

Lake Superior (LKS) NERR Nutrient Metadata
January to December, 2022
Latest Update: June 26th, 2023

Note: This is a provisional metadata document; it has not been authenticated as of its download date. Contents of this document are subject to change throughout the QAQC process and it should not be considered a final record of data documentation until that process is complete. Contact the CDMO (cdmosupport@baruch.sc.edu) 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/pigment sampling at those same four stations. 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. Samples are collected at the four long-term SWMP water quality stations.
- b) 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.

3) Research methods –

- a) Monthly Grab Sampling Program

Grab samples (sequential replicates) 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 collected concurrent with sampling, with a YSI EXO datasonde calibrated at the LKS NERR laboratory. At each station, seasonal depth profiles (bottom, middle, and top of

water column) were recorded on a field sheet. Depth profile data are only available by contacting the Reserve directly.

b) 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 or 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 buildup in the tubing.

Both monthly grab and diel samples were transported from the field to the laboratory in a cooler, then filtered within a few hours of arrival in the LKS NERR laboratory and at the latest 24 hours from collection. Samples were filtered in low light to prevent chlorophyll *a* degradation. Samples were frozen at $\leq -20^{\circ}\text{C}$. Chlorophyll *a* filters were folded and enclosed in aluminum wrapped centrifuge tubes and kept in the freezer at $\leq -20^{\circ}\text{C}$ until extraction within 28 days. The LKS NERR laboratory conducted all Chlorophyll *a* and Total Suspended Solid analysis for all grab and diel samples every month in 2022.

The University of Minnesota-Duluth's Natural Resources Research Institute (NRRI) Central Analytical Laboratory conducted nutrient analysis for all sampling in 2022. Samples were filtered at the LKS NERR then either transported via cooler to NRRI (30-minute drive) the same day and placed in a freezer at NRRI, or frozen at the LKS NERR then transported within 3 days to NRRI.

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 Thompson, 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 from 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) *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 8 m deep, 126 m 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 and active mining in the upper watershed
- 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 1.5-2.0 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 7 m, river approximately 360 m 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 Waste Water Treatment Plant (WLSSD 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

Barker's 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 1,207 m across Superior Bay at this location, navigation channel is at least 7 m deep
- f) *bottom habitat or type*: mix of sand and soft sediments
- g) *pollutants*: 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 often closed throughout the summer due to *E. coli* standard exceedance
- 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 wild rice

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

All LKS 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 00:00 -current	NA	NA
BL	P	LKSBLWQ	46° 44' 55.14 N, 92° 06' 0.97 W	05/08/2012 00:00 -current	NA	NA
OL	P	LKSOLWQ	46° 39' 24.66 N, 92° 12' 5.98 W	05/08/2012 00:00 -current	NA	NA
PO	P	LKSPOWQ	46° 40' 20.50 N, 92° 8' 8.21 W	05/28/2013 00:00 -current	NA	NA

5) Coded variable definitions –

lksbanut = Lake Superior NERR Barker's 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 –

SITE	Barker's Island	Blatnik Bridge	Oliver Bridge	Pokegama Bay	Barker's Island
First Year Sampled	2014	2012	2012	2013	2014
Monitoring Program	Grab	Grab	Grab	Grab	Diel
April	04/26/22 9:06	Not taken – ice	Not taken – ice	Not taken – ice	04/25/22 10:00 to 04/26/22 8:00
May	06/02/22 11:22	06/02/22 8:09	06/02/22 9:49	06/02/22 10:25	05/30/22 10:00 to 05/31/22 8:00

June	06/28/22 9:33	06/28/22 7:35	08/28/22 8:15	06/28/22 8:50	06/27/22 10:30 to 06/28/22 8:30
July	08/02/22 10:28	08/02/22 7:29	08/02/22 8:07	08/02/22 8:56	07/25/22 10:00 to 07/26/22 8:00
August	8/31/22 9:50	08/31/22 7:35	08/31/22 8:15	08/31/22 9:00	08/29/22 10:00 to 8/30/22 8:00
September	09/28/22 7:45	09/28/22 8:05	09/28/22 8:37	09/28/22 9:05	09/27/22 10:00 to 09/28/22 8:00
October	10/26/22 13:22	10/26/22 11:56	10/26/22 8:45	10/26/22 9:35	10/25/22 10:00 to 10/26/22 8:00

Grab sample times in the table above are the time of the first replicate grab. The second replicate grab sample was collected within four minutes of the first. Diel samples are collected every 2 hours between the listed start and end times.

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 are on-going, with 15-minute data for dissolved oxygen, temperature, specific conductance, salinity, pH, turbidity, and chlorophyll-a.

The SWMP weather station and datasonde site was established in Pokegama Bay. 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 August 2021. 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.

8) Distribution –

NOAA retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The NERRS retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the NERR

site where the data were collected should be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; *accessed* 12 October 2021.

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

II. Physical Structure Descriptors

9) Entry verification –

Raw results for chlorophyll-a (ug/L) and total suspended solids (mg/L) are hand recorded in laboratory notebooks or bench sheets. 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, bench sheets, or notebooks were independently checked by a second person for copy errors.

Nutrient data from the NERR Central Analytical laboratory are provided in an excel spreadsheet over email. These data undergo a unit conversion then are copied over to the NutrientQAQC Excel macro (see below).

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 NERR 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 NERR Central Analytical Laboratory by 1000 to yield mg/l.

Hannah Ramage was responsible for these data management tasks.

10) Parameter titles and variable names by category –

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

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:			
	*Orthophosphate	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Total Nitrogen	TN	mg/L as N
	Total Phosphorus	TP	mg/L as P
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
DIN	NO23F+NH4F

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 CHLA_N. MDLs for TSS are calculated only using blanks. NRRI Central Analytical Laboratory, a Minnesota state certified laboratory, revisits MDL values for every parameter annually, and reports a single value for each parameter for the year.

Parameter	Start Date	End Date	MDL	Last Revisited	Laboratory
TP	01/01/2022	12/31/2022	0.004	Reviewed annually	NRRI
NH4F	01/01/2022	12/31/2022	0.008	Reviewed annually	NRRI
PO4F	01/01/2022	12/31/2022	0.003	Reviewed annually	NRRI
NO2F	01/01/2022	12/31/2022	0.007	Reviewed annually	NRRI
NO3F	01/01/2022	12/31/2022	0.005	Reviewed annually	NRRI
TN	01/01/2022	12/31/2022	0.02	Reviewed annually	NRRI
CHLA_N	03/29/2022	12/31/2022	0.06	03/29/22	LKS NERR
TSS	01/01/2022	12/31/2022	1	10/26/22	LKS NERR

13) Laboratory methods –

a) Parameter: NH4F

NRRI Central Analytical Laboratory

Method Reference: *U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 351.2. EPA-600/4-79-020, Revised March 1983.*

Method Descriptor: *When ammonium is heated with salicylate and hypochlorite in an alkaline phosphate buffer. An emerald green color is produced which is proportional to the ammonium concentration. The presence of EDTA in the buffer prevents precipitation of calcium and magnesium. The color is intensified by adding sodium nitroprusside.*

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.*

b) Parameter: NO2F and NO3F

NRRI Central Analytical Laboratory

Method Reference: *S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes. Method 353.2. EPA 600 4-79-020, Revised 1983.*

Method Descriptor: *Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone also can be determined by removing the cadmium column.*

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.*

c) Parameter: PO4F

NRRI Central Analytical Laboratory

Method Reference: *Standard Methods for the Examination of Water and Wastewater, Method 4500-P E. 18th Ed. 1992. American Public Health Association, Washington, D.C.*

Method Descriptor: *Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid (phosphomolybdic acid) that is reduced to intensely colored molybdenum blue by ascorbic acid.*

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.*

d) Parameter: CHLA_N

LKS NERR Laboratory Method: *SOP Chlorophyll a Non-acidification Method Rev 1 (based on 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 μ m). 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 (0.7 Glass Fiber) and stored at -20 °C for up to 30 days, filters are placed in a foil wrapped centrifuge tube to prevent light interference.*

e) Parameter: TSS

LKS NERR Method: *SOP Solids: Total Dissolved Solids and Total Suspended Solids Rev 1 (based on 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 μ m). 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.*

f) Parameter: TP and TN

NRRI Central Analytical Laboratory

Method References:

Ameel, J. R. Axler, and C. Owen. 1993. Persulfate digestion for determination of total nitrogen and phosphorus in low-nutrient waters. American Environmental Laboratory. Oct. 1993.

Standard Methods for the Examination of Water and Wastewater, Method 4500-Norg D. (proposed). 19th Ed. 1995. American Public Health Association, Washington, D.C.

Method Descriptor: *An alkaline persulfate digestion simultaneously oxidizes ammonia and organic N to nitrate, and liberates phosphorus compounds as ortho-phosphate. Methods for the determination of NO₃ and PO₄ are then performed.*

Preservation Method: *Digestion best performed with 12 hours of collection, otherwise, samples are preserved by freezing.*

14) Field and Laboratory QAQC programs –

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, 25 replicates, so 20% of samples were collected in replicate for both programs combined. Variability between replicates is analyzed using Relative Percent Difference (RPD) and is summarized in the table below.

		TP	PO4F	TN	NH4F	NO23F	NO2F	CHLA_N	TSS
all sites combined	min	0	0	0	0	0	0	0	0
	max	25	35	9	44	67	22	54	118
	average	6	7	2	9	6	6	11	17
BA	min	0	0	0	0	0	0	0	0
	max	10	8	3	44	2	12	24	29
	average	5	4	1	11	1	7	5	10
BL	min	0	0	0	0	0	0	0	0
	max	10	23	5	5	4	19	54	46
	average	3	8	2	4	2	10	15	11
OL	min	0	0	0	0	0	0	0	0
	max	16	9	9	20	7	22	36	28
	average	5	3	4	8	2	4	7	8
PO	min	0	0	0	0	0	0	0	0
	max	25	35	3	22	67	13	51	118
	average	11	16	2	13	17	3	19	50

ii) **Laboratory variability** – Laboratory replicates are evaluated for CHLA_N, TSS and all dissolved nutrient parameters. In 2022, the LKS NERR laboratory analyzed 17 CHLA-N samples in duplicate (13% of samples) and 23 TSS samples in duplicate (17% of samples). Laboratory variability (RPD) was calculated for each and is one QC parameter that determines whether data is flagged as suspect or rejected. For all dissolved nutrient parameters, the NRRI Central Analytical Laboratory performed at least 4 laboratory replicates per sample batch. SWMP samples are processed alongside other samples in an analytical run so exact calculations of the percent of LKS NERR samples that were run in duplicate cannot be directly assessed.

iii) **Inter-organizational splits** – None were conducted in 2022.

b) **Accuracy**

i) **Sample spikes** – The NRRI, Central Analytical Laboratory reports a quality control standard, up to ten check standard values, and at least three sample spike recoveries per sample run. These are evaluated to assess whether data should be flagged. In 2022, all quality control standards were within 94 -104% recovery. All check standards were with 90 – 116 % recovery. All sample spike recoveries were within 80 – 116 %.

ii) **Standard reference material analysis** – None in 2022

iii) **Cross calibration exercises** - None in 2022

iv) **Blanks** – Each month at least 1 filter blank and matrix blank is assessed for contamination during the filtration or analysis process. Annually, a method blank, which is a sample of pure water treated like a sample through the whole process from collection to analysis is assessed for each parameter. In 2022, no blanks exceeded method detection limits for any parameter analyzed in the LKS NERR laboratory or sent for analysis to the NRRI Central Analytical Laboratory.

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
<i>Wind speed</i>	
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 for 2022: Standard protocol at the LKS NERR is to either refrigerate samples at 4°C and analyze for dissolved nutrients within 24 hours, or freeze and store at ≤-20°C for nutrient analysis within 28 days. NERRS SOP allows dissolved nutrient samples to be held for up to 28 days (CHLA_N for 30) at -20°C, plus allows for up to 5 days for collecting, processing, and shipping samples. TN and TP may be held at any temp for up to 6 months. Samples held beyond that time period are flagged suspect and coded CHB and are marked with an asterisk in the table below.

Sample Descriptor	Date Analyzed							
	TP	TN	PO4F	NH4F	NO2F	NO23F	CHLa_N	TSS
4/25–4/26, all grab and diel samples	5/19	5/19	5/10	5/11	5/25	5/6	5/17	5/17
5/30–6/2, all grab and diel samples	6/10	6/10	6/9	6/14	7/6*	6/9	6/9	6/30

6/27–6/28, all grab and diel samples	9/6	9/6	6/30	7/12	8/30*	7/6	7/1	7/11
7/25–8/2, all grab and diel samples	9/26	9/26	8/23	8/16	8/30*	8/11	8/4	8/3
8/29–8/31, all grab and diel samples	9/26	9/26	9/7 & 9/15	9/12	10/10*	9/16	9/16	9/2
9/27–9/28, all grab and diel samples	10/31	11/1	10/13 & 10/27	11/3*	10/28	10/26	10/14	10/7
10/25–10/26, all grab and diel samples	11/18	11/16	11/15	11/3	10/28	11/14	11/9	10/28

In the case that a value is both below the MDL and beyond sample hold time, it is flagged/coded <-4> [SBL] (CSM).

These samples were not analyzed for all parameters due broken sample containers or technical issues during filtration or analysis:

- lksbanut 9/27/2022 22:00 all parameters

Only samples at Barker's Island were collected during the April 2022 event because ice was still covering most of the estuary and the boat was not yet launched for access to all SWMP sites. There were two events when diel samples were not collected in the same time frame as the grab samples (May and July) because of wind/waves which prevented safe access to sampling sites. There were no rain events or drastic shifts in weather or river flow between samples days in either event.