 06/30/2022 @ 12:01 | 1 | B | 25% |
| FL | 07/29/2022 @ 13:33 | 1 | B | 25% |
| TS | 10/11/2022 @ 21:45 | 2 | NA | 25% |

**Data coded (CSM)**

**Chloride**

All chloride data for the months of April, May, June, and July are flagged <5> (CSM) as these data have been post-corrected. It was determined that these samples were analyzed using incorrect standards and, therefore, their raw values were inaccurate. These data were found to be consistently offset by approximately 56%. To account for this, staff have applied a post-correction multiplier of 0.56 to raw values, yielding the values represented in this dataset.

**pH**

All pH data for the months of April, May, June, July, August, and September are flagged <1> (CSM). The pH sensor on the handheld YSI multiparameter meter was failing and readings were found to take several minutes to nearly one-half hour to stabilize to ambient water conditions. Given the age and condition of this meter, these pH data are considered suspect, and are flagged as such. This handheld meter was intended to be replaced with a new YSI ProDSS multiparameter meter, however, due to supply chain complications and challenges following the 2020 coronavirus pandemic, this unit was not delivered in full until November 2022. All field parameters evaluated in November and December were obtained using the new handheld meter.

**Sample hold times for 2022:** NERRS SOP allows nutrient samples to be held for up to 24 hours if held at 4°C with no preservation, for NH4F and NO23F 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. However, available laboratory equipment at the Reserve only operates to a temperature of -4 °C. Per the Reserve’s analysis method, PO4 must be analyzed within 48 hours at 4°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.

The following tables describe the analysis dates for both Tier I and Tier II parameters for SWMP monthly and diel samples collected in 2022. 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** | **NH4F** | **NO23F** | **CLF** | **CHLA\_N, PHEA** | **SO4F** |
| --- | --- | --- | --- | --- | --- |
| April 2022, SWMP Monthly | 04/21/2022 | 04/26/2022 | 04/27/2022 | 06/09/2022\* | 04/27/2022 |
| 04/05-04/07, all diel samples | 04/21/2022 | 04/26/2022 | 04/27/2022 | 06/09/2022\* | 04/27/2022 |
| May 2022, SWMP Monthly | 06/15/2022 | 06/17/2022\* | 06/21/2022\* | 07/27/2022\* | 06/21/2022\* |
| 05/31-06/02, all diel samples | 06/15/2022 | 06/17/2022 | 06/21/2022 | \*\* | 06/21/2022 |
| June 2022, SWMP Monthly | 07/05/2022 | 07/26/2022\* | 06/21/2022  07/07/2022 | 07/27/2022\* | 06/21/2022  07/08/2022 |
| 06/14-06/15, all diel samples | 07/05/2022 | 07/26/2022\* | 06/21/2022 | 07/27/2022\* | 06/21/2022 |
| July 2022, SWMP Monthly | 07/25/2022 | 07/26/2022 | 07/27/2022 | 08/10/2022 | 07/26/2022 |
| 07/13 – 07/14, all diel samples | 07/25/2022 | 07/26/2022 | 07/27/2022 | 08/10/2022 | 07/26/2022 |
| August 2022, SWMP Monthly | 09/02/2022\* | 09/01/2022\* | 09/21/2022\* | 09/07/2022\*  09/27/2022 | 08/31/2022 |
| 08/03 – 08/04, all diel samples | 09/02/2022\* | 09/01/2022\* | 09/21/2022 | 09/07/2022\* | 08/31/2022 |
| September 2022 SWMP Monthly | 09/28/2022 | 09/29/2022 | 09/29/2022 | 09/27/2022  10/24/2022 | 09/29/2022 |
| 09/12-09/14, all diel samples | 09/28/2022 | 09/29/2022 | 09/29/2022 | 09/27/2022 | 09/29/2022 |
| October 2022, SWMP Monthly | 10/26/2022 | 10/27/2022 | 11/01/2022 | 10/24/2022  11/08/2022 | 10/27/2022 |
| 10/11-10/13, all diel samples | 10/26/2022 | 10/27/2022 | 11/01/2022 | 10/24/2022 | 10/27/2022 |
| November 2022, SWMP Monthly | 12/13/2022 | 12/07/2022 | 12/02/2022 | 12/08/2022  12/21/2022 | 12/02/2022 |
| 11/15-11/16, all diel samples | 12/13/2022 | 12/07/2022 | 12/02/2022 | 12/08/2022 | 12/02/2022 |
| December 2022, SWMP Monthly | 12/13/2022 | 12/07/2022 | 12/02/2022 | \*\*\* | 12/02/2022 |

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

\*\* Mishandling of samples resulted in the omission of CHLA/PHEA analysis for May diel samples.

\*\*\* Due to freezing temperatures, the ISCO unit was not deployed during the month of December.

**TABLE B – PO4 Analyses**

| **Month** | **Site\*** | **Analysis Date** | **Month** | **Site\*** | **Analysis Date** |
| --- | --- | --- | --- | --- | --- |
| April 2022 | FL | 04/08/2022\*\* | September 2022 | FL | 09/27/2022 |
| TN | 04/08/2022 | TN | 09/15/2022 |
| TS | 04/08/2022 | TS | 09/15/2022 |
| NP | 04/08/2022\*\* | NP | 09/27/2022 |
| BM | 04/08/2022 | BM | 09/20/2022 |
| All diels | 04/08/2022\*\* | All diels | 09/15/2022\*\* |
| May 2022 | FL | 06/13/2022\*\* | October 2022 | FL | 10/25/2022 |
| TN | 06/13/2022\*\* | TN | 10/13/2022 |
| TS | 06/13/2022\*\* | TS | 10/13/2022 |
| NP | 06/13/2022\*\* | NP | 10/25/2022 |
| BM | 06/13/2022\*\* | BM | 10/21/2022 |
| All diels | 06/13/2022\*\* | All diels | 10/13/2022 |
| June 2022 | FL | 07/22/2022\*\* | November 2022 | FL | 12/01/2022 |
| TN | 07/18/2022\*\* | TN | 11/17/2022 |
| TS | 07/18/2022\*\* | TS | 11/17/2022 |
| NP | 07/22/2022\*\* | NP | 12/01/2022\*\* |
| BM | 07/25/2022\*\* | BM | 11/22/2022 |
| All diels | 07/18/2022\*\* | All diels | 11/17/2022 |
| July 2022 | FL | 07/21/2022 | December 2022 | FL | 12/29/2022 |
| TN | 07/18/2022\*\* | TN | 12/16/2022 |
| TS | 07/18/2022\*\* | TS | 12/16/2022 |
| NP | 07/21/2022 | NP | 12/29/2022 |
| BM | 07/25/2022 | BM | 12/21/2022 |
| All diels | 07/18/2022\*\* | All diels | \*\*\* |
| August 2022 | FL | 08/26/2022 |
| TN | 08/04/2022 |
| TS | 08/04/2022 |
| NP | 08/30/2022 |
| BM | 08/22/2022\*\* |
| All diels | 08/04/2022 |

\* 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 month of December.