**Old Woman Creek (OWC) NERR Site Water Quality Metadata**

January through December 2020

Latest Update: June 3, 2023

**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 State Nature Preserve and NERR. Three of the sites are in the estuary proper- one in the upper reaches at Darrow Road (DR) one near the mouth, just south of State Route 6 (WM) and the third site is upstream from the WM site (OL). 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 a 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 2020 chemical monitoring program began on 03 March 2020 at sites BR, DR, OL, and WM. Sampling at all sites ended for the year on 31 November 2020 due to ice cover.

Replicate surface water grab samples for chemical and chlorophyll analysis were collected sequentially at each of the data logger sites. If collected concurrent with logger exchange, the samples were collected immediately prior to exchange to ensure that the samples for chemical analysis were undisturbed. Both samples were normally collected within 30 seconds of each other, except at site DR, where the samples were collected about 2-3 minutes apart (see table below). 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, conductivity, dissolved oxygen, and pH values were determined on the samples at time of collection using a field meter that was previously calibrated according to the manufacturer specifications. Sample turbidity was measured in the lab with a Hach 2100AN Turbidimeter. If samples were not to be filtered and analyzed within the next hour, they were stored in a refrigerator or in the dark on ice.

All monthly grab samples and diel samples collected in 2020 were analyzed in the Old Woman Creek analytical laboratory following 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 2020 (see table below). 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 a slightly shallower depth than the sonde sensors. Sampler intake and pump tubing was 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. The sample bottles for the sampler were cleaned using the same protocol outlined above and processing was the same as for the monthly grab samples. Samples were analyzed with the same equipment and following the same protocols as for the Monthly Grab Sampling Program.

4) Site location and character:

Old Woman Creek National Estuarine Research Reserve 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 (OWC) watershed is primarily row crop agriculture (~70%). All residences in the watershed (concentrated in one small village) have septic systems. Salinity in Old Woman Creek is normally 1 ppt or less. Lake Erie water levels and, as a result, Old Woman Creek estuary water levels were much higher than average and at time close to record values during 2019.

The data logger at the State Route 6 (WM) site (Latitude 41° 22' 57” N, Longitude 82° 30' 52” 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 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 the dominant aquatic macrophyte near this site but has been drowned out due to high water levels. Depth at this site will range from less than 10 cm to nearly 2.0 meter over the course of a year. Deeper water conditions typically occurred when the outlet of the estuary to Lake Erie was “closed” (i.e., no direct surface water exchange) due to development of a barrier beach. Water levels rose above flood level in fall 2015.

The data logger at site OL (Latitude 41° 22’ 54” N, Longitude 82° 30’ 52” W) is in the lower reaches of the estuary. This site is not in direct sight of the mouth, so northerly winds and resulting seiche activities are less noticeable at this site but can 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 20 cm to more than a meter during the year. Again, deeper water typically occurred when the estuary outlet was closed or during a significant rain event.

The data logger at site DR (Latitude 41° 21’ 54”N, Longitude 82° 30’ 17”W) is at the southern boundary of the reserve. The logger trap is suspended from one of the supports on the north side of the Darrow Road bridge. At this site, the creek is relatively narrow. Although water direction and flow are influenced at this site by changes in Lake Erie water levels, this site does not have direct contact with Lake Erie waters. The bottom sediments at his site are silty clay. No rooted aquatic vegetation is present near or upstream from this site. Depth at this site ranges from about 20 cm up to over 1 m.

The data logger at site BR (Latitude 41° 20’ 54” N, Longitude 82° 30’ 50”W) is located in the lower portion of the creek proper. Just upstream from the data logger, 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 at this site 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 algal growth on the bottom rocks during much of the year. Depth during base flow conditions was about 50 cm but could rise to 2.5 m during storm flow.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Station Code | SWMP Status | Station Name | Location | Active Dates | Reason Decommissioned | Notes |
| owcbrnut | P | Berlin Road | 41.3483, 82.5139 | 03/2002 - current | NA | NA |
| owcdrnut | P | Darrow Road | 41.3650, 82.5047 | 08/2007 – current | NA | NA |
| owcsunut | P | Route 2 | 41.3672, 82.5072 | 03/2002 – 08/2007 | Bridge repair work and access | No longer in service |
| owcolnut | P | Lower Estuary | 41.3817, 82.5144 | 4/2002 – current | NA | NA |
| owcwmnut | P | Route 6 | 41.3825, 82.5144 | 3/2002 – current | NA | NA |

**5) Code 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

monthly grab sample program = 1

diel grab sample program = 2

**6) Data Collection Period**

1. Monthly grab sampling

Sampling at all sites began on 03 March 2020 and ended on 31 November 2020. Samples were not collected in January, February, or December due to ice cover. April and May samples were not collected due to COVID restrictions.

Specific deployment dates and times (EST) are listed below. The two grab samples were collected sequentially within 1-3 minutes of each other.

|  |  |  |  |
| --- | --- | --- | --- |
| Station Code | Sample Date | Rep 1 | Rep 2 |
| owcbrnut | 03/03/2020 | 09:55 | 09:56 |
|  | April 2020 | Not collected |  |
|  | May 2020 | Not collected |  |
|  | 06/16/2020 | 08:28 | 08:32 |
|  | 07/15/2020 | 08:16 | 08:18 |
|  | 08/04/2020 | 08:31 | 08:33 |
|  | 09/01/2020 | 09:26 | 09:27 |
|  | 10/06/2020 | 09:09 | 09:10 |
|  | 11/10/2020 | 10:20 | 10:21 |
|  |  |  |  |
| owcdrnut | 03/03/2020 | 10:29 | 10:36 |
|  | April 2020 | Not collected |  |
|  | May 2020 | Not collected |  |
|  | 06/16/2020\* | 09:27 | 09:33 |
|  | 07/15/2020 | 08:44 | 08:52 |
|  | 08/04/2020 | 09:13 | 09:17 |
|  | 09/01/2020 | 09:42 | 09:43 |
|  | 10/06/2020 | 09:36 | 09:39 |
|  | 11/10/2020 | 10:53 | 10:54 |
|  | \*6/16 samples collected in reverse order, but the times were updated for the database | | |
|  |  |  |  |
| owcolnut | 03/03/2020 | 11:16 | 11:18 |
|  | April 2020 | Not collected |  |
|  | May 2020 | Not collected |  |
|  | 06/16/2020 | 10:23 | 10:27 |
|  | 07/15/2020 | 09:36 | 09:39 |
|  | 08/04/2020 | 10:11 | 10:12 |
|  | 09/01/2020 | 10:11 | 10:12 |
|  | 10/06/2020 | 10:15 | 10:28\*\* |
|  | 11/10/2020 | 12:50 | 12:51 |
|  | \*\*Sample replicates were collected further apart than usual. | | |
|  |  |  |  |
| owcwmnut | 03/03/2020 | 11:29 | 11:45\*\* |
|  | April 2020 | Not collected |  |
|  | May 2020 | Not collected |  |
|  | 06/16/2020 | 10:52 | 10:53 |
|  | 07/15/2020 | 10:11 | 10:17 |
|  | 08/04/2020 | 10:23 | 10:25 |
|  | 09/01/2020 | 10:11 | 10:12 |
|  | 10/06/2020 | 10:37 | 10:40 |
|  | 11/10/2020 | 12:12 | 12:15 |

\*\*Sample replicates were collected further apart than usual.

1. Diel Sampling

For the following dates and times (EST) in 2020, samples were collected at site WM at two-hour intervals over a 26-hour time period.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Station Code | Start Date (mm/dd/yyyy) | Start Time (EST) | End  Date | End Time |
| owcwmnut | 03/16/2020 | 4:00:00 | 03/17/2020 | 6:00:00 |
| owcwmnut | April 2020 | Not collected |  |  |
| owcwmnut | May 2020 | Not collected |  |  |
| owcwmnut | 06/23/2020 | 4:00:00 | 06/24/2020 | 6:00:00 |
| owcwmnut | 07/14/2020 | 4:00:00 | 07/15/2020 | 6:00:00 |
| owcwmnut | 08/04/2020 | 4:00:00 | 08/05/2020 | 6:00:00 |
| owcwmnut | 08/31/2020 | 4:00:00 | 09/01/2020 | 6:00:00 |
| owcwmnut | 10/04/2020 | 4:00:00 | 10/05/2020 | 6:00:00 |
| owcwmnut | 11/09/2020 | 4:00:00 | 11/10/2020 | 6:00:00 |

7) Associated projects:

As part of the SWMP long-term monitoring program, OWC 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. Data are available upon request from the Research Coordinator.

A more comprehensive set of chemical parameters are determined for each surface water grab and diel sample collected for this sampling program. Samples for phytoplankton determination are collected at the same time as surface water grab samples at the DR site and within 100 m of the WM site. This enhanced data set is available from the research coordinator at Old Woman Creek NERR.

From May 2015 to December 2020, three samples a day were collected from the owcbrnut and owcwmnut sites using an autosampler programmed to collect samples at 04:00, 12:00, and 20:00. The samples are transported to the National Center for Water Quality Research (NCWQR) weekly (usually Monday mornings) for analysis. Up to three samples per day are analyzed depending on weather (1 sample during base flow; 2-3 samples during storm events). These data are available from the OWC NERR Research Coordinator or from <https://ncwqr.org/monitoring/>. Starting June 2019, the analyses of samples mentioned above were done at OWC NERR. The sampling regiment also changed slightly following the schedule below:

For storm events (at least 10 per year):

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

owcwmnut x1 per day @ 12:00

Non-storm regular sampling:

owcbrnut x1 per day @ 12:00

owcwmnut x1 per week @ 12:00 on Mondays

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.

**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](http://www.nerrsdata.org); *accessed* 12 October 2020.

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, 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 any outliers, which would suggest either testing or contamination problems. The datasheets are kept on file at the Old Woman Creek Visitor Center.

The Reserve staff enter the data recorded on field datasheets into an Excel workbook designated for that sampling year. The 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. Field and laboratory workbooks are saved to the SWMP Coordinator’s computer, an external hard drive and a central Ohio Department of Natural Resources Division of Wildlife server, which is regularly backed up through the State of Ohio’s Information Technology Department. The SWMP Coordinator is responsible for the data QA/QC and for the nutrient analysis QA/QC.

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 Data Category**

Required NOAA/NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisk “\*”.

Data Category Parameter Variable Name Units of Measure

Phosphorus: \*Soluble Reactive Phosphorus SRP (PO4F) mg/l as P

(Orthophosphate)

Total Phosphorus TP mg/l as P

Nitrogen: \*Nitrite + Nitrate, Filtered NO23F mg/l as N

\*Nitrite, Filtered NO2F mg/l as N

\*Nitrate, Filtered NO3F mg/l as N

\*Ammonium, 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

Notes:

1. Time is coded based on a 2400 clock and is referenced to Eastern Standard Time (EST).
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 and Calculated Laboratory Parameters**

**a) Parameters Measured Directly**

Phosphorus Species: SRP (PO4F), TP

Nitrogen Species: NH4F, NO2F, NO3F

Other: CHLA\_N

**b) Calculated Variables**

NO3F NO23F- NO2F

DIN NO23F + NH4F

**12)**  **Limits of Detection**

The Minimum Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the Old Woman Creek Analytical Laboratory. The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. The table below presents the MDL’s for the 2020 analytical period. These values are reviewed and revised annually.

*Old Woman Creek (Hand Chemistry) MDLs*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameter | Start Date | End Date | MDL | Units | Date Revisited |
| NH4F | 1/1/2020 | 5/16/2020 | 0.002 | mg/L | 5/30/2019 |
| NO2F | 1/1/2020 | 5/16/2020 | 0.0001 | mg/L | 6/13/2019 |
| NO23F | 1/1/2020 | 5/16/2020 | 0.010 | mg/L | 6/6/2019 |
| PO4F | 1/1/2020 | 5/16/2020 | 0.0001 | mg/L | 4/12/2019 |
| TP | 1/1/2020 | 5/16/2020 | 0.002 | mg/L | 6/27/2019 |
| CHLA\_N | 4/19/2019 |  | 0.19 | µg/L | 4/19/2019 |

*Old Woman Creek (Discrete Analyzer) MDLs*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameter | Start Date | End Date | MDL | Units | Date Revisited |
| NH4F | 5/2/2020 | 12/31/2020 | 0.007 | mg/L | 10/26/2020 |
| NO2F | 5/2/2020 | 12/31/2020 | 0.003 | mg/L | 9/10/2020 |
| NO23F | 5/2/2020 | 12/31/2020 | 0.003 | mg/L | 10/23/2020 |
| PO4F | 5/2/2020 | 12/31/2020 | 0.003 | mg/L | 9/17/2020 |
| TP | 5/2/2020 | 12/31/2020 | 0.003 | mg/L | 10/26/2020 |
| CHLA\_N | 4/19/2019 |  | 0.19 | µg/L | 4/19/2019 |

\*MDLs for the Seal autoanalyzer were calculated in the fall of 2020, but applied to previous data for the year.

**13) Laboratory Methods**

**Filtration:**

Each water sample is filtered withing 24 hours of collection using vacuum filtration. Due to frequent high levels of suspended particles, the OWC analytical lab uses a 2-step filtration process. Briefly, whole water samples are first filtered through 0.7 µm glass fiber filters (GFF), and then through pre-soaked 0.45 µm membrane filters within 24 hours of collection. All dissolved parameters, including orthophosphate (PO4F), Nitrate + Nitrite (NO23F), Nitrite (NO2F), and Ammonium (NH4F) are measured from 0.45 µm filtrate. Chlorophyll-*a* concentrations (CHLA\_N) are measured from the material retained on the 0.7 µm GFF.

**Preservation:**

If samples are not able to be processed and analyzed within allowable hold times, they are preserved through freezing at -20˚C. Hold times for samples collected at OWC follow the National Estuarine Research Reserve Standard Operating Procedures (NERR 2021), which generally align with hold times recommended in Standard Methods (APHA 2017). Briefly, samples are stored in the lab at 4˚C and analyzed within 5 days of collection. If analysis within 5 days is not possible, hold times may be extended for an additional 28 days by freezing filtrate at -20˚C. For chlorophyll-*a*, freezing extends hold times by 30 days.

**Nutrients:**

**March 2020 samples:** All nutrients (PO4F, TP, NH4F, NO2F, NO23F) for March 2020 were measured using hand chemistry per the methods details below and in the Old Woman Creek Standard Operating Procedures and Quality Control document.

**a) Total Phosphorus (TP)** – measured on whole water samples

Digestion: Persulfate digestion on a hot plate following Standard Methods 4500-P B.5 (23rd edition, APHA 2017)

Analysis: Ascorbic acid reduction following Standard Methods 4500-P E (23rd edition; APHA 2017)

**b) Orthophosphate (PO4F)**

Method: Ascorbic acid reduction following Standard Methods 4500-P E (23rd edition; APHA 2017)

**c) Nitrate + Nitrite (NO23F)**

Method: Standard Methods 4500-NO3- E (23rd edition; APHA 2017)

**d) Nitrite (NO2F)**

Method: Methods 4500-NO2- B (23rd edition; APHA 2017)

**e) Ammonium (NH4F)**

Method:Standard Methods 4500-NH3 F (23rd edition; APHA 2017)

**June-November 2020 samples** (no April or May samples were collected) all nutrients were measured with a Seal Analytical AQ300 Discreate Autoanalyzer. All parameters are quantified spectrophotometrically. For each parameter the OWC analytical lab follows methods developed by Seal Analytical that suggest reagent volumes and masses appropriate for their equipment. However, these methods follow principals outlined in Standard Methods (APHA 2017) and USEPA (1993), which are listed, below.

**a) Total Phosphorus (TP)** – measured on whole water samples

Digestion: Persulfate digestion on a hot plate following Standard Methods 4500-P B.5 (23rd edition, APHA 2017)

Analysis: Ascorbic acid reduction following Standard Methods 4500-P F (23rd edition; APHA 2017)

**b) Orthophosphate (PO4F)**

Method: Ascorbic acid reduction following USEPA 365.1 Rev 2.0 (1993) and Standard Methods 4500-P F (23rd edition; APHA 2017)

Principal: Sample is combined with molybdate and antimony to form an antimony phosphor-molybdate complex. This complex is reduced by ascorbic acid to an intensely blue dye, phosphomolybdenum blue, which is measured at 880 nm.

**c) Nitrate + Nitrite (NO23F)**

Method: USEPA 132 A Rev 1.0 (1993) and Standard Methods 4500-NO3- F (23rd edition; APHA 2017)

Principal: Nitrate is chemically reduced to nitrite by passing the sample water through a cadmium coil. Reduced sample is then mixed with sulfanilamide and phosphoric acid, causing a reaction where nitrite forms a diazonium compound which, when combined with N-(1-naphthyl)-ethylenediamine, forms a pink dye that can be measured spectrophotometrically at 520 nm.

**d) Nitrite (NO2F)**

Method: USEPA 354.1 Rev 2.0 (1993); Standard Methods 4500-NO2-B (23rd edition; APHA 2017)

Principal: The sample is mixed with sulfanilamide and phosphoric acid. This causes a reaction where nitrite forms a diazonium compound which, when combined with N-(1-naphthyl)-ethylenediamine, forms a pink dye that can be measured spectrophotometrically at 520 nm.

**e) Ammonium (NH4F)**

Method:USEPA 350.1 Rev 2.0 (1993); Standard Methods 4500-NH3 H (23rd edition; APHA 2017)

Principal: Ammonia reacts with hypochlorite in an alkaline sample, forming chloramine. The chloramine is combined with salicylate and nitroferricyanide, forming a blue-green dye that is measured at 660 nm.

**Pigments:**

Chlorophyll-*a* is extracted from material retained on 0.7 µm GFF, which are placed in stoppered vials containing 90% acetone solvent and left to sit for a 2-7 day steeping period at -20˚C. Filters are transferred to test tubes and centrifuged (1 minute, 2840 RPM) to separate particulates. Chlorophyll-*a* is then determined fluorometrically from whole water samples using a Turner Design Trilogy model fluorometer following the CHL-NA (“non-acidification”) module. This module follows the Welschmeyer Method (Welschmeyer 1994), where the Trilogy provides a set of very narrow bandpass excitation and emission filters that nearly eliminate the spectral interference caused by the presence of pheophytin-*a* and chlorophyll-*b*, allowing for the direct measurement of chlorophyll-*a* without the need for acidification.

**a) Chlorophyll-*a* (CHLA\_N)**

Method:USEPA Method 445.0 (USEPA 1997); Notable deviations from Method 445.0 include:

* OWC skips the grinding step where the filter is homogenized because filter particles can interfere with fluorometer readings if not properly removed, and overheating during grinding can cause chlorophyll-*a* to degrade.
* OWC places filters in the freezer (-20˚C) instead of the fridge (4˚C), both when filters are placed in vials, and for steeping. Freezing lyses phytoplankton cells and releases chlorophyll-*a*, which is important because we do not grind our filters.

Principal: A solvent, in this case 90% aqueous acetone, is used to extract chlorophyll from phytoplankton cells retained on GFF. Extract is then placed in a fluorometer, which excites electrons in the chlorophyll extract with a lower wavelength light, and then measures their emission at a higher wavelength. With the Welschmeyer Method (Welschmeyer 1994), filters are included in the fluorometer to ensure that measured emission is only from chlorophyll-*a*, and not other phytoplankton pigments nor organic material in the water.

**14) Field and Laboratory QA/QC Programs**

1. **Precision**

**Field Variability**- For monthly grab sampling, two replicate samples are collected at all four sites (i.e., 100% of samples receive a field replicate). These samples are collected consecutively (within 4 minutes of each other at a maximum, but usually within 30 seconds of each other) and represent true replicates. For Diel sampling, only one sample is collected at each time (i.e., 0% of samples receive a field replicate).

**Lab Variability-** No lab replicates are analyzed for nutrient samples. For chlorophyll-*a* samples, one sample is analyzed as a lab duplicate for each run. This represents 9% of Monthly grab samples, and 7% of Diel samples that are run in duplicate for chlorophyll-*a*.

**Inter-organizational Splits-** OWC NERR did not participate in an inter-organizational split program with any other lab in 2022.

1. **Accuracy**

**Sample Spikes**- For Monthly grab sampling, a sample spike is included on every run (i.e., 10% of samples), for each nutrient parameter. OWC does not include spikes for Diel sampling, nor when analyzing chlorophyll-*a*.

**Cross Calibration Exercises**- Old Woman Creek NERR did not participate in any cross-calibration exercises with other labs during 2022.

**General Laboratory QA/QC-** For each nutrient analysis, a deionized water blank and a know standard are analyzed after every 10 unknown samples, and at the end of every run, to ensure that the analysis maintains accuracy throughout the entire run.

When Nitrate + Nitrite (NO23F) is analyzed, nitrate (NO3-) is reduced to nitrite (NO2-) when sample water us passed through a cadmium coil. The reduction efficiency of this process is measured by analyzing known nitrate and known nitrite standards of the same concentration. Theoretically, each standard should return the same value after analysis (i.e., 100% reduction efficiency), but this is almost never the case due to deterioration of the cadmium coil and interferences within the sample. If the reduction efficiency drops below 85%, the coil is regenerated, and the entire run is reanalyzed.

Total phosphorus is analyzed by digesting all phosphorus species to orthophosphate, which is then measured directly on the analyzer. During each total phosphorus run, a known standard and deionized water blank are included as samples to verify that the digestion is complete, and that it is not introducing any interferences into the analysis, respectively.

For chlorophyll-*a*, a filter blank (i.e., a sample which had deionized water passed through a 0.7 µm GFF filter) and a 90% acetone blank are included at the end of every run to assess whether there was any contamination in the sample, and evaluate any background fluorescence from the extraction solvent, respectively. Furthermore, each chlorophyll-*a* run includes a solid secondary standard at the beginning and end of each run. The Solid Secondary Standard provides a stable fluorescence signal that can be used to check the stability of the fluorometer, and track drift over time. As long as the solid secondary standard is within +/- 50 RFU of its originally calibrated value, OWC does not create a new calibration curve for chlorophyll-*a*.

**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.

**Change in reported data:** For the June 2020 through 2021 samples, all nutrient concentrations, except for TP, were originally corrected using the deionized water blank that is included during analysis. Subtracting the blank is a negligible change to the reported concentration, but occasionally results in a zero/negative measured value or causes the parameter to be below the MDL. In May of 2023 we determined during the data authentication process that subtracting the deionized water blank was not the most appropriate method because the analyzer used to measure nutrient concentrations includes a zero standard when creating the standard curve. On June 3, 2023, the measured concentrations without the blank removed were uploaded to the database in the authenticated dataset. Users should be aware that there would have been a slight change in some previously reported values as a result.

**NO2F and NO23F:** With the Seal discrete analyzer, 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, given acceptable error within these methods, it is possible for NO2 to be measured as slightly higher than NO2+3, if NO2 concentrations are especially high and NO3 concentrations are especially low. However, this occurred more often and to a greater degree than expected in 2020. Since it is not technically possible for NO2F to be greater than NO23F, in these instances NO2F and calculated NO3F values were rejected and flagged/coded <-3> (CSM). NO23F and calculated DIN where at least flagged/coded <1> (CSM) and rejected in some cases. These measurements may be valid for some users and uses; 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.

**Sample hold times for 2020:** Nutrient samples are held at 4°C or below and typically analyzed within three days. NERRS protocols allows nutrient samples to be held for up to 24 hours + 5 days for collecting, processing, and shipping. CHLA filters were held at -20°C. NERRS protocols allows CHLA samples to be held for up to 30 days, plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time are marked with an asterisk below, flagged suspect and coded CHB.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **Date Analyzed** | | | | | |
| **Sample Descriptor** | **PO4F** | **TP** | **NH4F** | **NO2F** | **NO(2)3F** | **CHLA\_N** |
| 3/3/2020, all grab samples | 3/4/2020 | 3/4/2020 | 3/4/2020 | 3/4/2020 | 3/4/2020 | 3/12/2020 |
| No Samples for April | / | / | / | / | / | / |
| No Samples for May | / | / | / | / | / | / |
| 6/16/2020, all grab samples | 6/17/2020 | 6/16/2020 | 6/17/2020 | 6/17/2020 | 6/17/2020 | 6/23/2020 |
| 7/15/2020, all grab samples | 7/16/2020 | 7/16/2020 | 7/16/2020 | 7/16/2020 | 7/16/2020 | 7/18/2020 |
| 8/4/2020, all grab samples | 8/5/2020 | 8/5/2020 | 8/5/2020 | 8/5/2020 | 8/5/2020 | 8/13/2020 |
| 9/1/2020, all grab samples | 9/2/2020 | 9/1/2020 | 9/2/2020 | 9/23/2020\* | 9/23/2020\* | 9/9/2020 |
| 10/6/2020, all grab samples | 10/8/2020 | 10/7/2020 | 10/8/2020 | 10/8/2020 | 10/8/2020 | 10/13/2020 |
| 11/10/2020, all grab samples | \*11/17/2020 | 11/12/2020 | \*11/18/2020 | \*11/17/2020 | \*11/17/2020 | 11/17/2020 |
| No Samples for December | / | / | / | / | / | / |
|  |  |  |  |  |  |  |
| 03/16-17/2020, all diel samples | 3/18/2020 | 3/18/2020 | 3/18/2020 | 3/18/2020 | 3/18/2020 | 3/31/2020 |
| No Samples for April | / | / | / | / | / | / |
| No Samples for May | / | / | / | / | / | / |
| 6/23/2020, all diel samples | 6/25/2020 | 6/24/2020 | 6/25/2020 | 6/25/2020 | 6/25/2020 | 6/30/2020 |
| 7/14-15/2020, all diel samples | 7/16/2020 | 7/16/2020 | 7/16/2020 | 7/16/2020 | 7/16/2020 | 7/18/2020 |
| 8/4-5/2020, all diel samples | 8/5/2020 | 8/5/2020 | 8/5/2020 | 8/5/2020 | 8/5/2020 | 8/15/2020 |
| 8/31-9/1/2020, all diel samples | 9/2/2020 | 9/1/2020 | 9/2/2020 | \*9/23/2020 | \*9/23/2020 | 9/9/2020 |
| 10/4-5/2020, all diel samples | 10/8/2020 | 10/7/2020 | 10/8/2020 | 10/8/2020 | 10/8/2020 | 10/13/2020 |
| 11/9-10/2020, all diel samples | \*11/17/2020 | 11/12/2020 | \*11/18/2020 | \*11/17/2020 | \*11/17/2020 | 11/17/2020 |

\*samples held beyond NERRS SOP guidance.

Barrier Beach Status and Water Exchange

The water quality of the OL and WM sites at OWC are influenced by whether the barrier beach is open (i.e., surface exchange is occurring between the estuary and the lake). When the barrier 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 data. This is evident in less stable values throughout the diel cycles. 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 and specific conductivity. The Oberlin Beach Association is a private beach association whose property contains a portion of the barrier beach. During 2020, the association used a mini excavator to open the barrier beach as documented by the dates below:

|  |  |  |
| --- | --- | --- |
| **Beach Status** | **Date From** | **Date To** |
| Open | 01/01/2020 | 03/07/2020 |
| Closed | 03/08/2020 | 03/11/2020 |
| Open | 03/12/2020 | 03/15/2020 |
| Closed | 03/16/2020 | 03/18/2020 |
| Open | 03/19/2020 | 05/01/2020 |
| Closed | 05/02/2020 | 05/15/2020 |
| \*Open | 05/16/2020 | 06/07/2020 |
| Closed | 06/08/2020 | 09/03/2020 |
| \*\*Opened | 09/03/2020 | 09/04/2020 |
| Closed | 09/04/2020 | 09/08/2020 |
| Open | 09/09/2020 | 09/11/2020 |
| Closed | 09/12/2020 | 10/22/2020 |
| Open | 10/22/2020 | 11/21/2020 |
| Closed | 11/22/2020 | 11/23/2020 |
| Open | 11/23/2020 | 12/15/2020 |
| Closed | 12/15/2020 | 12/23/2020 |
| Open | 12/24/2020 | 12/31/2021 |

\*Narrow but deep channel present

\*\*Channel unnaturally created by private beach association 10:00-16:00

The DR June replicate grab samples were actually collected in the reverse order, with replicate 2 being collected first. The times were changed for the purposes of the NERRS database.

**References**

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Welschmeyer, N.A. (1994). Fluorometric analysis of chlorophyll *a* in the presence of chlorophyll *b* and pheopigments. Limnology and Oceanography 39:1985-1992.

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