Lake Superior (LKS) **NERR Nutrient Metadata**
January to December, 2018
Latest Update: 6/15/2020

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

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

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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 sampling. The nutrient sampling has two programmatic parts:

a) Monthly Grab Sampling Program: Identifies nutrient difference along the river-to-Lake gradient throughout the ice free season. This program also collects samples from under ice periodically in the winter. Samples are collected at the four water quality stations.
b) Diel Sampling Program: Lake Superior does not experience strong tides, therefore 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 station, every month.

3) Research methods –

a) Monthly Grab Sampling Program

Grab samples were collected from a boat or canoe 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. In winter, a hole is first augured through the ice. Sample bottles are acid-washed amber one-liter poly bottles. Ambient water quality data was concurrent with sampling, with an YSI EXO datasonde calibrated at the LKS NERR laboratory. At each station, depth profiles (bottom, middle, and top of water column) were recorded on a field sheet and are reported in the water quality Annual Metadata document.

a) Diel Sampling Program

Diel samples were taken from the dock located at Reserve offices with an ISCO autosampler (Barkers Island SWMP station). The sampler was set to sample, 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 ISCO sample bottle container for the duration of sampling during warm summer months. Cold months inhibit use of the ISCO sampler because of ice build up in the tubing.

Both monthly and diel samples were filtered within a few hours of arrival in the LKS NERR laboratory and at the latest 24 hours from collection. Bottles were kept cold and covered to prevent exposure to light. Chlorophyll *a* filters were folded and enclosed in aluminum wrapped centrifuge tubes and kept in the freezer until extraction. The LKS NERR laboratory conducted the analysis for nutrients in April, May, and September. In June through August the LKS NERR laboratory analyzed chlorophyll-a but filtered and transported nutrient samples to University of Minnesota-Duluth's Natural Resources Research Institute (NRRI) Central Analytical Laboratory for analysis. Samples were transported the day of sampling directly to the analytical lab's freezer. 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).

Oliver Bridge (OL)

a) -92.20166, 46.65685
b) 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 estuary site, receives flow of the St. Louis River (relatively undeveloped riparian area)
e) river approximately 8m deep, 126m wide
f) bottom habitat or type currently undocumented (suspected sand or soft sediment)
g) approximately 12 miles downstream of the Fond du Lac dam, historic paper mills above dam and active mining in the upper watershed
h) 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

Blatnik Bridge site (BL)

a) -92.10027, 46.748649
b) 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 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) 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) this site is within the lower estuary, in the industrial harbor, the site is influenced by Lake seiche

Barkers Island site (BA)

a) -92.06352, 46.721772
b) 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 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) site is downstream of the Superior WWTP and WLSSD WWTP, and near several storm water outfalls and Faxon Creek (an entirely urban stream) it is also adjacent to a public beach
h) 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

Pokegama Bay site (PO)

a) -92.135614, 46.672360
b) 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 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 type is mostly red clay and silt, Pokegama Bay wetlands historically included large beds of wild rice
g) 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)
h) 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.

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**	**08/09/2012 00:00 -current**	**NA**	**NA**
BL	**P**	**LKSBLWQ**	**46° 44' 55.14 N, 92° 06' 0.97 W**	**08/09/2012 00:00 -current**	**NA**	**NA**
OL	**P**	**LKSOLWQ**	**46° 39' 24.66 N, 92° 12' 5.98 W**	**07/27/2012 00:00 -current**	**NA**	**NA**
PO	**P**	**LKSPOWQ**	**46° 40' 20.50 N, 92° 8' 8.21 W**	**10/01/2013 00:00 -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	2014	7/22/2014 12:00 to 7/23/2014 10:00
April	4/23/19 9:31	4/23/19 10:34	4/23/19 11:40	4/23/19 7:54	04/22/19 16:00 to 04/23/19 14:00
May	5/28/19 9:30	5/28/19 10:15	5/28/19 9:00	5/28/19 11:15	05/29/19 10:00 to 05/30/10 08:00
June	6/25/19 10:15	6/25/19 11:02	6/25/19 11:55	6/25/19 12:17	06/24/19 10:00 to 06/25/19 8:00
July	7/30/19 10:53	7/30/19 10:05	7/30/19 9:30	7/30/13 12:45	07/29/19 12:00 to 07/30/19 10:00
"August"	9/04/19 8:33	9/04/19 9:20	9/04/19 7:55	9/04/19 10:33	09/02/19 10:00 to 09/03/19 8:00
September	9/24/19 8:09	9/24/19 8:35	9/24/19 9:06	9/24/19 9:25	09/23/19 12:00 to 09/24/19 10:00

7) Associated researchers and projects–

As part of the SWMP long-term monitoring program, Lake Superior 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.

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/phycocyanin fluorescence.

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 completed last in 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 2013-2018 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. Four of the sampling location for this project are SWMP stations.

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 2019.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page www.nerrsdata.org. Data are available in comma separated version format.

II. Physical Structure Descriptors

9) Entry verification –

Results for nutrient analyses from LKS NERR laboratory 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 a Miscroft 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.

Nutrient results and QAQC material from the NRRI Central Analytical Laboratory are received in a Microsoft Excel worksheet. Data are converted to mg/L then copied and pasted in to the NutrientQAQC macro. All data transfers from one Excel worksheet to another are checked by a second person.

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.

Example of conversion documentation: The NRRI Central Analytical Laboratory calculates and reports results in ppb (parts per billion). For purposes of consistency in the NERR System, Lake Superior NERR calculates the concentrations as mg/l. Therefore, Lake Superior NERR staff divides the concentrations reported by the NRRI Central Analytical Laboratory by 1000 to yield mg/l.

10) Parameter titles and variable names by category –

Required NOAA NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisk "*".

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:			
	*Orthophosphate, Filtered	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
	Total Nitrogen	TN	mg/L as N
	Total Phosphorus	TP	mg/L as N
Plant Pigments:			
	*Chlorophyll a	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 they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3.

11) Measured or calculated laboratory parameters –

a) **Parameters measured directly**

Nitrogen species:	NH4F, NO2F, NO23F, TN
Phosphorus species:	PO4F, TP
Other:	CHLA_N, TSS

b) **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, and PO4F. MDLs for TSS are calculated only using blanks. 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. The NRRI Central Analytical Laboratory reported minimum detection limits to the LKS NERR. Their MDLs are revisited at least annually.

Parameter	Laboratory	Start Date	End Date	MDL	Last Verified
NH4F	NRRI	1/1/2019	12/31/2019	0.002	
NO2F	LKS	1/1/2019	6/23/2019	0.003	2/6/2020
NO2F	NRRI	6/24/2019	9/5/2019	0.002	
NO2F	LKS	9/5/2019	12/31/2019	0.003	2/6/2020

NO23F	NRRI	1/1/2019	12/31/2019	0.002	
PO4F	NRRI/LKS	1/1/2019	12/31/2019	0.002	2/4/2020 (LKS)
TP	NRRI	1/1/2019	12/31/2019	0.002	
TN	NRRI	1/1/2019	12/31/2019	0.005	
CHLA	LKS	1/1/2019	12/31/2019	0.025	5/9/2019
TSS	LKS	1/1/2019	12/31/2019	1	10/29/2019

13) Laboratory methods –

a) **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-NH_3).*

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 um membrane filter) and stored at 4 ℃ for up to 24 hours or filtered and stored at - 20 ℃ for up to 28 days.*

b) **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

NRRI Central Analytical Laboratory: *Standard Methods 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-NO_3 F).*

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 um membrane filter) and stored at 4 ℃ for up to 24 hours or filtered and stored at - 20 ℃ for up to 28 days.*

c) **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)

NRRI Central Analytical Laboratory: *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 an pH<1. The reduced blue phospho-molybdenum complex is colorimetrically read at 880 nm.*

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

d) **Parameter: TN/TP**

NRRI Central Analytical Laboratory: *Standard Method 4500-PJ followed by SM 4500 PE (for TP) and SM 4500 NO3 F (for TN)*

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-J).*

Method Descriptor: *A whole water sample is digested simultaneously for Total Nitrogen and Total Phosphorus using a persulfate method. After digestion, samples are ready for automated analysis for NO3 and PO4 (see above).*

Preservation Method: *Samples stored at 4 °C for up to 24 hours or stored at - 20 °C for up to 28 days.*

e) **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 um). 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 placed in a foil wrapped centrifuge tube to prevent light interference.*

f) **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 um). The filter and residue retained is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids.*

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

14) Field and Laboratory QAQC programs –

[Instructions/Remove: This section describes field variability, laboratory variability, the use of inter-organizational splits, sample spikes, standards, and cross calibration exercises. Include any information on QAQC checks performed by your lab.]

a) **Precision**

i) **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, 24 replicates were taken, so 20% 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	TN Rep RPD	PO4F Rep RPD	TP Rep RPD	CHLA_N Rep RPD	TSS Rep RPD
all sites combined	min	0.0	0.0	0.0	0.0	0.0	2.6	0.0	0.0
	max	62.1	85.7	44.4	7.2	40.0	53.7	57.0	168.4
	average	9.9	18.4	10.0	2.0	11.4	12.1	10.3	41.5
BA	min	0.0	0.0	2.3	0.7	0.0	3.4	0.0	0.0
	max	62.1	40.0	8.2	3.5	40.0	8.7	25.1	46.2
	average	23.2	29.2	5.1	1.7	8.6	5.3	7.7	21.9
BL	min	0.0	0.0	1.1	0.4	0.0	2.6	1.0	0.0
	max	13.3	40.0	1.7	4.1	13.3	8.0	12.2	142.9
	average	4.8	8.1	1.3	2.1	2.2	6.0	4.1	60.6
OL	min	0.0	0.0	0.0	0.3	0.0	9.2	3.0	4.0
	max	21.1	85.7	25.0	1.2	18.2	14.1	57.0	66.7
	average	8.5	27.9	9.3	0.7	5.9	12.2	18.0	29.0
PO	min	0.0	0.0	0.0	0.0	14.3	5.7	0.6	1.1
	max	15.4	18.2	44.4	7.2	40.0	53.7	32.2	168.4
	average	3.1	8.3	24.3	3.4	28.7	25.1	11.5	54.6

i) **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. The NRRI Central Analytical Laboratory reported laboratory splits (8% of total samples analyzed).

ii) **Inter-organizational splits** – The LKS NERR Laboratory participated in the 2018 NOAA/NERRS Analytical Laboratory Intercomparison Study for Nitrate+Nitrite, Nitrite, and Orthophosphate and was within all warning limits (2 Standard deviations of all samples across laboratories) for all parameters.

b) **Accuracy**

i) **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.

The NRRI Central Analytical Laboratory reported at least one LCS per sample batch, all were within 91 – 109% recovery.

ii) **Standard reference material analysis –** None in 2019
iii) **Cross calibration exercises** – None in 2019

15) QAQC flag definitions –
[Instructions/Remove: This section details the primary and secondary QAQC flag definitions and requires no additional information. Include the following excerpt.]

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 –
[Instructions/Remove: This section details the secondary QAQC Code definitions used in combination with the flags above and requires no additional information. Include the following excerpt.]

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.

April and May NH4F data is rejected due equipment malfunction resulting in drift throughout the run. Due to the malfunction the LKS NERR laboratory was unable to

analyze NO23F in April and May. Again, the LKS NERR laboratory was unable to analyze September samples (9/23 – 9/24/2019) for NH4F and NO23F due to the same malfunction.

Sample hold times for 2019: Samples are held at -20°C. 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.

	Date Analyzed							
Sample Descriptor	**NH4F**	**NO2F**	**NO23F**	**TN**	**PO4F**	**TP**	**CHLA_N**	**TSS**
4/23/2019, all grab samples	6/27/2019*				02/04/2020*		5/13/2019	4/23/2019
4/22-4/23/2019, all diel samples	6/27/2019*				02/04/2020*		5/13/2019	4/23/2019
5/28/2019, all grab samples	6/27/2019				02/04/2020*		6/5/2019	6/4/2019
5/28-5/30/2019, all diel samples	6/27/2019				02/04/2020*		6/5/2019	6/4/2019
6/25/2019, all grab samples	6/27 – 6/28/2019	7/2/2019	7/2/2019	7/11 and 7/18/2019	7/10 and 7/11/2019	7/10/2019	6/27/2019	6/26/2019
6/24-6/25/2019, all diel samples	6/27 – 6/28/2019	7/2/2019	7/2/2019	7/11 and 7/18/2019	7/10 and 7/11/2019	7/10/2019	6/27/2019	6/26/2019
7/30/2019, all grab samples	8/08/2019	7/31/2019	7/31/2019	8/21/2019	8/13/2019	8/21/2019	8/1/2019	8/1/2019
7/29-7/30/2019, all diel samples	8/08/2019	7/31/2019	7/31/2019	8/21/2019	8/13/2019	8/21/2019	8/1/2019	8/1/2019
9/04/2019, all grab samples	10/3/2019*	9/25/2019	9/25/2019	9/24/2019	10/8 and 10/9/2019*	9/26/2019	10/3/2019	9/10/2019
9/02-9/03/2019, all diel samples	10/3/2019*	9/25/2019	9/25/2019	9/24/2019	10/8 and 10/9/2019*	9/26/2019	10/3/2019	9/10/2019
9/24/2019, all grab samples		02/06/2020*			02/06/2020*		10/3/2019	9/26/2019
9/23-9/24/2019, all diel samples		02/06/2020*			02/06/2020*		10/3/2019	9/26/2019

*sample held longer than allowed by NERRS protocols