**Lake Superior** (LKS) **NERR Nutrient Metadata**

**January to December, 2017**

**Latest Update:** June 7, 2021

**I. Data Set and Research Descriptors**

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

Hannah Ramage, Monitoring Coordinator (Laboratory Contact)

14 Marina Drive, Superior, WI 54880

705-399-4088

[Hannah.ramage@ces.uwex.edu](mailto:Hannah.ramage@ces.uwex.edu)

Shon Schooler, Research Coordinator (June 2011 – August 2018)

14 Marina Drive, Superior, WI 54880

715-399-4087

[sschoole@uwsuper.edu](mailto:sschoole@uwsuper.edu)

Dustin Haines, Research Coordinator (August 2019 - )

14 Marina Drive, Superior, WI 54880

715-399-4087

[dustin.haines@wisc.edu](mailto:dustin.haines@wisc.edu)

**2) Research objectives** –

The Lake Superior NERR is situated on the freshwater estuary at the confluence of the St. Louis River and Lake Superior, the largest and most pristine of the Great Lakes. The Reserve is a diverse, 16,697-acre complex that contains a variety of representative terrestrial and aquatic habitats allowing for extensive research and educational opportunities. The Reserve provides opportunities for research and monitoring, experiential learning, and training, while continuing to contribute to the protection of the ecological health of the St. Louis River Estuary and Lake Superior coastal habitats.

The Lake Superior NERR implements the NERR System-Wide Monitoring Program (SWMP) along a river-to-Lake gradient. SWMP includes a continuous meteorological station, four continuous water quality monitoring stations, and monthly nutrient/pigment sampling at those same four stations. The nutrient sampling has two programmatic parts:

1. Monthly Grab Sampling Program: Identifies nutrient difference along the river-to-Lake gradient throughout the ice free season. Samples are collected at the four long-term SWMP stations.
2. Diel Sampling Program: Lake Superior does not experience strong tides, therefore 12 diel samples are simply collected with an auto-sampler every two hours, beginning the day before or day of grab sample collections. Diel samples are collected at the same SWMP station, every month.

Water samples for nutrient/pigment analysis were collected by NERR staff at these four stations, filtered and analyzed in the LKS NERR Laboratory.

**3) Research methods** –

1. Monthly Grab Sampling Program

Grab samples (sequential replicates) were collected from a boat once a month at the depth of the sonde deployment (1.5 meters beneath the surface, except at Pokegama which is shallower) using a horizontal sampler. Sample bottles are acid-washed amber one-liter poly bottles. Ambient water quality data was collected concurrent with sampling, with a YSI EXO datasonde calibrated at the LKS NERR laboratory. At each station, depth profiles (readings every 2m) were recorded on a field sheet. Depth profile data are only available by contacting the Reserve directly.

1. Diel Sampling Program

Diel samples were taken from the dock located at Barker’s Island SWMP station, at the same depth as the water quality datasonde, with an ISCO autosampler. The sampler was set to sample twelve times, with pre-reverse, every two hours for 24 hours beginning either the day before of the day of monthly grab samples. Sample bottles are acid washed one-liter translucent poly bottles. Ice was added to the sample bottle container for the duration of sampling during warm summer months.

Both monthly grab and diel samples were transported in a cooler, then filtered within a few hours of arrival in the LKS NERR laboratory. Samples were filtered in low light to prevent chlorophyll *a* degradation. Samples were either refrigerated at 4°C and analyzed for nutrients within 24 hours, or frozen at ≤-20°C and analyzed within 28 days. Chlorophyll *a* filters were folded and enclosed in aluminum foil and kept frozen at ≤-20°C until extraction. The LKS NERR laboratory conducted the analysis for all required parameters for 2017. Additionally, due to local research and management interest, the LKS NERR conducted Total Suspended Solid analysis for all grab and diel samples every month.

**4) Site location and character –**

The Lake Superior NERR is located within the estuary of the St. Louis River. The St. Louis River Watershed covers approximately 3,634 square miles in northeast Minnesota and 263 square miles in northwest Wisconsin. The watershed is mostly forested, with some urban areas, especially at the estuary, and active iron mining in the upper reaches. In the upper watershed the river flows through lake clays and glacial deposits for approximately 100 miles. Near the city of Thomson, the river channel narrows and the river flows through a rocky rapid-filled gorge. Approximately 23 river miles upstream from Lake Superior is the Fond du Lac dam, the most downstream of several dams. Below the gorge and dams the river begins to take on the characteristics of a freshwater estuary. Near the mouth of the river on Lake Superior is the largest working harbor on the Great Lakes (by tonnage). A long baymouth sand bar protects the estuary form the wind and waves of Lake Superior. The natural entry through the bar is the Superior Entry to the southeast, while the Duluth Entry is an engineered entry with a lift bridge toward the northwest end.

Lake Superior does not produce a noticeable “tide” as on the ocean coasts, however, seiches, which occur when wind or atmospheric pressure causes oscillations in the water of Lake Superior, are common. For example, the USGS Sontek at the Duluth entry to the harbor has measured streamflow at between 4.0 cfs and -3.5 cfs. There tends to be a larger seiche period of about eight hours, while smaller seiches can be seen at approximately four and two hours. The change in water level as a result is usually less than a foot, however, a strong seiche can reverse the direction of the river’s flow as far upstream as Fond du Lac (approximately 12 river miles). The USGS stream gage on the St. Louis River at Scanlon (upstream of the Fond du Lac dam) recorded an annual mean discharge of 2,384 cfs for the period of record (1909 to 2017). In comparison, 2017 was a high water year, with an annual mean discharge of 3,575 cfs.

Oliver Bridge (OL)

a) *latitude & longitude:* 46.65685, -92.20166

b) *tidal range:* This site is located on the downstream side of a bridge piling at Oliver, WI. The site is 11 miles upstream of Lake Superior and upstream of the majority of the estuary, receives downstream river flow below the Fond du Lac dam, but is influenced to some extent by Lake seiche.

c) *salinity range:* 0.08 – 0.2 PPT

d) *freshwater input:* freshwater estuary site, receives flow of the St. Louis River (relatively undeveloped riparian area)

e) *water depth:* river approximately 8m deep, 126m wide

f) *bottom habitat or type:* currently undocumented (suspected sand or soft sediment)

g) *pollutants:* approximately 12 miles downstream of the Fond du Lac dam, historic paper mills above dam

h) *watershed:* this site is the furthest upstream site monitored in the St. Louis River Estuary by LKS, approximately 11 miles upstream from the mouth at Lake Superior, this site does experience seiche

i) *associated sonde depth:* the sonde is deployed at a depth of 1.5 m from the surface at this site

Blatnik Bridge site (BL)

a) *latitude & longitude:* 46.748649, -92.10027

b) *tidal range:* this site is located on the downstream side of a mid-river bridge protection cell off of Rice’s Point,

and is influenced by seiche

c) *salinity range:* 0.1 – 0.25 PPT

d) *freshwater input:* freshwater estuary site, receives flow of the St. Louis River and tributaries to the estuary (urban)

e) *water depth:* approximately 7m, river approximately 360 meters wide

f) *bottom habitat or type:* currently undocumented (suspect mostly sand)

g) *pollutants:* site is located within the urban area of Superior, WI, and Duluth, MN; site is immediately

downstream of the Western Lake Superior Sanitary District WWTP discharge.

h) *watershed:* this site is within the lower estuary, in the industrial harbor, the site is influenced by Lake seiche

i) *associated sonde depth:* the sonde is deployed at a depth of 1.5 m from the surface at this site

Barkers Island site (BA)

a) *latitude & longitude:* 46.721772, -92.06352

b) *tidal range:* this site is located on the northwest end of Barkers Island in the St. Louis River, upstream of the Superior entry to the estuary, and is influenced by Lake seiche

c) *salinity range:* 0.08 to 0.2 PPT

d) *freshwater input:* freshwater estuary, receives flow from the St. Louis River and tributaries (urban)

e) *water depth:* approximately 2 m, approximately 1207m across Superior Bay at this location, navigation channel is at least 7m deep

f) *bottom habitat or type:* mix of sand and soft sediments

g) *pollutants:* site is downstream of the Superior WWTP and WLSSD WWTP

h) *watershed:* this site is the furthest downstream site monitored by LKS NERR in the St. Louis River Estuary, also within the lower industrial harbor. The Nemadji River (433 square mile watershed, mostly forested) also enters the St. Louis River Estuary near the Superior entry

i) *associated sonde depth:* the sonde is deployed at a depth of 1.5 m from the surface at this site

Pokegama Bay site (PO)

a) *latitude & longitude:* 46.672360, -92.135614

b) *tidal range:* this site is located in the Pokegama River, upstream of its mouth at the St. Louis River

c) *salinity range:* 0.06 – 0.21 PPT

d) *freshwater input:* freshwater estuary, receives flow from a 20,144-acre sub-watershed of the St. Louis River

e) *water depth:* approximately 1 to 2 m in the channel as it winds through shallower wetlands

f) *bottom habitat or type:* mostly mobile red clay and silt, Pokegama Bay wetland historically included large beds of wildrice

g) *pollutants:* this site is downstream of Village of Superior’s waste water lagoons and is impaired due to Total Phosphorus exceedances.

h) *watershed:* the Pokegama River is a tributary to the St. Louis River, entering the estuary on the Wisconsin side of Clough Island. The Pokegama River watershed measures approximately 20,144 acres, 51% of which is wetland, 37% forested, 4% developed and 6% agricultural use (the remainder is open water or bare land). This site is on a red clay tributary to the St. Louis River, the mouth of which enters between the Oliver and Blatnik sites, and is affected by Lake seiche.

i) t *associated sonde depth:* he sonde is deployed at a depth of approximately 0.6 m from the surface at this site

All Lake Superior NERR historical nutrient/pigment monitoring stations:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Station Code | SWMP Status | Station Name | Location | Active Dates | Reason Decommissioned | Notes |
| BA | P | LKSBAWQ | 46° 43' 18.38 N, 92° 03' 48.67 W | 05/05/2012 -current | NA | NA |
| BL | P | LKSBLWQ | 46° 44' 55.14 N, 92° 06' 0.97 W | 05/08/2012 -current | NA | NA |
| OL | P | LKSOLWQ | 46° 39' 24.66 N, 92° 12' 5.98 W | 05/08/2012 -current | NA | NA |
| PO | P | LKSPOWQ | 46° 40' 20.50 N, 92° 8' 8.21 W | 05/28/2013 -current | NA | NA |

**5) Coded variable definitions** –

lksbanut = Lake superior NERR Barkers Island nutrients

lksponut = Lake Superior NERR Pokegama River nutrients

lksolnut = Lake Superior NERR Oliver Bridge nutrients

lksblnut = Lake Superior NERR Blatnik Bridge nutrients

Monthly Grab Sample Program = 1

Diel Grab Sample Program = 2

**6) Data collection period** – Grab and diel samples were collected at the date and times specified in the table below. In all cases, replicate grab samples were collected within four minutes of the first sample.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Grab Samples | | | | Diel samples |
| **SITE** | **Oliver Bridge** | **Pokegama Bay** | **Blatnik Bridge** | **Barkers Island** | **Barkers Island** |
| **First Year**  **Sampled** | 2012 | 2013 | 2012 | 2012 | 2014 |
| **March** | 3/3/17 12:27 | 3/3/17 11:15 | 3/9/17 12:10 | 3/9/17 12:24 | not taken - ice |
| **April** | 4/22/17 9:41 | 4/22/17 10:50 | 4/22/17 11:37 | 4/22/17 13:41 | 04/21/17 13:00 to 04/22/17 11:00 |
| **May** | 5/24/17 10:01 | 5/24/17 10:49 | 5/24/17 9:23 | 5/24/17 11:52 | 05/23/17 10:00 to 05/24/17 08:00\* |
| **June** | 6/29/17 10:04 | 6/29/17 10:44 | 6/29/17 11:25 | 6/29/17 11:57 | 06/28/17 9:00 to 06/29/17 5:00 |
| **July** | 7/25/17 9:54 | 7/25/17 10:33 | 7/25/17 9:01 | 7/25/17 8:43 | 07/24/17 15:00 to 07/25/17 13:00 |
| **August** | 8/28/17 9:15 | 8/28/17 10:21 | 8/28/17 11:08 | 8/28/17 11:44 | 08/28/17 10:00 to 08/29/17 8:00 |
| **September** | 9/22/17 11:31 | 9/22/17 12:10 | 9/22/17 10:43 | 9/22/17 12:54 | 09/22/17 11:00 to 09/23/17 09:00 |
| **October** | 10/18/17 11:03 | 10/18/17 10:30 | 10/18/17 9:47 | 10/18/17 12:00 | 10/17/17 10:00 to 10/18/17 08:00 |
|  |  |  |  |  |  |

\* May diel samples were not physically collected due to a distributor arm malfunction with the ISCO.

**7) Associated researchers and projects–**

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

The System-Wide Monitoring Program datasonde deployments at the four SWMP sites is on-going, with 15-minute data for dissolved oxygen, temperature, specific conductance, salinity, pH, turbidity, and chlorophyll-a. Research projects were carried out by students this field season for comparison of water quality sensor readings and laboratory methods for chlorophyll *a*. It was found that there was a suitable correlation between YSI EXO2 sonde chlorophyll-a sensor results and laboratory obtained chlorophyll-a results collected during the nutrient sampling.

The SWMP weather station and datasonde site was established in Pokegama Bay and is the central location of a developing Great Lakes climate change Sentinel Site. The weather station records 15-minute data on temperature, relative humidity, wind speed and direction, rain, photosynthetically-active radiation and total solar radiation. Permanent vegetation surveys were established in the wetlands surrounding the SWMP site, with vegetation community data collection beginning in summer 2014. Vegetation surveys were again completed at these locations in August, 2016 and September 2017. One focus of this project is wild rice, and the resulting data will be used to measure reference site conditions to compare to wild rice restoration efforts throughout the estuary.

The St. Louis River Estuary is listed as an Area of Concern under the Great Lakes Water Quality Agreement. One of the impairments for which it was listed is “Excessive Loading of sediment and nutrients”. Other agencies working in the St. Louis River Estuary to remove impairments include the Wisconsin and Minnesota Department of Natural Resources, the United States Environmental Protection Agency Mid-Continent Ecology Lab, United States Fish and Wildlife Service and the United State Geological Survey. The LKS NERR participates with partnerships in the area with these agencies as well as with the City of Superior, Douglas County, and several non-profits.

Under-ice sampling at 30 sites was carried out from 2013-2017 with researchers from UM-Duluth’s Natural Resources Research Institute (NRRI) and Large Lakes Observatory (LLO). The objective of this project is to follow algal community changes under ice, and document areas of low dissolved oxygen in winter. There are few winter sampling projects undertaken along Lake Superior. Partners who participated in sample analyses were; Lake Superior NERR, GLERL, LLO, USGS and NRRI.

The LKS NERR cooperates with researchers at University of Wisconsin and University of Minnesota studying the biogeochemical processes in the estuary. Researchers are looking at the spatial and seasonal patterns of nutrient and organic matter processing. One outcome will be the identification of the role of anthropogenic stressors. The results will enhance our ability to interpret data from water quality monitoring in the estuary to inform management strategies. The USGS is working on a biophysical model of the St. Louis River Estuary. The USGS will be collecting data throughout the estuary until 2018 to build this model. The Lake Superior NERR is assisting by coordinating collection of SWMP data to alternate with USGS sampling and tending additional equipment, such as a non-SWMP sonde at the Superior Entry to the estuary.

The LKS NERR Research Coordinator, assisted by the Monitoring Coordinator and Coastal Training Program Coordinator, plan to coordinate a monitoring network in the estuary in order to best match management needs with monitoring data. The result will be a list of prioritized needs matched with organizations best suited to meet those needs.

The St. Louis River Estuary has recently been chosen as a NOAA Blueprint Habitat Focus Area (<http://www.habitat.noaa.gov/habitatblueprint/pdf/hb_st_louis_river_factsheet.pdf>). NOAA offices will work in cooperation with local entities to meet multiple habitat objectives on a watershed scale.

**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 process 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 2016.

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** –

Nutrient sample analysis conducted in LKS NERR Laboratory from March to May 2017 was carried out by previous personnel (previous Monitoring Coordinator and student technicians) who were unable to complete the data entry, compilation and QAQC process. Therefore, Hannah Ramage (current Monitoring Coordinator), who did not perform the analysis, compiled and all nutrient data and performed QAQC.

Results for nutrient analyses were managed by the Automated Analyzer Control and Evaluation Software (AACE), version 7.09, which operates the SEAL AA3. The AACE software allows for analysis post-processing, QAQC, and exportation of reports via pdf. It also exports data as .slk files in mg/L. This file is easily saved as an excel file and data can be copied and pasted into the NutrientQAQC excel macro (see below) without any unit conversions. Raw results for chlorophyll-a (ug/L) and total suspended solids (mg/L) were hand recorded in laboratory notebooks. These results are later entered digitally into an excel spreadsheet. Depth profile data is hand recorded on a datasheet in the field and later entered into an excel spreadsheet. All data transfers from hand recorded datasheets or notebooks, and from AACE .slk files were independently checked by a second person.

After nutrient data was transferred or entered into a Microsoft Excel worksheet, the data was processed using the NutrientQAQC Excel macro. 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 –**

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

Data Category Parameter Variable Name Units of Measure

Phosphorus and Nitrogen:

\*Orthophosphate PO4F mg/L as P

\*Ammonium, Filtered NH4F mg/L as N

\*Nitrite, Filtered NO2F mg/L as N

\*Nitrate, Filtered NO3F mg/L as N

\*Nitrite + Nitrate, Filtered NO23F mg/L as N

Plant Pigments:

Chlorophyll CHLA\_N µg/L

Other Lab Parameters:

Total Suspended Solids TSS mg/L

Notes:

1. Time is coded based on a 2400 clock and is referenced to Standard Time.

2. Reserves have the option of measuring either NO2 and NO3 or substituting NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3.

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

1. **Parameters measured directly**

Nitrogen species: NH4F, NO2F, NO23F

Phosphorus species: PO4F

Other: CHLA, TSS

1. **Calculated parameters**

NO3F NO23F-NO2F

**12) Limits of detection** –

The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results. The LKS NERR Laboratory revisits MDLs annually using EPA 821-R-16-006 procedures for NH4F, NO2F, NO23F, PO4F and TSS. The estimated MDL for CHLA\_N is taken from the Turner Designs, Trilogy Laboratory Fluorometer User’s Manual Version 1.2, as purchasing large amounts of Chlorophyll-a standard to perform MDL analysis is cost prohibitive.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Start Date | End Date | MDL | Last Revisited |
| NH4F | 01/01/17 | 12/31/17 | 0.01 | 4/4/18 |
| NO2F | 01/01/17 | 12/31/17 | 0.005 | 4/4/18 |
| NO23F | 01/01/17 | 12/31/17 | 0.008 | 4/3/18 |
| PO4F | 01/01/17 | 12/31/17 | 0.003 | 4/3/18 |
| CHLA\_N | 01/01/17 | 12/31/17 | 0.14 | 4/20/21\* |
| TSS | 01/01/17 | 12/31/17 | 1.0 | 12/21/17 |

\*The CHLA\_N MDL was evaluated/calculated in 2021 and used retroactively since one hadn’t been calculated for 2017-2019 data.

**13) Laboratory methods** –

* 1. **Parameter: NH4F**

LKS NERR Laboratory Method: *SOP Ammonia by Seal AA3 Auto analyzer Rev. 1*

*Ammonia in Water, Waste Water and Soil Extracts, Seal Analytical Auto Analyzer Application Method No. G-102-93 Rev. 7 (based on Standard Method 4500-NH3-G)*

NRRI Central Analytical Laboratory: *Standard Methods 4500-NH3- G*

Method Reference: *Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012, American Public Health Association, American Water Works Association, Water Environment Federation, Port City Press, Baltimore, Maryland (Section 4500-NH3).*

Method Descriptor: *This is an automated procedure were* *ammonia is reacted with alkaline phenol, hypochlorite and dichloro-isocyanuric acid to produce a blue compound measured at 660 nm. Nitroprusside is used as a catalyst. The LKS NERR method varies from Standard Method 4500-NH3 G with the use of salicylate instead of phenol.*

Preservation Method: *Samples filtered (0.45 µm membrane filter) and stored at 4°C for up to 24 hours or filtered and stored at -20°C for up to 28 days.*

* 1. **Parameter: NO2F and NO23F**

LKS NERR Laboratory Method: *SOP Nitrate and Nitrite by Seal AA3 Auto analyzer Rev. 0*

*Nitrate and Nitrite in Water and Waste Water and other aqueous extracts, Seal Analytical Application Method No. G\_200-97 Rev. 6 (based on Standard Method 4500 NO3-F*

Method Reference: *Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012, American Public Health Association, American Water Works Association, Water Environment Federation, Port City Press, Baltimore, Maryland (Method 4500-NO3F).*

Method Descriptor: *This is an automated procedure for the determination of nitrate plus nitrite, in which nitrate in a filtered sample is reduced to nitrite by a copper-cadmium reductor column at a pH of 8.5. The nitrite ion then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with the N-1-naphthylethylenediame dihydrochloride to form a reddish-purple azo dye which is read colorimetrically at 550 nm. The nitrite value is determined by eliminating or by-passing the reductor column and standardizing with an appropriate nitrite standard.*

Preservation Method: *Samples filtered (0.45 µm membrane filter) and stored at 4°C for up to 24 hours or filtered and stored at -20°C for up to 28 days.*

* 1. **Parameter: PO4F**

LKS NERR Laboratory Method: *SOP Phosphate by Seal AA3 Auto analyzer Rev. 1*

*Phosphate in water or Bray soil extracts, Seal Analytical Method No. G-297-03 Rev 4 (based on Standard Method 4500-P-E)*

EPA or other Reference Method: *Standard Methods 4500-P-E*

Method Reference: *Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012, American Public Health Association, American Water Works Association, Water Environment Federation, Port City Press, Baltimore, Maryland (Method 4500-P-E).*

Method Descriptor: *This automated procedure for the determination of orthophosphate is based on the colorimetric method in which a blue color is formed by the reaction of orthophosphate, molybdate ion and antimony ion followed by reduction with ascorbic acid at a pH<1. The reduced blue phospho-molybdenum complex is colorimetrically read at 880 nm.*

Preservation Method: *Samples filtered (0.45 µm membrane filter) and stored at 4°C for up to 24 hours or filtered and stored at -20°C for up to 28 days.*

* 1. **Parameter: CHLa\_N**

LKS NERR Laboratory Method: *SOP Chlorophyll a Non-acidification Method Rev 1 (based on EPA Method 445.0)*

EPA or other Reference Method: EPA Method *445.0*

Method Reference: *US.EPA 1997. Method 445.0, In Vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence, Revision 1.2, September, 1997. Arar, E.J. and Collins, G.B., National Exposure Research Laboratory, Office of Research and Development, United States Environmental Protection Agency, Cincinnati, Ohio, 45268.*

Method Descriptor: *Chlorophyll a containing phytoplankton in surface water are concentrated by filtering through a glass fiber filter (Whatman GF/F, 0.7 µm). Pigments are extracted in 90% acetone for 24 hours. The filter slurry is centrifuged for clarification and fluorescence is measured. The Turner Design Trilogy fluorimeter 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.*

Preservation Method: *Samples filtered and stored at -20°C for up to 30 days, filters are wrapped in foil to prevent light interference.*

* 1. **Parameter: TSS**

LKS NERR Method: *SOP Solids: Total Dissolved Solids and Total Suspended Solids Rev 1 (based on Standard Methods 2540)*

EPA or other Reference Method: *Standard Methods 2540*

Method Reference: *Standard Methods for the Examination of Water and Wastewater, 22nd Edition, Method 2540, APHA, AWWA, WEF, Port City Press, Baltimore, Maryland, 2012.*

Method Descriptor: *A well-mixed sample is filtered through a weighed standard glass fiber filter (1.5 µm). The filter and residue retained is dried to a constant weight at 103 to 105oC. The increase in weight of the filter represents the total suspended solids.*

Preservation Method: *Refrigerate sample at 4ºC for no more than 7 days. Analyzed as soon as possible due to the impracticality of preservation.*

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

* 1. **Precision**
     1. **Field variability** – True field replicates (successive grab samples taken within 4 minutes of one another) were collected at every SWMP station for the Monthly Grab Sampling Program. Field replicates were not collected for the Diel Sampling Program. In total, 32 replicates, so 22% of samples were collected in replicate for both programs combined. Variability among replicates is analyzed using Relative Percent Difference and is summarized in the table below.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | NH4F Rep RPD | NO2 Rep RPD | NO23F Rep RPD | PO4F Rep RPD | CHLA\_N  Rep  RPD | TSS Rep RPD |
| all sites combined | min | 0.0 | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 |
| max | 75.9 | 109.1 | 63.3 | 64.2 | 150.0 | 200.0 |
| average | 18.5 | 14.7 | 10.9 | 28.2 | 19.6 | 33.3 |
|  |  |  |  |  |  |  |  |
| BA | min | 0.0 | 4.9 | 1.2 | 19.4 | 0.0 | 0.0 |
| max | 46.8 | 18.2 | 16.3 | 64.2 | 20.2 | 200.0 |
| average | 16.6 | 10.8 | 5.6 | 44.8 | 26.9 | 59.6 |
|  |  |  |  |  |  |  |  |
| BA | min | 1.5 | 0.0 | 1.0 | 0.0 | 3.4 | 0.0 |
| max | 35.6 | 109.1 | 63.3 | 57.1 | 34.6 | 28.6 |
| average | 12.2 | 25.4 | 17.0 | 29.7 | 16.6 | 18.8 |
|  |  |  |  |  |  |  |  |
| OL | min | 0.0 | 0.0 | 1.9 | 0.0 | 0.0 | 0.0 |
| max | 47.1 | 10.5 | 11.0 | 51.9 | 24.8 | 142.9 |
| average | 17.1 | 3.1 | 7.5 | 21.0 | 13.5 | 22.7 |
|  |  |  |  |  |  |  |  |
| PO | min | 0.0 | 0.0 | 2.3 | 0.0 | 0.0 | 1.2 |
| max | 75.9 | 81.5 | 38.1 | 26.7 | 28.6 | 106.4 |
| average | 26.9 | 19.3 | 13.6 | 17.1 | 21.2 | 32.3 |

* + 1. **Laboratory variability** – For each analysis conducted in the LKS NERR laboratory, at least two laboratory replicates were performed per sample batch (5%). High variability (>10% RPD) is one QC parameter that determines whether data is flagged as suspect or rejected.
    2. **Inter-organizational splits** – None in 2017.
  1. **Accuracy**
     1. **Sample spikes** – The LKS NERR Laboratory analyzed at least one Laboratory Control Sample (LCS), made from a purchased standard solution independent of the calibration standards, every sample batch for all nutrient parameters. Percent Recovery was calculated as 100\*(instrument reading/true value) for each laboratory parameter. Any analysis with an LCS percent recovery of >110% or <90% are at least flagged suspect. Any analysis with an LCS percent recovery of >120% and <80% are flagged rejected.
     2. **Standard reference material analysis –** None in 2017
     3. **Cross calibration exercises** – None in 2017

**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.

**Sample Hold Times:** Standard protocol at the LKS NERR is to either refrigerate samples at 4°C and analyze for nutrients within 24 hours, or freeze and store at ≤-20°C for analysis within 28 days. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30) at -20°C, plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect and coded CHB. They are also marked with an asterisk below. Although TSS sample hold times are largely unknown standard protocol was to analyze within 7 days.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Collection Date** | **Sample Type** | **Date Analyzed** | | | | | |
| *NH4F* | *NO2F* | *NO23F* | *PO4F* | *CHLA-N* | *TSS* |
| 3/3/2017 | grab | 3/4/2017 | Not analyzed | 3/16/2017 | 3/16/2017 | 3/24/2017 | unknown |
| 4/22/2017 | grab | 4/23/2017 | 4/24/2017 | 4/24/2017 | 4/24/2017 | 5/23/17 | unknown |
| 4/21 - 4/22/17 | diel |
| 5/24/2017 | grab | 6/5/2017 | \*7/12/17 | \*7/13/17 | Not analyzed | 5/26/2017 | 6/1/2017 |
| Not collected | diel |
| 6/29/2017 | grab | 7/11/2017 | 7/12/2017 | 7/13/2017 | Not analyzed | 7/7/2017 | 7/3/2017 |
| 6/28 - 6/29/17 | diel |
| 7/25/2017 | grab | Not analyzed | Not analyzed | Not analyzed | Not analyzed | 8/3/2017 | 7/27/2017 |
| 7/24 - 7/25/17 | diel |
| 8/28/2017 | grab | \*10/26/17 | \*10/20/17 | \*10/26/17 | \*10/26/17 | 9/21/2017 | 8/31/2017 |
| 8/28 - 8/29/17 | diel |
| 9/22/2017 | grab | \*10/26/17 | 10/20/17 | \*10/26/17 | \*10/26/17 | 10/26/17 | 9/26/2017 |
| 9/22 - 9/23/17 | diel |
| 10/18/2017 | grab | 11/7/2017 | 11/7/2017 | 11/8/2017 | 11/8/2017 | 11/9/2017 | 10/24/2017 |
| 10/17 - 10/18/17 | diel |

Nutrient sample analysis conducted in LKS NERR Laboratory from March to May 2017 was carried out by previous personnel (previous Monitoring Coordinator and student technicians) who were unable to complete the data compilation and QAQC process. Therefore, Hannah Ramage (current Monitoring Coordinator), who did not perform the analysis, compiled and all nutrient data and performed QAQC. AACE program files and data post-processing were conducted when needed to ensure the best quality data. New data quality protocols were created for the laboratory and data coding and flagging was carried out in reference to those protocols.

The decisions to code nutrient results <-3> [GQD] (CSM) or <1> [GQS] (CSM) or <1> [GQS] (CHB) if a sample was also held too long, unless specifically noted below, were made using the LKS NERR Laboratory’s individual QC procedure for analyses performed on the Seal AA3 Autoanalyzer. This procedure includes analysis of 5 QC parameters:

1. **Correlation Coefficient (r):** The correlation coefficient (r) between the light absorbance of calibrants (mAU) and the expected calibration concentration (mg/L) of the analyte.
2. **Laboratory Control Sample (LCS)** performance: The calculated percent recovery of a known concentration of analyte that is made from a separate source than the calibrants.
3. **Laboratory Duplicate** Performance: The Relative Percent Difference (RPD) between two results from the same sample.
4. **Blank performance**: Method, field, filter or pure water blanks that are included in a run of samples
5. **Peak shape and noise**: the absorbance peaks generated by the analysis and baseline noise

There were data that met the characterization above to be marked suspect, but that were below MDL as well. In these cases detailed below data were flagged/coded <-4> [SBL] (CSM).

**NH4F**

|  |  |
| --- | --- |
| lksolnut | 5/24/2017 10:01 |
| lksolnut | 5/24/2017 10:02 |
| lksponut | 5/24/2017 10:50 |
| lksolnut | 8/28/2017 9:15 |
| lksponut | 8/28/2017 10:21 |
| lksponut | 8/28/2017 10:23 |

**NO2F**

|  |  |
| --- | --- |
| lksblnut | 5/24/2017 9:22 |
| lksblnut | 5/24/2017 9:23 |
| lksolnut | 5/24/2017 10:01 |
| lksolnut | 5/24/2017 10:02 |
| lksponut | 5/24/2017 10:49 |
| lksponut | 5/24/2017 10:50 |
| lksbanut | 6/29/2017 11:57 |
| lksblnut | 6/29/2017 11:25 |
| lksblnut | 6/29/2017 11:27 |
| lksolnut | 6/29/2017 10:04 |
| lksolnut | 6/29/2017 10:06 |
| lksponut | 6/29/2017 10:44 |
| lksponut | 6/29/2017 10:47 |
| lksbanut | 6/28/2017 9:00 |
| lksbanut | 6/28/2017 11:00 |
| lksbanut | 6/28/2017 13:00 |
| lksbanut | 6/28/2017 15:00 |
| lksbanut | 6/28/2017 17:00 |

For additional details regarding the LKS NERR laboratory QC procedures for specific data, please contact the Monitoring Coordinator.

March samples were not analyzed for NO2F due to technical issues.

May and June samples were not analyzed for PO4F due to a cracked coil in the autoanalyzer on the relevant channel.

There were no nutrient parameters analyzed in July because samples were not properly filtered in time, and therefore were unpreserved.