**Old Woman Creek (OWC) NERR Nutrient Metadata**

**January through December 2021**

**Latest Update:** **April 5, 2024**

**I. Data Set and Research Descriptors**

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**2) Research objectives** –

1. Monthly grab sampling program

Samples for chemical analysis are taken at least monthly at the four existing datalogger sites within or near the Old Woman Creek National Estuarine Research Reserve (NERR). Three of the sites are located in the estuary proper - one near the mouth, just south of State Route 6 (WM), one just upstream from the WM site (OL), and a third in the upper reaches at Darrow Road (DR). The final site (BR) is just upstream of the first riffle zone above the estuary in Old Woman Creek proper. The purpose of this part of the nutrient monitoring program is to document the spatial and temporal distribution of nutrient levels as water moves through this Great Lakes estuary.

1. Diel sampling program

At site WM, samples are collected at 2-hour intervals over a 26-hour period once per month. The purpose of this part of the monitoring program is to examine temporal changes in nutrient levels in the estuary over the course of a day.

**3) Research methods** –

1. Monthly grab sampling program

The 2021 chemical monitoring program began on 08 March 2021 at sites BR, DR, OL, and WM. Sampling at all sites ended on 03 January 2022 due to ice cover. However, because this last sample date occurred in 2022, nutrient parameters from this date are included in the 2022 dataset. The last sampling date in the 2021 dataset occurred on 06 December 2022.

Replicate surface water grab samples for chemical and chlorophyll analysis were collected sequentially at each site. Both replicates were normally collected within 30 seconds of each other, except at site DR, where samples are usually collected within a few minutes of each other (Table 2). At DR, samples were collected using a 3-L Van Dorn bottle.

Sample bottles (previously washed in a commercial grade dishwasher with phosphate-free detergent and citric acid rinse aid or with 10% HCl, rinsed six (6) times with distilled water, then allowed to air dry upside down prior to sampling) were rinsed with the sample water three times before the sample was collected for analysis. Temperature, dissolved oxygen, specific conductance, and pH values were determined on the samples at time of collection using a field meter (YSI Pro Plus, Yellow Spring Inc, Yellow Springs, OH) that was previously calibrated according to manufacturer specifications. Sample turbidity was measured in the lab with a Hach 2100AN Turbidimeter. If samples could not be filtered within an hour after collection, they were stored in a refrigerator or in the dark on ice.

All monthly grab samples and diel samples collected in 2021 were analyzed on-site at the Old Woman Creek analytical laboratory following National Estuarine Research Reserve System (NERRS) guidance as described in the Old Woman Creek Standard Operating Procedures and Quality Control v2.

1. Diel sampling program

An ISCO Model 5800 refrigerated sampler was used to collect water samples at site WM once a month, from March through December 2021 (Table 3). The sampler collected a single, 900-ml sample at 2-hour intervals for a 26-hour period. The sampler intake was suspended adjacent to the WM data sonde at the same depth as the sonde sensors. Sampler intake and pump tubing were replaced as needed. Prior to collecting each sample, the ISCO sampler was programmed to rinse the collection line three times. Water temperature, pH, and DO were taken from the associated YSI data logger at owcwmwq and the nearest 15-minute readings. Otherwise, protocols were the same as for the Monthly Grab Sampling Program, including bottle cleaning, processing, and analysis.

**4) Site location and character –**

Old Woman Creek NERR is located on the southern shore of Lake Erie, slightly east of the city of Huron, Ohio (Latitude 41° 23'N; Longitude 82° 33'W). Land use in the Old Woman Creek watershed is primarily row crop agriculture (~70%). All residences in the watershed (concentrated in Berlin Heights, population 714 according to the 2010 census) have septic systems. Salinity in Old Woman Creek is normally ≤0.3 psu. Water levels in the estuary vary with Lake Erie water levels and are influenced by the opening and closing of the barrier beach, but are rarely deeper than 2 m according to bathymetric surveying from 1990. Long-term water quality and nutrient monitoring currently occurs at four sites, though a fifth has been monitored in the past (Table 1).

Site WM near State Route 6 (Latitude 41° 22' 57” N, Longitude 82° 30' 53” W) is very close to the mouth of Old Woman Creek. In this portion of the Reserve, the creek is very shallow but extends over a large surface area. This site frequently experiences the influx of Lake Erie waters. The bottom sediments at this site are silty clay. No rooted aquatic vegetation is present directly adjacent to the site, although both emergent and submerged vegetation are present within 3 m of the site. *Phragmites* *australis* was historically the dominant aquatic macrophyte near this site but has been drowned out due to high water levels and herbicide treatments in 2019. Depth at this site ranged from 0.6 m to 2.3 m during 2021. Deeper water conditions typically occur when the outlet of the estuary to Lake Erie is “closed” (i.e. no direct surface water exchange) due to development of a barrier sand beach.

Site OL (Latitude 41° 22’ 55” N, Longitude 82° 30’ 51” W) is in the lower reaches of the estuary. It is not in direct sight of the mouth, so northerly winds and resulting seiche events are less noticeable at this site but can still occur. The bottom sediments are silty clay. This site is located near the northern tip of a *Nelumbo* *lutea* bed, and during many years these plants are within 3 m of the site. This site varied in depth from 0.80 to 1.84 m during 2021. Similar to water levels at site WM, deeper water typically occurred when the estuary outlet was closed or during significant rain events.

Site DR (Latitude 41° 21’ 54”N, Longitude 82° 30’ 17”W) is at the southern boundary of the Reserve. Water samples are collected from the Darrow Road bridge where it crosses the creek. The creek is relatively narrow here and although water direction and flow are influenced by changes in Lake Erie water levels, this site does not have direct contact with Lake Erie waters. The bottom sediments are silty clay. No rooted aquatic vegetation is present near or upstream from this site, though coontail (*Ceratophyllum demersun*) has occasionally been observed at site DR. Depth at this site ranged from 0.9 to 2.3 m during 2021.

Site BR (Latitude 41° 20’ 56” N, Longitude 82° 30’ 44”W) is located in the lower portion of the creek proper where Berlin Road crosses Old Woman Creek. The site is just upstream of the first riffle area above the estuary. Unlike the other three sites, Lake Erie water levels have no impact on this site. The bottom of the creek here is a combination of rocks interspersed with clay-silt that has been washed in from upstream. There are no aquatic macrophytes at or near this site, but there can be periphyton growth on the bottom rocks during much of the year. A USGS stream gauge is located ~ 6m upstream from this site and discharge and gauge height data can be found at: <https://waterdata.usgs.gov/oh/nwis/uv?site_no=04199155>. Based on data collected from this gauge, depth at this site ranged from 0.4 to 3.1 m throughout 2021.

**Table 1:** Location of sites that are part of the Old Woman Creek System-wide Monitoring Program (SWMP). Station Code refers to seven-letter site notation used by the CDMO while Station Name is the short-hand name for each site. The Status of all sites is primary (P). The date that monitoring began at each site and, when applicable, the date that the site was decommissioned are listed. If a site has not been decommissioned, not applicable (NA) has been added to the Reason Decommissioned column.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Station Code** | **SWMP Status** | **Station Name** | **Location (latitude, longitude)** | **Active Dates** | **Reason Decommissioned** | **Notes** |
| owcbrwq | P | Berlin Road | 41° 20’ 56” N,  82° 30’ 44” W | 03/01/2002 – current | NA | NA |
| owcdrwq | P | Darrow Road | 41° 21’ 54” N,  82° 30’ 17” W | 08/01/2007 – current | NA | NA |
| owcolwq | P | Lower Estuary | 41° 22’ 55” N,  82° 30’ 51” W | 04/01/2002 – current | NA | NA |
| owcwmwq | P | Route 6 | 41° 22' 57” N,  82° 30' 53” W | 05/01/1995 – current | NA | NA |
| owcsuwq | P | Route 2 | 41° 22’ 02” N,  82° 30’ 26” W | 05/01/1995 – 08/23/2007 13:15 | Bridge repair; could not access site | NA |

**5) Coded variable definitions** –

owcnut = Old Woman Creek nutrients

|  |  |
| --- | --- |
| **Sampling Station** | **Sampling Site Code** |
| State Route 6 | owcwmnut |
| Lower Estuary | owcolnut |
| Darrow Road | owcdrnut |
| Berlin Road | owcbrnut |

*Coded Project Identifiers Within the Dataset:*

Whether samples were collected as part of the Monthly or Diel sampling program are denoted in the “Monitoring Program” column of the dataset using the following numbering scheme.

Monthly grab sample program = 1

Diel grab sample program = 2

**6) Data collection period** –

1. Monthly grab sampling

Sampling at all sites began on 08 March 2021 while the last samples analyzed in 2021 were collected on 06 December 2021. The last sampling to occur before ice cover made sampling unfeasible occurred on 03 January 2022, but data from this period are included in the 2022 dataset. Specific deployment dates and times (EST) are listed (Table 2). The two grab samples were collected sequentially.

**Table 2:** Monthly grab sampling occurred at four sites including BR (owcbrnut), DR (owcdrnut), OL (owcolnut), and WM (owcwmnut). Two replicates were collected on each sample date. Collection time for each replicate is listed based on a 2400 clock in Eastern Standard Time (EST).

|  |  |  |  |
| --- | --- | --- | --- |
| **Site** | **Replicate** | **Sample Date (mm/dd/yyyy)** | **Time (EST)** |
| BR | 1 | 03/08/2021 | 10:23:00 |
| BR | 2 | 03/08/2021 | 10:24:00 |
| BR | 1 | 04/06/2021 | 08:57:00 |
| BR | 2 | 04/06/2021 | 08:59:00 |
| BR | 1 | 05/04/2021 | 09:01:00 |
| BR | 2 | 05/04/2021 | 09:10:00 |
| BR | 1 | 06/02/2021 | 07:18:00 |
| BR | 2 | 06/02/2021 | 07:19:00 |
| BR | 1 | 06/29/2021 | 08:48:00 |
| BR | 2 | 06/29/2021 | 08:49:00 |
| BR | 1 | 08/03/2021 | 09:25:00 |
| BR | 2 | 08/03/2021 | 09:26:00 |
| BR | 1 | 08/30/2021 | 08:15:00 |
| BR | 2 | 08/30/2021 | 08:18:00 |
| BR | 1 | 10/05/2021 | 08:25:00 |
| BR | 2 | 10/05/2021 | 08:27:00 |
| BR | 1 | 11/02/2021 | 07:52:00 |
| BR | 2 | 11/02/2021 | 07:54:00 |
| BR | 1 | 12/06/2021 | 13:39:00 |
| BR | 2 | 12/06/2021 | 13:40:00 |
| DR | 1 | 03/08/2021 | 10:50:00 |
| DR | 2 | 03/08/2021 | 10:56:00 |
| DR | 1 | 04/06/2021 | 09:26:00 |
| DR | 2 | 04/06/2021 | 09:28:00 |
| DR | 1 | 05/04/2021 | 09:27:00 |
| DR | 2 | 05/04/2021 | 09:37:00 |
| DR | 1 | 06/02/2021 | 07:40:00 |
| DR | 2 | 06/02/2021 | 07:47:00 |
| DR | 1 | 06/29/2021 | 09:09:00 |
| DR | 2 | 06/29/2021 | 09:14:00 |
| DR | 1 | 08/03/2021 | 09:54:00 |
| DR | 2 | 08/03/2021 | 09:59:00 |
| DR | 1 | 08/30/2021 | 08:27:00 |
| DR | 2 | 08/30/2021 | 08:31:00 |
| DR | 1 | 10/05/2021 | 08:52:00 |
| DR | 2 | 10/05/2021 | 08:54:00 |
| DR | 1 | 11/02/2021 | 08:08:00 |
| DR | 2 | 11/02/2021 | 08:10:00 |
| DR | 1 | 12/06/2021 | 13:50:00 |
| DR | 2 | 12/06/2021 | 13:56:00 |
| OL | 1 | 03/08/2021 | 11:33:00 |
| OL | 2 | 03/08/2021 | 11:34:00 |
| OL | 1 | 04/06/2021 | 10:39:00 |
| OL | 2 | 04/06/2021 | 10:44:00 |
| OL | 1 | 05/04/2021 | 10:39:00 |
| OL | 2 | 05/04/2021 | 10:43:00 |
| OL | 1 | 06/02/2021 | 08:33:00 |
| OL | 2 | 06/02/2021 | 08:35:00 |
| OL | 1 | 06/29/2021 | 09:57:00 |
| OL | 2 | 06/29/2021 | 10:03:00 |
| OL | 1 | 08/03/2021 | 11:01:00 |
| OL | 2 | 08/03/2021 | 11:02:00 |
| OL | 1 | 08/30/2021 | 09:00:00 |
| OL | 2 | 08/30/2021 | 09:01:00 |
| OL | 1 | 10/05/2021 | 09:38:00 |
| OL | 2 | 10/05/2021 | 09:40:00 |
| OL | 1 | 11/02/2021 | 08:51:00 |
| OL | 2 | 11/02/2021 | 08:54:00 |
| OL | 1 | 12/06/2021 | 14:38:00 |
| OL | 2 | 12/06/2021 | 14:42:00 |
| WM | 1 | 03/08/2021 | 11:45:00 |
| WM | 2 | 03/08/2021 | 11:46:00 |
| WM | 1 | 04/06/2021 | 10:58:00 |
| WM | 2 | 04/06/2021 | 11:03:00 |
| WM | 1 | 05/04/2021 | 10:52:00 |
| WM | 2 | 05/04/2021 | 10:55:00 |
| WM | 1 | 06/02/2021 | 09:08:00 |
| WM | 2 | 06/02/2021 | 09:13:00 |
| WM | 1 | 06/29/2021 | 10:18:00 |
| WM | 2 | 06/29/2021 | 10:20:00 |
| WM | 1 | 08/03/2021 | 11:22:00 |
| WM | 2 | 08/03/2021 | 11:23:00 |
| WM | 1 | 08/30/2021 | 09:11:00 |
| WM | 2 | 08/30/2021 | 09:14:00 |
| WM | 1 | 10/05/2021 | 09:56:00 |
| WM | 2 | 10/05/2021 | 09:58:00 |
| WM | 1 | 11/02/2021 | 09:16:00 |
| WM | 2 | 11/02/2021 | 09:18:00 |
| WM | 1 | 12/06/2021 | 14:49:00 |
| WM | 2 | 12/06/2021 | 14:54:00 |

1. Diel sampling

For the following dates and times (EST) in 2021, samples were collected at site WM at two-hour intervals over a 26-hour time period (Table 3).

**Table 3:** Diel sampling occurred once per month at site WM (owcwmnut). Samples were collected at two-hour intervals beginning at 4:00 AM on the start date and concluding at 6:00 AM on the end date. Collection time for each replicate is listed based on a 2400 clock in Eastern Standard Time (EST).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Site** | **Start Date (mm/dd/yyyy)** | **Start Time (EST)** | **End Date (mm/dd/yyyy)** | **End Time (EST)** |
| WM | 03/02/2021 | 4:00:00 | 03/03/2021 | 6:00:00 |
| WM | 04/13/2021 | 4:00:00 | 04/14/2021 | 6:00:00 |
| WM | 05/09/2021 | 4:00:00 | 05/10/2021 | 6:00:00 |
| WM | 06/06/2021 | 4:00:00 | 06/07/2021 | 6:00:00 |
| WM | 07/12/2021 | 4:00:00 | 07/13/2021 | 6:00:00 |
| WM | 08/08/2021 | 4:00:00 | 08/09/2021 | 6:00:00 |
| WM | 09/12/2021 | 4:00:00 | 09/13/2021 | 6:00:00 |
| WM | 10/10/2021 | 4:00:00 | 10/11/2021 | 6:00:00 |
| WM | 11/07/2021 | 4:00:00 | 11/08/2021 | 6:00:00 |
| WM | 12/19/2021 | 4:00:00 | 12/20/2021 | 6:00:00 |

**7) Associated researchers and projects–**

As part of the long-term System-Wide Monitoring Program, the Old Woman Creek NERR also monitors 15-minute meteorological and water quality data which may be correlated with this nutrient/pigment dataset. Water quality data sondes are deployed at each of the nutrient sampling sites. These sondes measure and record water temperature, specific conductivity, dissolved oxygen, pH, turbidity, and depth at 15-minute intervals throughout the sampling period (approximately March – December). A meteorological tower is located on Reserve property within 1 km of the DR, OL, and WM nutrient collection sites and within 5 km of the BR nutrient collection site. Air temperature, humidity, barometric pressure, wind speed and direction, precipitation, and photosynthetically active radiation data are collected at 15-minute intervals throughout the year. These data are available at [www.nerrsdata.org](http://www.nerrsdata.org). Microwave radar water level sensors (Waterlog Nile Series) are located at the DR and adjacent to the WM sites; sensors collect water depth data every 15 minutes under ice-free conditions. An acoustic Doppler current profiler is located adjacent to the WM site and collects water flow data every 15 minutes. Data are available upon request from the Research Coordinator (please see Section 1 Part 1).

Since May 2015, ongoing work in the Reserve has been dedicated to quantifying the nutrient processing ability of the Old Woman Creek wetland to understand how storm events influence nutrient loading into Lake Erie. Between May 2015 and June 2019, three samples per day were collected from site BR (owcbrnut) and site WM (owcwmnut) using an autosampler programmed to collect samples at 04:00, 12:00, and 20:00. These were transported each week to the National Center for Water Quality Research at Heidelberg University (Tiffin, OH) where the number of samples analyzed depended on whether a storm occurred over the previous week. If a storm event had occurred, 2-3 samples per day were analyzed until the creek had receded to near pre-storm levels, while only 1 sample per day was analyzed if the creek remained at baseflow. Beginning in June 2019, water samples were analyzed on-site at the Old Woman Creek analytical lab and the sampling analysis frequency was modified to the schedule, below:

For storm events (≥10 per year), the following analysis schedule was followed until recession to pre-storm levels:

BR (owcbrnut) x3 per day @ 04:00, 12:00, and 20:00

WM (owcwmnut) x1 per day @ 12:00

During non-storm, baseflow conditions, sample analysis frequency was as follows:

BR (owcbrnut) x1 per day @ 12:00

WM (owcwmnut) x1 per week @ 12:00 on Mondays

These modifications to sampling frequency were based analysis of the 2015-2018 data showing that baseflow nutrient concentrations were stable over the course of 24 hours at site BR, or from one week to the next at site WM. Throughout the entirety of this ongoing project, water samples have been analyzed for soluble reactive phosphorus (PO4F), total phosphorus (TP), nitrite (NO2F), nitrite+nitrate (NO23F), and ammonium (NH4F). Nitrate (NO3F) and dissolved inorganic nitrogen (DIN) were quantified by calculation. Data are available by request from the Reserve’s Research Coordinator (please see Section 1 Part 1).

The chemical data have been incorporated into several research projects and publications related to plankton eukaryotic microorganisms, the breakdown of selected organic contaminants, of *Phragmites* control on non-target communities, biomonitoring study of the aquatic vegetation of the estuary, nutrient cycling, nutrient assimilation, and nutrient and sediment loading reduction through agricultural conservation practices. The data are also used to produce an annual watershed health report card for the Old Woman Creek watershed.

In 2021, Old Woman Creek was one of 12 Reserves that participated in project comparing extracted chlorophyll-*a* concentrations with those measured from *in-situ* sensors. All chlorophyll-*a* data measured for the Diel sampling program were also used for this chlorophyll working group program. The diel and chlorophyll working group datasets are the same, except that two additional collection periods (01/11-12/2021, 02/08-09/2021) occurred for the latter. Data were collected following the same sampling frequency and methodology except that no nutrients were measured on the January and February 2021 sampling dates. Those interested in these extra two months of chlorophyll-*a* data, which are compatible with the diel program, should contact the Reserve’s Research Coordinator (please see Section 1 Part 1).

**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 2021.

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** –

All field data are recorded by hand on a field datasheet during sample collection. All laboratory chemical analysis data are transcribed by hand on a laboratory datasheet; field measurements of water temperature, pH, specific conductance, and dissolved oxygen are transcribed to that datasheet. Any anomalies observed in the field or in the lab are also recorded on their respective datasheets. Duplicate readings are visually inspected to identify outliers, which would suggest either testing or contamination problems. The datasheets are kept on file at the Old Woman Creek Visitor Center.

Reserve staff enter the data recorded on field datasheets into an Excel workbook designated for that sampling year. Reserve staff enter the data recorded on the laboratory datasheets into Excel workbooks designated for each site that include all years of data collected for each site. Parameters measured in ppb (µg/L) are converted to ppm (mg/L) in the Excel workbook, except for Chlorophyll-*a*. A different Reserve staff member checks the field and laboratory data for accuracy. Field and laboratory workbooks are saved to the System-Wide Monitoring Program Coordinator’s computer, an external hard drive, and a central Ohio DNR Office of Coastal Management server, which is regularly backed up through the State of Ohio’s Information Technology Department. The System-Wide Monitoring Program Coordinator is responsible for the nutrient analysis QAQC.

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.

**10) Parameter titles and variable names by category –**

Nutrient and chlorophyll-*a* concentrations, along with water quality parameters measured from whole water samples (Table 4), are available to download through the Centralized Data Management Office (CDMO) or by request from the Reserve’s Research Coordinator (please see Section 1 Part 1).

**Table 4:** Parameters quantified in Old Woman Creek during 2021 monthly grab and diel sampling. Centralized Data Management Office (CDMO) parameter name, as listed on the downloaded data, are provided along with the units for each parameter.

**Data Category Parameter CDMO Parameter Units**

**Phosphorus and Nitrogen:**

\*Soluble Reactive Phosphorus PO4F mg/L as P

(Orthophosphate), Filtered

Total Phosphorus TP mg/L as P

\*Nitrite + Nitrate (NO2+3), Filtered NO23F mg/L as N

\*Nitrite (NO2), Filtered NO2F mg/L as N

\*Nitrate (NO3), Filtered NO3F mg/L as N

\* Ammonium (NH4), Filtered NH4F mg/L as N

Dissolved Inorganic Nitrogen DIN mg/L as N

**Plant Pigments:** \*Chlorophyll-*a* CHLA\_N μg/L

**Field Parameters:** Water Temperature WTEM\_N ºC

pH PH\_N pH

Dissolved Oxygen DO\_N mg/L

Specific Conductivity SCON\_N μS/cm

Turbidity TURB\_N NTU

\*Required NOAA/NERR System-Wide Monitoring Program nutrient parameters

**11) Measured or calculated laboratory parameters** –

**a) Parameters measured directly**

Phosphorus Species: PO4F, TP

Nitrogen Species: NH4F, NO2F, NO23F

**b) Calculated parameters**

NO3F NO23F–NO2F

DIN NO23F+ NH4F

**12) Limits of detection** –

The Minimum Detection Limits (MDL), which are the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the Old Woman Creek Analytical Laboratory (Table 5). The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. MDL are determined annually, except for CHLA\_N, which was last determined on 12/21/2020.

**Table 5:** Minimum detection limits (MDL) for parameters measured at the Old Woman Creek Analytical Lab and reported to the CDMO. Variable name, as it appears when downloaded from the CDMO, is listed in parentheses in the Parameter column. Each time MDLs are assessed, the newly determined MDL replaces the old one. Start and End Dates represent the temporal range over which each MDL is applicable. All dates when the MDL was determined are included here, even if it did not change before or after assessment.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Parameter** | **Start Date**  **(mm/dd/yyyy)** | **End Date**  **(mm/dd/yyyy)** | **MDL** | **Units** |
| NH4 (NH4F) | 01/01/21 | 05/23/21 | 0.007 | mg/L |
| 05/24/21 | 12/31/21 | 0.005 |
| NO2+3 (NO23F) | 01/01/21 | 05/24/21 | 0.003 | mg/L |
| 05/25/21 | 12/31/21 | 0.002 |
| NO2 (NO2F) | 01/01/21 | 05/24/21 | 0.0001 | mg/L |
| 05/25/21 | 12/31/21 | 0.0001 |
| PO4 (PO4F) | 01/01/21 | 05/24/21 | 0.0017 | mg/L |
| 05/25/21 | 12/31/21 | 0.0022 |
| TP | 01/01/21 | 05/25/21 | 0.003 | mg/L |
| 05/26/21 | 12/31/21 | 0.005 |
| Chlorophyll-*a* (CHLA\_N) | 01/01/21 | 12/31/21 | 0.19 | µg/L |

**13) Laboratory methods** –

After collection, whole water samples were brought back to the lab where a raw 60 ml subsample was taken for the determination of TP and turbidity. The remainder of each whole water sample was then filtered within 24 hours using vacuum filtration. Water was first filtered through a 0.7 µm MilliporeSigma glass fiber filter (GFF) which was immediately added to 90% aqueous acetone and placed in the freezer (~-20˚C) for chlorophyll-*a* extraction and quantification. Filtrate from the GFF was then filtered through a 0.45 µm Metricel GN-6 membrane filter that had been pre-soaked in deionized water. This 0.45 µm membrane filter filtrate was stored in HDPE plastic bottles in the fridge (~4˚C) until analysis or, in instances where analysis was not possible within NERR SOP hold times, stored frozen (~-20˚C) until analysis.

Chlorophyll-*a* concentrations (CHLA\_N) were determined following methods described in USEPA Method 445.0, rev. 1.2. Briefly, GFF filters were steeped in 90% aqueous acetone in the freezer (~-20˚C) for 2-7 days, until analysis. After steeping, samples were inverted and transferred to centrifuge tubes. Chlorophyll-*a* was quantified fluorometrically from the centrifuged (1 minute, 2840 RPM) supernatant using a Turner Designs (San Jose, CA) Trilogy Fluorometer. Samples were not acidified, so reported concentrations are total chlorophyll-*a*, including pheophytin.

All nutrients (PO4F, TP, NH4F, NO2F, NO23F) were analyzed using a Seal Analytical (Mequon, WI) AQ 300 discrete analyzer following established methods outlined below. During analysis, confidence and rigor were achieved by following several QAQC procedures. For each run, the site DR water sample was spiked with a known concentration to evaluate whether there was any interference in sample water that impacted analysis results. A deionized water blank and known middle standard (i.e. equal to half of the high standard) were included at the beginning and end of every run, as well as every 10 samples. A check standard equal to the high standard on the calibration curve was also included at the end of every run. If one of these three QAQC checks (deionized water blank, middle standard, check standard) were greater than 15% off, samples were re-analyzed. Another QAQC check specific to nitrate+nitrite (NO23F) is the cadmium coil efficiency. Nitrate is reduced to nitrite when in contact with cadmium and is then measured as nitrate plus nitrite. This reduction is often less than 100% efficient and can be quantified by running a known nitrate standard and comparing it to a known nitrite standard of the same concentration. If the cadmium coil efficiency, which is measured as (nitrate/nitrite)\*100 is ever below 85%, samples are re-analyzed.

The only nutrient Old Woman Creek measured in 2021 from whole water samples was TP. Phosphorus occurs in many organic forms, which must be converted to orthophosphate before analysis. This oxidation of organic phosphorus, or digestion, was accomplished via potassium persulfate digestion in Erlenmeyer flasks at 350˚C. Digested samples were analyzed on the Seal AQ300 within 12 hours. In addition to the aforementioned QAQC procedures, a digested blank and digested high standard were included in total phosphorus runs to ensure the digestion process did not introduce any interference and that all phosphorus was recovered from the sample.

Turbidity (TURB\_N) was measured in the lab within 24 hours of sample collection using a Hach (Loveland, CO) 2100AN turbidimeter. All other reported field parameters (WTEM\_N, PH\_N, DO\_N, SCON\_N) were measured *in situ* using YSI (Yellow Springs, OH) EXO 2 or EXO 3 sondes deployed as part of the NERR System-Wide Monitoring Program. For more details on sonde deployment, calibration, and data collection, water quality metadata can be downloaded from the CDMO’s website at: [www.nerrsdata.org](http://cfcdmo.baruch.sc.edu/).

Details relevant to each methodology are listed below. A more detailed description of lab hygiene and methods specific to the Old Woman Creek Analytical Lab can be found in the associated SOP downloaded with this metadata. Additional questions can be directed to the Reserve’s Research Coordinator (please see Section 1 Part 1).

**Summary:** For each parameter measured directly, the Seal Analytical method number (when appropriate), reference method, method principal, and preservation method are listed below. Nutrients are measured spectrophotometrically using a Seal Analytical AQ300 discrete analyzer, while chlorophyll-*a* samples are determined fluorometrically with a Turner Designs Trilogy fluorometer. Dissolved nutrients (SRP, NH4F, NO2F, NO23F) are measured from 0.45 µm filtrate, while chlorophyll-*a* (CHLA\_N) is measured from 0.7 µm filtrate. Total phosphorus (TP) is measured from whole water samples.

* 1. **Parameter: Total Phosphorus, TP**

**Seal Analytical Method:** *EPA-119-D rev A*

**Method Reference:** *US.EPA 1983. USEPA-600/4-79-020. Method 170.1*

**Method Principal:** Prior to analysis, all organic forms of phosphorus were converted to orthophosphate through digestion. 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 880 nm.

**Preservation Method:** Whole water samples are stored at ~4˚C for up to 4 days. Occasionally, analysis is not possible within this timespan, in which case samples are stored at ~-20˚C for up to 28 days.

* 1. **Parameter: Orthophosphate / Soluble Reactive Phosphorus (PO4) PO4F**

**Seal Analytical Method:** *EPA-118-D rev 0*

**Method Reference:** *USEPA 365.1 rev 2.0; Standard Methods 4500-P F (23rd edition)*

**Method Principal:** 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 880 nm.

**Preservation Method:** Filtered within 24 hours of collection and stored at ~4˚C for up to 4 days. Occasionally, analysis is not possible within this timespan, in which case samples are stored at ~-20 ˚C for up to 28 days.

* 1. **Parameter: Ammonium (NH4), NH4F**

**Seal Analytical Method:** *EPA-148-A rev 2*

**Method Reference:** *USEPA 350.1 rev 2.0; Standard Methods 4500-NH3 G (23rd edition)*

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

**Preservation Method:** Filtered within 24 hours of collection and stored at ~4˚C for up to 4 days. Occasionally, analysis is not possible within this timespan, in which case samples are stored at ~-20 ˚C for up to 28 days.

* 1. **Parameter: Nitrite (NO2), NO2F**

**Seal Analytical Method:** *EPA*-*116-D rev A*

**Method Reference:** *USEPA 354.1 rev 2.0 (1993); Standard Methods 4500-NO2 B (23rd edition)*

**Method Principal:** Nitrite is determined through formation of a reddish-purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine (NEDD). The absorbance of this complex is measured spectrophotometrically at 520 nm.

**Preservation Method:** Filtered within 24 hours of collection and stored at ~4˚C for up to 4 days. Occasionally, analysis is not possible within this timespan, in which case samples are stored at ~-20 ˚C for up to 28 days.

* 1. **Parameter: Nitate+Nitrite (NO2+3), NO23F**

**Seal Analytical Method:** *EPA-132-A rev 1*

**Method Reference:** *EPA-132-A rev 1.0*

**Method Principal:** Sample is buffered to pH 7.5 using an imidazole buffer containing copper (II) sulfate. The nitrate in the buffered sample is chemically reduced to nitrite using a copperized cadmium coil. An aliquot of reduced sample is mixed with sulfanilimide in dilute phosphoric acid, and the nitrite reacts to form a diazonium compound. This compound couples with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a reddish-purple azo dye. This species is measured spectrophotometrically at 520 nm.

**Preservation Method:** Filtered within 24 hours of collection and stored at ~4˚C for up to 4 days. Occasionally, analysis is not possible within this timespan, in which case samples are stored at ~-20 ˚C for up to 28 days.

* 1. **Parameter: Chlorophyll-*a*, CHLA\_N**

**Method Reference:** *USEPA Method 445.0 rev 1.2*

**Method Principal:** Phytoplankton cells are retained on a 0.7 µm GFF, and then chlorophyll-a pigments are extracted from the filter in acetone solvent. Chlorophyll-a fluorescence can then be quantified.

**Preservation Method:** Filtered within 24 hours of collection and stored in 90% acetone at -20˚C for 2 to 7 days. Chlorophyll-a samples were not held for longer than 7 days during 2021.

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

1. **Precision**
   * 1. **Field variability** - For the System-wide Monitoring Program, two replicate samples are collected at all four sites (Table 2). These samples are collected consecutively and represent true replicates.
     2. **Laboratory variability** – QAQC checks as detailed above
     3. **Inter-organizational splits -** Old Woman Creek NERR did not participate in an inter-organizational split program with any other lab during 2021.
2. **Accuracy**
3. **Sample spikes** – QAQC checks as detailed above and refer to the Old Woman Creek Standard Operating Procedures and Quality Control document.
4. **Standard reference material analysis** – none in 2021
   * 1. **Cross calibration exercises** - Old Woman Creek NERR did not participate in any cross-calibration exercises with other labs during 2021.

**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.

***QAQC Flagging Notes***

Barrier Beach Status and Water Exchange

A dynamic barrier beach exists between Old Woman Creek and Lake Erie that will close and open depending on precipitation, lake water levels, and deposition of sand. Water quality of sites OL and WM is especially influenced by whether the barrier beach is open (i.e., surface exchange is occurring between the estuary and the lake). When the beach is open, wind-driven surface water exchange and larger seiche events usually result in cycles of water inflow from the lake and outflow to the lake that can be detected in the water quality and nutrient data. The change from closed to open can be rapid and dramatic, usually because of precipitation. The transition from open to closed is gradual and usually marked by a gradual increase in water depth. On October 9, a member of the public was observed opening the beach by digging.

|  |  |  |
| --- | --- | --- |
| **Status** | **Date From** | **Date To** |
| Open | 01/01/2021 | 03/19/2021 |
| Closed | 03/20/2021 | 03/20/2021 |
| Open | 03/21/2021 | 04/01/2021 |
| Closed | 04/02/2021 | 04/11/2021 |
| Open | 04/12/2021 | 04/14/2020 |
| Closed | 04/15/2021 | 04/25/2021 |
| Open | 04/26/2021 | 06/21/2021 |
| Closed | 06/22/2021 | 06/28/2021 |
| Open | 06/29/2021 | 07/01/2021 |
| Closed | 07/02/2021 | 07/17/2021 |
| Open | 07/18/2021 | 07/29/2021 |
| Closed | 07/30/2021 | 08/27/2021 |
| Open | 08/28/2021 | 08/31/2021 |
| Closed | 09/01/2021 | 10/08/2021 |
| Open\* | 10/09/2021 | 10/28/2021 |
| Closed | 10/29/2021 | 11/01/2021 |
| Open | 11/02/2021 | 12/02/2021 |
| Closed | 12/03/2021 | 12/07/2021 |
| Open | 12/08/2021 | 12/31/2021 |

\*Channel created anthropogenically by digging

NO2, NO3, and NO2+3

NO2+3 is quantified by passing water through a cadmium coil. NO3 is reduced to NO2 by the cadmium, after which NO2 is directly quantified colorimetrically. This reduction efficiency, which is calculated by running a known concentration of NO3 standard and comparing it to a known concentration of NO2 standard, is never 100%. Therefore, it is possible for NO2 to be measured as higher than NO2+3, if NO2 concentrations are especially high and NO3 concentrations are especially low. This did not happen in 2021 but historically, NO2F, NO23F, and NO3F values were flagged as <1> (CSM) in instances when this did occur. These measurements are valid, but the data user should understand that NO2 makes up the majority of the NO2+3 fraction in these samples. For more information on laboratory methods, please refer to Part 2 Section 13 of this document.

***Site specific flagging:***

Berlin Road (BR)

PO4F and TP were uncharacteristically high on 08/30/2021. These concentrations are likely correct though, because PO4F and TP concentrations were uncharacteristically high at site DR on the same date as well. It is possible that moderate precipitation over the previous 4-5 days explains such high phosphorus concentrations. Regardless, these values were flagged <0> (CSM) because they reflect correct environmental conditions and are not high because of lab errors.

Darrow Road (DR)

PO4F and TP were uncharacteristically high on 08/30/2021. These concentrations are likely correct though, because PO4F and TP concentrations were uncharacteristically high at site BR on the same date as well. It is possible that moderate precipitation over the previous 4-5 days explains such high phosphorus concentrations. Regardless, these values were flagged <0> (CSM) because they reflect correct environmental conditions and are not high because of lab errors.

Lower Estuary (OL)

Replicate 1 for PO4F measured on 05/04/2021 was much higher than historical concentrations. It appears that there was an error for this replicate and it is likely that the other replicate provides a more accurate quantification of SRP concentrations on 05/04/2021. Therefore, SRP was flagged as <-3> [GQD](CSM) on this date.

Wetland Mouth (WM)

Replicate 2 for NO2F measured on 03/08/2021 was much higher than historical concentrations, as well as samples analyzed for the diel sampling program from 5-6 days prior. It appears that there was an error for this replicate and it is likely that the other replicate provides a more accurate quantification of NO2F concentrations on this 03/08/2021. Therefore, NO2F and NO3F were flagged as <-3> [GQD](CSM) and <-3> [GCR] (CSM) on this date.

PO4F samples collected on 07/12-13/2021 as part of the diel sampling program were high. At times, they were at their highest on this date as any time over the previous 5 years. Samples collected during this time span group relatively closely however, and there is no obvious reason why this data should not be accepted. Therefore, PO4F concentrations during these timestamps are flagged <1> (CSM).

***Sample hold times***

Whole water samples were filtered within 24 hours of collection (Table 6). Unless noted otherwise, all water samples (whole water and filtrate) were held at 1-4 °C, and filters for chlorophyll-*a* analysis were immediately placed in -20°C after filtering for extraction (see Section II, Part 13 for a more detailed description of methods used to quantify chlorophyll-*a*). NERR protocols allows nutrient samples to be held for up to 28 days (chlorophyll-*a* for 30) at -20°C, plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time are flagged <1> (CHB).

**Table 6:** Nutrient and chlorophyll-*a* sample hold times for 2021. Sampling methods, frequency, and location followed the monthly grab sampling program (“Grab”) and diel sampling program (“Diel”). Samples were filtered within 24 hours of the collection date. Parameters include soluble reactive phosphorus (PO4F), total phosphorus (TP),ammonium (NH4F), nitrite (NO2F), nitrite+nitrate(NO23F), and chlorophyll-*a* (CHLA\_N).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Collection Date** | **Program** | **Date Analyzed** | | | | | |
| **PO4F** | **TP** | **NH4F** | **NO2F** | **NO23F** | **CHLA\_N** |
| 03/08/2021 | Grab | 03/10/2021 | 03/08/2021 | 03/09/2021 | 03/10/2021 | 03/09/2021 | 03/10/2021 |
| 04/06/2021 | Grab | 04/07/2021 | 04/06/2021 | 04/07/2021 | 04/07/2021 | 04/07/2021 | 04/08/2021 |
| 05/04/2021 | Grab | 05/05/2021 | 05/04/2021 | 05/04/2021 | 05/06/2021 | 05/06/2021 | 05/06/2021 |
| 06/02/2021 | Grab | 06/03/2021 | 06/02/2021 | 06/04/2021 | 06/04/2021 | 06/04/2021 | 06/04/2021 |
| 06/29/2021 | Grab | 06/30/2021 | 06/30/2021 | 06/30/2021 | 06/30/2021 | 06/30/2021 | 07/01/2021 |
| 08/03/2021 | Grab | 08/04/2021 | 08/04/2021 | 08/04/2021 | 08/04/2021 | 08/05/2021 | 08/05/2021 |
| 08/31/2021 | Grab | 08/31/2021 | 08/31/2021 | 08/31/2021 | 09/01/2021 | 09/01/2021 | 09/02/2021 |
| 10/05/2021 | Grab | 10/06/2021 | 10/05/2021 | 10/06/2021 | 10/06/2021 | 10/06/2021 | 10/07/2021 |
| 11/02/2021 | Grab | 11/03/2021 | 11/02/2021 | 11/03/2021 | 11/03/2021 | 11/18/2021\* | 11/05/2021 |
| 12/06/2021 | Grab | 12/07/2021 | 12/07/2021 | 12/07/2021 | 12/09/2021 | 12/09/2021 | 12/07/2021 |
| 03/02-03/2021 | Diel | 03/04/2021 | 03/03/2021 | 03/04/2021 | 03/04/2021 | 03/04/2021 | 03/05/2021 |
| 04/13-14/2021 | Diel | 04/15/2021 | 04/14/2021 | 04/15/2021 | 04/15/2021 | 04/21/2021\*\* | 04/20/2021 |
| 05/09-10/2021 | Diel | 05/11/2021 | 05/10/2021 | 05/11/2021 | 05/11/2021 | 05/11/2021 | 05/12/2021 |
| 06/06-07/2021 | Diel | 06/08/2021 | 06/07/2021 | 06/08/2021 | 06/08/2021 | 06/09/2021 | 06/09/2021 |
| 07/12-13/2021 | Diel | 07/13/2021 | 07/13/2021 | 07/14/2021 | 07/15/2021 | 07/15/2021 | 07/19/2021 |
| 08/08-09/2021 | Diel | 08/10/2021 | 08/10/2021 | 08/10/2021 | 08/10/2021 | 08/11/2021 | 08/12/2021 |
| 09/12-13/2021 | Diel | 09/14/2021 | 09/14/2021 | 09/14/2021 | 09/15/2021 | 09/15/2021 | 09/16/2021 |
| 10/10-11/2021 | Diel | 10/13/2021 | 10/12/2021 | 10/13/2021 | 10/13/2021 | 10/14/2021 | 10/14/2021 |
| 11/07-08/2021 | Diel | 11/09/2021 | 11/08/2021 | 11/09/2021 | 11/10/2021 | 11/12/2021 | 11/10/2021 |
| 12/19-20/2021 | Diel | 12/22/2021 | 12/20/2021 | 12/21/2021 | 12/22/2021 | 12/22/2021 | 12/27/2021 |

\*For monthly grab samples collected on 11/02/2021, NO23F samples were frozen between 11/05-18/2021, so were within NERR protocol hold times.

\*\*This sample was held beyond NERR protocol hold times and is flagged <1> (CHB).