Lake Superior (lks) **NERR Nutrient Metadata**
February to November, 2015
Latest Update: May 19, 2016

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@belle.baruch.sc.edu) or Reserve with any additional questions.

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons -These are the staff members responsible for the design, implementation and continuation of the 2015 data set.

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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. This includes a meteorological station, and four continuous water quality monitoring stations with monthly nutrient and chlorophyll *a* sampling, and monthly sampling at one site consisting of 12 nutrient and chlorophyll *a* samples collected over a 24-hour period. Lake Superior does not experience tides, therefore diel samples are simply collected with an auto-sampler every two hours, beginning the day before grab samples are taken.

In 2015, four continuous water quality stations were operational, along with a meteorological station. The NERR analytical laboratory was operational (in-house analyses initiated July, 2014). Surface water samples were taken by NERR staff, filtered and analyzed in the NERR laboratory.
3) Research methods – Detail the specifics of sample collection, collection intervals, sample processing, QAQC of the equipment and analyzers.

a) Monthly Grab Sampling Program

Grab samples 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 taken at this time as well, utilizing a YSI EXO datasonde calibrated at the NERR laboratory. Depth profiles were taken, and data recorded on a field data sheet. Analyses of all samples were carried out at the NERR laboratory.

b) Diel Sampling Program

Diel samples were taken from the dock located at our offices with an ISCO autosampler (Barkers Island SWMP station). The sampler was set to sample, with pre-reverse, every two hours. Sample bottles are acid washed one-liter opaque poly bottles. Ice was added to the sample bottle container for the duration of sampling. Analyses of all samples were carried out at the NERR laboratory.

All samples were filtered within a few hours of arrival in the laboratory. Bottles were kept cold and covered to prevent exposure to light. Chlorophyll *a* filters were folded and enclosed in aluminum foil and kept in the freezer until extraction, which was carried out the next day.

4) Site location and character – Description of NERR site in general and the sampling sites associated with each YSI data logger / nutrient collection.

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 and active iron mining in the upper watershed. 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 fresh water estuary. Near the mouth of the river on Lake Superior is the largest working harbor on the Great Lakes. 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 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 of the seiche 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, affected by reservoir regulation) recorded an annual mean discharge of 2363 cfs for the period of record (1908 to 2015). For the 2015 water year the annual mean discharge was 1,407 cfs.

Oliver Bridge site (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 the 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

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

Blatnick 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 therefore 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 7 m, river approximately 360 meters wide

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

g) Site is located within the urban areas 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 seiche flows

Barkers Island site (ba)

a) -92.06352, 46.721772

b) this site is located on the northwest end of Barkers Island, upstream of the Superior entry to the estuary, and 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 2m, approximately 1207m across Superior Bay at this location, navigation channel 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

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 to 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 include large beds of wildrice

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 Blatnick sites, and is affected by Lake seiche.

5) Coded variable definitions – station code names and monitoring program codes:

lksponut = Lake Superior NERR Pokegama River nutrients

monthly grab sample program = 1

diel grab sample program = 2

6) Data collection period – Replicates were collected at each site, with the second sample being collected a few minutes after the first sample. Depth profiles are taken at the same time as sample collection. Diel samples are usually taken between 10AM the day prior to grab sampling and 8AM the day of grab sampling. At LKS NERR, SWMP nutrient sampling began in 2012 with samples taken at ol, ba and bl. For po, nutrient sampling began in the 2013 field season.

SITE	Oliver Bridge grab	Pokegama Bay grab	Blatnick Bridge grab	Barkers Island grab	Barkers Island diel
February	2/3/2015 12:30	2/3/2015 11:50	2/3/2015 13:15	2/3/2015 13:59	not taken - ice
April	4/28/2015 10:44	4/28/2015 11:00	4/28/2015 12:26	4/28/2015 13:01	04/27 10:00 to 04/28 10:00
May	5/26/2015 10:16	5/26/2015 11:08	5/26/2015 11:52	5/26/2015 12:32	05/25 10:00 to 05/26 08:00
June	6/23/2015 9:03	6/23/2015 9:43	6/23/2015 10:46	6/23/2015 11:20	06/22 10:00 to 06/23 08:00
July	7/21/15 9:19	7/21/15 10:26	7/21/15 11:09	7/21/15 11:37	07/20 10:00 to 07/21 08:00
August	8/26/2015 8:53	8/26/2015 9:41	8/26/2015 10:20	8/26/2015 23:03	08/25 10:00 to 08/26 08:00
September	9/24/2015 10:08	9/24/2015 9:14	9/24/2015 11:30	9/24/2015 12:11	09/23 10:00 to 09/24 08:00
October	10/20/2015 8:55	10/20/2015 9:37	10/20/2015 10:56	10/20/2015 12:06	10/19 10:00 to 10/20 08:00
November	11/17/2015 8:56	11/17/2015 9:47	11/17/2015 10:32	11/17/15 10:58	11/16 10:00 to 11/17 08:00

7) Associated researchers and projects –

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, pH, turbidity, and chlorophyll. Research projects were carried out by students this field season for comparison of water quality sensor readings and laboratory methods for chlorophyll/chlorophyll *a* and turbidity/solids. It was found that though the data from the sensor was comparable to that of the laboratory in each case, the correlation was weak, making it difficult to infer concentrations of chlorophyll *a* or suspended solids from sonde data.

The SWMP weather station and data sonde 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, 2015. 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 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.

The Lake Superior NERR Science and Interpretive Center was opened on a part-time basis in the summer of 2014. A Great Lakes educational display was borrowed from GLERL, Ann Arbor, Michigan. The NERR received a PAC grant in 2015 to proceed with updates to the building, and design and construction of a Lake Superior/St. Louis River informational display. The project should be complete by 2017.

8) Distribution – This section addresses data ownership and data liability by including the following excerpt from the Ocean and Coastal Resource Management Data Dissemination Policy for the NERRS System-wide Monitoring Program in the metadata.

> 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 2012.
>
> 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 – This section explains how data acquisition, data entry, and data verification (QAQC) were performed before data were sent to the CDMO to be archived into the permanent database.

Laboratory analyses are run in the LKS NERR, primarily by the Monitoring Coordinator, Tracey Ledder, with assistance from the water quality technician, Joe Ripley. Raw results for nutrient analyses are managed by the Automated Analyzer Control and Evaluation Software (AACE), version 6.10, which operates the SEAL AA3. Data reports are exported through .slk files and Adobe Acrobat in mg/L. Raw results for chlorophyll a (ug/L) and suspended solids (mg/L) are recorded in the corresponding laboratory notebook as the samples are read.

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 – Only list those parameters that are reported in the data. See Table 2 in the "Nutrient and Chlorophyll Monitoring Program and Database Design" SOP version 1.6 (January 2012) for a full list of available parameters.

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
	Total Nitrogen	TN	mg/L as N
	Total Phosphorus	TP	mg/L as P
	Total Suspended Solids	TSS	mg/L
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
Field Parameters:			
	Water Temperature	WTEM_N	ºC

Notes:

1. Time is coded based on a 2400 clock and is referenced to Standard Time.
2. Reserves have the option of measuring 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 – This section lists all measured and calculated variables (field parameters not listed). See Table 2 in the "Nutrient and Chlorophyll Monitoring Program and Database Design" SOP version 1.7 (March 2016) document for a full list of directly measured and computed variables.

a) **Parameters measured directly**

Nitrogen species:	NH4, NO2, NO23, TN
Phosphorus species:	PO4F, TP
Other:	CHLA, TSS, WTEM

b) **Calculated parameters**

NO3	NO23-NO2

12) Limits of detection – This section explains how the laboratory determines the minimum detection limit (MDL).

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the Lake Superior NERR Laboratory. The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. These values are reviewed and revised periodically.

Parameter	Start Date	End Date	MDL mg/L
PO4F	1/1/15	12/31/15	0.00065
TP	1/1/15	12/31/15	0.092
NH4F	1/1/15	12/31/15	0.0087
NO2F	1/1/15	12/31/15	0.0083
NO23F	1/1/15	12/31/15	0.0056
TN	1/1/15	12/31/15	0.107
TSS	1/1/15	12/31/15	1.0
CHLA_N	1/1/15	12/31/15	0.1

13) Laboratory methods – This section lists the laboratory and reference method, the method reference, a brief description of method and a brief description of the sample preservation method used ***for each parameter that is directly determined.*** Samples are filtered as soon as they are brought in from the field. Nutrient samples are usually analyzed that same day.

a) **Parameter: NH4F**

LKS NERR Laboratory Method: *Ammonia by AA3*

EPA or other Reference Method: *Standard Methods* 4500-NH_3

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: *The filtered sample (0.45 um membrane filter) is reacted with salicylate and dichloro-isocyanuric acid to produce a blue compound measured at 660 nm. Nitroprusside is used as a catalyst.*

Preservation Method: *Samples filtered and stored at 4 °C up to 24 hours.*

b) **Parameter: NO2F**

LKS NERR Laboratory Method: *Nitrate and Nitrite by AA3*

EPA or other Reference Method: *Standard Method 4500-NO_3^- 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 (0.45 um membrane filter) 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 can be determined by eliminating or by-passing the reductor column and standardizing with an appropriate nitrite standard.*

Preservation Method: *Samples filtered and stored frozen at –20 °C up to 14 days.*

c) **Parameter: NO23F**

LKS NERR Laboratory Method: *Nitrate and Nitrite by AA3*

EPA or other Reference Method: *Standard Method 4500-NO_3^- 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 (0.45 um membrane filter) 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.*

Preservation Method: *Samples filtered and stored frozen at –20 °C up to 14 days.*

d) **Parameter: PO4F**

LKS NERR Laboratory Method: *Phosphate by AA3*

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

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).*

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 followed by a reduction with ascorbic acid at a pH <1. The reduced blue phosphor-molybdenum complex is colorimetrically read at 880 nm.*

Preservation Method: *Samples filtered (0.45 um membrane filter) and stored frozen at –20 °C up to 14 days.*

e) **Parameter: UncCHLa**

LKS NERR Laboratory Method: *Chlorophyll a*

EPA or other Reference 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-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 with the aid of mechanical grinding. The filter slurry is centrifuged for clarification and fluorescence is measured. The Turner Design Trilogy provides a set of very narrow bandpass excitation and emission filters that nearly eliminate the spectral interference caused by the presence of pheophytin a and chlorophyll b.*

Preservation Method: *Samples filtered and stored frozen at –20 °C up to 14 days.*

f) **Parameter: TSS**

LKS NERR Method: *Solids*

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. Preferably analyze as soon as possible due to the impracticality of preservation.*

14) Field and Laboratory QAQC programs – This section describes field variability, laboratory variability, the use of inter-organizational splits, sample spikes, standards, and cross calibration exercises.

a) **Precision**

i) **Field variability** –Grab samples were taken in duplicate as successive grabs at each SWMP site. Field variability is expected to be higher than "normal" as these sites experience flow reversal due to seiche on a regular basis.

1) Ammonium – RPD in field duplicates ranged from 0.3 to 200%, with a mean of 20.8. Largest variability was at BA in August (200) and OL in July (110.4).

2) Nitrate/Nitrite – RPD in field duplicates ranged from 0 to 49.4%, with a mean of 4.6. Largest variability was at OL in July (49.4).

3) Nitrite – RPD in field duplicates ranged from 0.0 to 40.0%, with a mean of 6.9. Largest variability was at BL in April (40.0)

4) Phosphate – RPD in field duplicates ranged from 0.0 to 163.2%, with a mean of 17.6. Largest variability was at BL in October (163.2) and BA in May (128.1).

5) Chlorophyll *a* – RPD in field duplicates ranged from 0.4 to 54%, with a mean of 10.8. Largest variability was at PO in August (54), and BA in May (28.9).

6) Total Phosphorus –RPD in field duplicates ranged from 0.0 to 200%, with a mean of 58.8. Largest variability was at OL in July (200), and BA and OL in August (200). Almost half of the duplicate sets had one or both values at or below the MDL and could not be calculated.

7) Total Nitrogen – RPD in field duplicates ranged from 0.2 to 139.1%, with a mean of 26.8. Largest variability was at BA (139.1) and BL (132.4) in August.

6) Suspended Solids – RPD in field duplicates ranged from 0.0 to 90.0, with a mean of 26.4. Largest variability was at BL (90), PO (50) and BA (40) in July.

ii) **Laboratory variability** – Laboratory duplicates were prepared and analyzed, once for each batch of samples.

1) Ammonium – Eight laboratory duplicates were analyzed, results ranged from 0.0 to 155.6 RPD, with a mean RPD of 26.0.

2) Nitrate/Nitrite – Eight laboratory duplicates were analyzed, results ranged from 0.2 to 14.3 RPD, with a mean of 3.5 RPD.

3) Nitrite – Eight laboratory duplicates were analyzed, results ranged from 0.0 to 1409 RPD, with a mean RPD of 4.7.

4) Phosphate – Eight laboratory duplicates were analyzed, results ranged from 0.0 to 55.3.6 RPD, with a mean RPD of 10.8.

5) Chlorophyll – Eight laboratory duplicates were analyzed, results ranged from 1.8 to 12.7 RPD, with a mean RPD of 4.6.

6) Total Phosphorus – Six laboratory duplicates were analyzed, results ranged from 5.7 to 40.0 RPD, with a mean RPD of 16.3. Several duplicates had one or both results below the MDL.

7) Total Nitrogen – Six laboratory duplicates were analyzed, results ranged from 1.2 to 98.2 RPD, with a mean RPD of 50.3.

8) Total Suspended Solids – Eight laboratory duplicates were analyzed, results ranged from 7.4 to 35.3 RPD, with a mean RPD of 17.5.

iii) **Inter-organizational splits** – None in 2015.

b) **Accuracy**

i) **Sample spikes** – Laboratory Control Samples (LCS), made from a purchased standard solution independent of the calibration curve, were analyzed at a rate of 10% of samples. The difference between the expected and observed concentrations were calculated as RPD.

1) Ammonia – Twenty-one LCS were analyzed; RPD ranged from -8 to -29, with an overall mean of -11.4%. All LCS results were lower than the expected.

2) Nitrate/Nitrite – Twenty-six LCS were analyzed; RPD ranged from 0.7 to 22%, with an overall mean of 6.6%. Most of the LCS results were higher than the expected.

3)Nitrite – Twenty-five LCS were analyzed; RPD ranged from 0 to 12.7, with an overall mean of 2.7%.

4) Phosphate – Twenty-five LCS were analyzed; RPD ranged from 0 to 17.4, with an overall mean of 2.0%. Most of the LCS results were lower than the expected.

5) Total Phosphorus – Seventeen LCS were analyzed; RPD ranged from 5.3 to >100, with an overall mean of 13.7. Most of the LCS results were higher than the expected.

ii) **Standard reference material analysis –** This will result from samples sent out from EPA to each lab. None in 2015.

iii) **Cross calibration exercises** – LKS NERR did not participate in cross calibration exercises in 2015.

15) QAQC flag definitions – This section details the primary and secondary 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 – This section details the secondary QAQC Code definitions used in combination with the flags above. 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 – Additional notes regarding the data set in general, circumstances not covered by the flags and comment codes, or specific data that were coded with the CSM "See Metadata" comment code.

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.

The 2015 sampling was the first full season the Lake Superior NERR analytical laboratory was operational (April through November, with one Under Ice sampling). This was a fairly high water year. Most of the data problems are related to learning the equipment (the SEAL AA3 was installed June 2014) and maintenance required. For example, making and use of cadmium columns, and maintaining even flow to the waste container from the flow cell of the nutrient autoanalyzer.

There were particular problems with the ammonia analyses and many samples have been flagged as <1> suspect due to low RPDs for laboratory control samples and baseline drift. The baseline issues appear to have been related to the flow of sample through the detector to waste. The sample batches affected include the July 22-23 batch, the August 25-26 batch, and the November 12-13 batch. Unstable baselines can result in the software not detecting the primer, and, therefore, not recognizing peaks for that run. When this occurred, the peak heights were manually measured and Excel was used to create a calibration curve and peak concentrations for these runs.

The nitrite analyses in May, July, August, September, October and November showed filter blanks slightly higher than to double the laboratory reagent water blank. The analytical results for nitrite are typically low. Therefore, for those samples which the filter blank was greater than the MDL and greater than 10% of the analytical result, the result was flagged <1> suspect.

The nitrate/nitrite analyses in May, July, September, October and November showed filter blanks slightly higher than to three times the machine response for laboratory reagent water. Therefore, for those samples for which the filter blank was greater than the MDL and greater than 10% of the analytical result, the result was flagged <1> suspect.

The phosphate analysis in the Under Ice sampling showed low recovery for Laboratory Control Samples (-17%). The samples for this batch were flagged <1> suspect due to poor quality control results.

The chlorophyll *a* analytical results from the Under Ice sampling in February were often much higher than the standard curve, and much higher than results we had acquired in other Under Ice samplings. These samples were flagged <1> suspect as they were out of range of the standard curve.

The optional parameters Total Phosphorus (Filtered) and Total Nitrogen (Filtered) are parameters of interest to State partners in this estuary. Both Wisconsin and Minnesota have Water Quality Standards for TP. The Lake Superior NERR laboratory, therefore, began to digest filtered samples and analyze them for TP and TN in 2015. Many of these samples are flagged <1> suspect due to high filter blanks for TN which was determined to be partly caused by the membrane filters we were using (nitrocellulose) and membrane filters were

changed after 2015. Cadmium column problems also affected TN analyses. Analytical issues in TP analyses occurred with precipitate clogging tubing and blowing joints due to reaction with surfactant and potassium persulfate used in the digestion. Even if tubing joints did not blow, the precipitation resulted in higher backgrounds for digested samples (cloudiness), for these runs the results are therefore flagged <1> suspect. MDLs were also higher than they should be due to the elevated background. Surfactant concentrations in reagents and wash water were too high and will be lowered in 2016 for TP and TN analyses.

Total Dissolved Solids (analyzed but not reported to CDMO) are of interest in this estuary as the tributaries run through the Old Lake Superior red clay plain and therefore streams carry silt and clays that pass through the TSS filter. Total Dissolved Solids were initially analyzed using aluminum weighing dishes (Under Ice to May). Filter blanks and laboratory reagent water blanks were high, with a visible residue on the dishes apparently from a reaction with the aluminum itself. The NERR lab switched (June) to borrowed glass dishes which did not show a residue for blanks but which were too large for our analytical balance, and often resulted in unreliable weights. In July through November, we switched to smaller glass dishes that show little blank residue and fit the balance.