Lake Superior NERR (lks)Nutrient Metadata
May through November, 2013
Latest Update: May 14, 2014

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 2013 data set.

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Laboratory Analyses by the EPA Mid-Continent Ecology Lab, Duluth, MN
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2) Research objectives – A brief description of the nature of the monitoring program resulting in this data set (monitoring along land use, vertical, salinity or habitat gradients).

a) Monthly Grab Sampling Program
b) Diel Sampling Program

The LSNERR is situated on the freshwater estuary at the confluence of the S. 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 will provide 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 Freshwater Estuary and Lake Superior coastal habitats.

The Lake Superior NERR will implement the NERR System-Wide Monitoring Program (SWMP) along a river-to-Lake gradient. This will include four continuous water quality monitoring stations with monthly nutrient and chloropyll sampling, a meterological station, and monthly sampling at one site consisting of 12 nutrient and chlorophyll samples collected over a 24-hour period. Data will be archived at the Centralized Data Management Office (CDMO) as per established protocols.

In 2013, four continuous water quality stations were made operational, as was the meteorological station. The LSNERR offices and lab space were under construction beginning in August. Nutrient and chlorophyll *a* sampling was carried out under a GLRI-funded study investigating nutrient, chlorophyll and suspended solids levels in the St. Louis River Area of Concern. Samples were taken from approximately 50 sites around the

estuary and nearshore Lake Superior, once a month, over the ice free season. This study included the LSNERR SWMP sites at no charge to the LSNERR. Samples were filtered (or not, as required by each analytical method) and analyzed by the US Environmental Protection Agency, National Health and Environmental Health Effects Research Laboratory, Mid-Continent Ecology Division (EPA MED-lab), Duluth, MN.

3) Research methods – Information on sample collection, collection intervals, sample processing, QAQC of the equipment and analyzers.

a) Monthly Grab Sampling Program
Grab samples were collected once a month from a boat at the depth of sonde deployment (1.5 meters beneath the surface) using a horizontal sampler. Ambient water quality data was taken at this location as well, utilizing a datasonde calibrated at the EPA MED-lab and recording data on a data sheet. Secchi depth was also recorded. Depth profiles taken the previous year indicated that the St. Louis River does not stratify during ice free months. Analyses of all samples were carried out at the EPA MED-lab according to that lab's standard operating procedures.

b) Diel Sampling Program
Not implemented yet in 2013

4) Site location and character – Description of the LS 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. In the upper watershed the river flows through lake clays and glacial deposits for approximately 100 miles. Near the city of Thomson the 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 lowest of several dams. Below the gorge and dams the river begins to take on the characteristics of a fresh water estuary. The Lower St. Louis River estuary, at the mouth of the river on Lake Superior, is the largest working harbor on the Great Lakes.

Lake Superior does not produce a "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 has measured streamflow 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 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. The USGS stream gage on the St. Louis River at Scanlon (upstream of the Fond du Lac dam) recorded a yearly median discharge of 2278 cfs for the period of record (1909 to 2012).

Oliver Bridge site (ol)

a) -92.20166, 46.65685

b) This site is located on the downstream side of a bridge piling at Oliver, Wisconsin. 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 may be 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 area)

e) water depth approximately 8m, 126 meters across

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

g) approximately 12 miles downstream of the Fond du Lac dam

h) This site is the farthest upstream site monitored in the St. Louis River Estuary, approximately 11 miles from the mouth at Lake Superior. This site may experience some influence due to seiche.

Pokegama River site (po)

a) -92.135614, 46.672360
b) This site is located near the Pokegama River boat landing in the Superior Municipal Forest, at the MET station. The Pokegama River is tributary to the St. Louis River estuary and therefore is influenced to some extent by Lake seiche
c) Salinity range thought to be similar, 0.1 to 0.2 PPT
d) Freshwater estuary site, the Pokegama River watershed is approximately 20,144 acres and largely forested. Wild rice was abundant in the bay and along the river channel in 2013.
e) Water approximately 2 m depth at mid-river, 5 meters across
f) Bottom habitat or type undocumented, much red clay
g) Site is located upstream of the urban area of Superior, WI/ Duluth, MN, and is mostly forested.
h) This site is within the St. Louis River estuary.

Blatnick Bridge site (bl)

a) -92.10027, 46.748649
b) This site is located on the downstream side of a middle river piling off of Rice's Point, and therefore is influenced by Lake seiche
c) salinity range 0.1 to 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, approximately 360 meters wide
f) bottom habitat or type currently undocumented (suspected sand)
g) Site is located within the urban area of Superior, WI/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 activity.

Barkers Island site (ba, formerly ls)

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 therefore 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 1207 meters across Superior Bay at this point
f) bottom habitat or type undocumented (suspect sand or soft sediment)
g) Site is downstream of the Superior WWTP and the WLSSD WWTP
h) This site is the furthest downstream site monitored in the St. Louis River Estuary, also within the lower industrial harbor. The Nemadji River (433 square mile watershed) also enters the St. Louis River estuary near the Superior Entry.

5) Coded variable definitions – Explain the station code names and monitoring program codes.

Lksbanut = Lake Superior NERR Barkers Island nutrients
monthly grab sample program = 1
diel grab sample program = 2

6) Data collection period – The date and time each sample was collected. Field duplicates were taken one after the other while at that site. At LSNERR, SWMP nutrient monitoring first began for ol, ba, and bl in 2012. For po, 2013 is the first year of nutrient sampling.

SITE	May	June	July	August	Sept	Oct	Nov
Oliver Bridge	5/28/13	6/17/13	7/23/13	8/19/13	9/17/13		11/4/13
Pokegama Bay	5/28/13	6/17/13	7/23/13	8/19/13	9/17/13	10/31/13	
Blatnick Bridge	5/29/13	6/18/13	7/22/13	8/20/13	9/16/13	10/30/13	
Barkers Island	5/29/13	6/18/13	7/22/13	8/20/13	9/16/13	10/30/13	

7) Associated researchers and projects (link to other products or programs) **–** Brief description of other research (data collection) that correlates or enhances the nutrient data.

Samples were taken monthly at these four sites (ol, po, bl, ba) for nutrient and chlorophyll *a* analyses from May through November, 2013, by staff of the EPA MED-lab under cooperative effort by partners in the St. Louis River Area Of Concern. One of the beneficial use impairments for which the estuary was listed as an AOC is excessive sediment and nutrients. Therefore, many partners in the estuary are working on establishing historic conditions and current conditions in regards to sedimentation and erosion as well as nutrient loads. Other on-going activities in the AOC include contaminated site remediation, habitat restoration fish, wildlife and benthic community studies.

The System-wide Monitoring Program datasonde deployments occurred at all four of these sites by September. Chlorophyll *a* laboratory analyses results will be compared to sonde readings at the same site and time in order to better understand the limitations and use of the sonde Chlorophyll *a* fluorescence data.

The LSNERR 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.

Other research in which LSNERR participated in 2013 included the biological control of purple loosestrife, a study of the microbial communities related to mercury methylation in sediment, a geospatial analyses of stressor gradients and stakeholder participation patterns in the estuary, an erosion study by UW-Superior, and exploratory use of periphytometers with the USGS to explore nutrient limitations.

Other agencies working in the St. Louis River estuary include the Wisconsin and Minnesota Departments of Natural Resources, the United States Environmental Protection Agency Mid-Continent Ecological Lab, United Stated Fish and Wildlife Service and the United States Geological Survey. The LSNERR 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 – This section will address data ownership and data liability by <u>including the following excerpt</u> from the Ocean and Coastal Resource Management Data Dissemination Policy for the NERRS System-wide Monitoring Program in the metadata.

> NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature, including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal

Resource Management, National Ocean Service, National Oceanic and Atmospheric Administration. 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.

Also include the following excerpt in the metadata which will address how and where the data can be obtained.

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 http://cdmo.baruch.sc.edu/. Data are available in text tab-delimited 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.

The results of the nutrient sample analyses were received from the EPA MED-lab in Microsoft Excel worksheets. 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.

The EPA MED Laboratory calculates and reports results in μg/L. For purposes of consistency in the NERR System, Lake Superior NERR entered the concentrations as mg/l for nitrate, phosphate and ammonium by dividing the reported value by 1000.

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 The EPA MED-lab had intended to analyze for Total Phophorus and Total Nitrogen under this study but ultimately had difficulty with the analytical instrumentation and these parameters were not reported in the overall study.

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 + Nitrate, Filtered	NO23F	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/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 – This section lists all measured and calculated variables. Only list those parameters that are collected and reported, do not list field parameters. See Table 2 in the "Nutrient and Chlorophyll Monitoring Program and Database Design" SOP version 1.6 (January 2012) document for a full list of directly measured and computed variables.

a) **Parameters measured directly**

Nitrogen species:	NH4, NO23
Phosphorus species:	PO4F
Other:	CHLA,

b) **Calculated parameters**

None

12) Limits of detection – This section explains how the laboratory determines the minimum detection limit (MDL), lists the method detection limits used and dates they were in use.

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, were established by the EPA MED 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
PO4F	5/1/13	12/31/13	0.0025 mg/L
NH4F	5/1/13	12/31/13	0.0040 mg/L
NO23F	5/1/13	12/31/13	0.0013 mg/L
CHLA_N	5/1/13	12/31/13	1.2 ug/L

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.***

a) **Parameter: NH4F**

EPA MED- Laboratory Method: *MED-D-SOP-NH4 Salicylate*
EPA or other Reference Method: *LACHAT Quick Chem 10-107-06-2-C*
Method Reference: *Lachat Instruments, 1992. Quick Chem Method No. 10-107-06-2-6, "Ammonia in surface water, wastewater". Manual for the QuickChem Automated Ion Analyzer. Milwaukee, WI.*
Method Descriptor: *Ammonium in a filtered sample, when heated with salicylate and hypochlorite in an alkaline phosphate buffer, produces an emerald green color which is proportional to the ammonium concentration. Ammonium concentration is detected using a 660nm filter.*
Preservation Method: *Samples filtered through a 0.45 um membrane filter and stored frozen for analyses within 28 days of collection.*
Quality Control: *Laboratory replicates and spiked samples should be prepared for at least 5% of samples analyzed. Duplicate field samples and blanks should be collected for at least 5% of the total number collected. Check standards and QA samples should be analyzed at least 5% of the total number of samples analyzed.*

b) **Parameter: NO23F**

Laboratory Method: *Phosphate and Nitrate using Lachat Flow Injection System*
EPA or other Reference Method: *(QuikChem Method 10-107-04-1-C, 1992) Nitrate+Nitrite in waters*
Method Reference: *APHA. 1995. Standard Methods for the examination of water and wastewater. Method 4500-NO_3^- E.*
Method Descriptor: *Nitrate is reduced to nitrite by a copper-cadmium reductor column at a pH of 8.0. The nitrate then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye, the absorbance of which is proportional to the concentration.*
Preservation Method: *Dissolved nutrient water samples are prepared by filtering collected water through a 0.45um membrane filter and store frozen until analysis within 180 days of collection.*
Quality Control: *Laboratory replicates and spike samples should be prepared for at least 5% of the number of samples to be analyzed. Duplicate field samples and blanks should be collected for at least 5% of the samples collected. Standard checks and QA samples should be analyzed for at least 5% of the number of samples analyzed.*

c) Parameter: PO4F

Laboratory Method: *Phosphate and Nitrate using Lachat Flow Injection System*
EPA or other Reference Method: *(QuikChem Method 10-115-01-1-B, 1992) Orthophosphate in waters*
Method Reference: *APHA. 1995. Standard Methods for the examination of water and wastewater. Method 4500-P E.*
Method Descriptor: *The orthophosphate ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions. The complex formed is reduced with ascorbic acid to form blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.*
Preservation Method: *Dissolved nutrient water samples are prepared by filtering collected water through a 0.45um membrane filter and store frozen until analysis within 180 days of collection.*
Quality Control: *Laboratory replicates and spike samples should be prepared for at least 5% of the number of samples to be analyzed. Duplicate field samples and blanks should be collected for at least 5% of the samples collected. Standard checks and QA samples should be analyzed for at least 5% of the number of samples analyzed.*

d) Parameter: TN and TP (no complete analyses results)

Laboratory Method: *Persulfate Digestion for Total Phosphorus and Total Nitrogen Analyses using Lachat Flow Injection System*
EPA or other Reference Method: *(QuikChem Method 10-107-04-1-C) Nitrate+Nitrite in Waters and (QuikChem Method 10-115-01-1-F) Total Phosphorus by persulfate digestion*

Method Reference: *Standard Methods 4500-N org/ 4500-P section 5 APHA 1995.*
Method Descriptor: *Persulfate digestion oxidizes all nitrogen compounds to nitrate and all phosphorus compounds to orthophosphate. Nitrogen oxidation occurs under alkaline conditions at 100-110°C, while phosphorus oxidizes under acidic conditions at 14-17psi. Both analytes are determined colorimetrically using the respective Lachat QuikChem Methods.*
Preservation Method: *Samples stored frozen until analysis within 180 days of collection??.*
Quality Control: *Laboratory replicates and spike samples should be prepared for at least 5% of the number of samples to be analyzed. Duplicate field samples and blanks should be collected for at least 5% of the samples collected. Standard checks and QA samples should be analyzed for at least 5% of the number of samples analyzed.*

e) Parameter: CHLA_N

EPA MED-Laboratory Method: *Fluorometric Chlorophyll a Analysis, Reference CHG-034*
EPA or other Reference Method: *EPA Method 445.0, Welschmeyer (1994)*
Method Reference: *In Vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence (Revision 1.2) 1997.*
Method Descriptor: *Phytoplankton contained in a measured volume of sample water are concentrated onto a glass fiber filter by filtration at low vacuum. Pigments contained in the phytoplankton are extracted in 90% buffered acetone for 16 to 24 hours at -10oC following sonication of the filter. Extracts are clarified by filtration and the fluorescence is read and used to calculate chlorophyll a in the original water sample. Concentrations of chlorophyll a are reported in ug/L.*
Preservation Method: *Samples are processed as soon after collection as possible and are stored in foil-covered scintillation vials at -10oC or lower until analysis. Filters may be stored for as long as 3 ½ weeks without significant loss of chlorophyll a.*
Quality Control: *Calibration checks are run daily. Field duplicates and field blanks are run once per batch.*

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** – All samples were collected in replicate (successive grab samples). Results show field variability, as calculated by Relative Percent Difference (RPD), to differ by parameter.
  - (1) Ammonium – RPD in field replicates ranged from 1% to 151%, with an average of 28%. Two samples from OL and one from BA exceeded 60% RPD.
  - (2) Nitrite/nitrate – RPD in field replicates ranged from 0% to 136%, with an average of 12%. Two samples from PO exceeded 35% RPD.
  - (3) Phosphate – RPD in field replicates ranged from 4% to 200%, with an average of 81%. Eight samples from among all of the sites exceeded 70%, due to results at or below the MDL.
  - (4) Chlorophyll *a* – RPD in field replicates ranged from 0% to 75%, with an average of 14% RPD. One sample from PO and one from BBA exceeded 30% RPD.
- ii) **Laboratory variability** – The EPA MED-lab ran analyses of laboratory duplicates at a rate of 8% across the entire study, which consisted of 283 samples. There were 48 SWMP samples taken within this larger study.
  - (1) Ammonium – The majority of laboratory duplicates were less than 10% RPD. There were 2 sets of duplicates in which concentrations were near the MDL and the RPDs exceeded 30%.
  - (2) Nitrite/Nitrate – The average laboratory duplicate RPD was 2.2%. One set, in which the concentration was at the MDL, gave an RPD of 23.5%.
  - (3) Phosphate – Most laboratory duplicates were less than 10% RPD, however 5 sets greatly exceeded 10% RPD while being at the MDL.
  - (4) Chlorophyll *a* – only two laboratory duplicates were run with 2.5% and 15.8% RPD.
- iii) **Inter-organizational splits** – None in 2013.

b) **Accuracy**

i) **Sample spikes** – Sample spikes were analyzed during ammonium, nitrite/nitrate and phosphate analyses for the overall study of which the SWMP sites were a part. The EPA MED-lab acceptance criterion is 90-110% recovery.

(1) Ammonium – Ammonium sample spikes averaged 105% recovery, with a range of 97.6% to 113.4%.

(2) Nitrite/nitrate – Nitrite/nitrate sample spikes averaged 101.7% recovery, with a range of 91.2% to 109.2%.

(3) Phosphate – Phosphate sample spikes results ranged from 64% to 124% recovery, with eight spikes failing to meet the criterion. Seven of the eight failed spikes were analyzed in the second laboratory batch of overall study samples. Those SWMP samples corresponding to this batch were flagged as "Suspect".

ii) **Standard reference material analysis –** The EPA MED-lab analyzed laboratory control standards for each analysis. The acceptance criterion was 90-110% recovery.

(1) Ammonium – The LCS was a solution of 0.0925 mg/L. Recoveries ranged from 90.6% to 106.2%, with an average of 96.9%.

(2) Nitrite/nitrate – The LCS was a solution of 0.250 mg/L. Recoveries ranged from 105.4% to 109.2%, with an average of 108.8%.

(3) Phosphate – The LCS was a solution of 0.0195 mg/L. Recoveries ranged from 91.4% to 109.0%, with an average of 100% recovery.

(4) Chlorophyll *a* – A low (8.0 ug/L) and a high (75 ug/L) concentration check standard was run every day of analyses, both before and after the analytical run. The check standards all passed.

iii) **Cross calibration exercises** – *None in 2013.*

15) QAQC flag definitions – This section details the primary and secondary QAQC flag definitions. 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 – 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

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 – Use this section for further documentation of the research data set. Include any 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. You may include the metadata worksheets here if so desired. You may also include information on major storms or precipitation events that could have affected the data recorded at the sample sites.

Include the following excerpt:

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.

The region experienced severe floods in June, 2013, about one year to the day of the extreme flood of 2012. Discharge data for the USGS gauge on the St. Louis River at Scanlon (upstream of the estuary) shows that discharge increased from about 2000 cfs to 9,220 cfs by June 25th and slowly descended again by about July 7th. Precipitation data from the USGS gauge at Nemadji River showed approximately 2 inches of rain June 20th, with almost another inch through June 29th.

Early ice and foggy weather in late October made access to sites particularly difficult and small boats were pulled from the water in early November.

Samples were flagged "Suspect <1>" for the following reasons relating to quality control results reported by the EPA MED-lab;
- Ammonia samples below 0.016 mg/L were flagged <1> as filter blanks were detected ammonia up to 0.0152 mg/L.
- Nitrite/nitrate samples below 0.005 mg/L were flagged <1> for filter blanks in which the analyte was detected up to 0.0048 mg/L, though laboratory water blanks were non-detect.
- Phosphate samples below 0.026 mg/L were flagged <1> due to filter blanks detecting the analyte up to 0.0256 mg/L, additionally only two filter blanks were analyzed for the study of 283 samples. Phosphate samples within the larger study batch SLR153 to SLR283 were flagged <1> as seven spike samples failed the laboratory criterion, though LCS were within criteria.
- Chlorophyll *a* pre- and post-check samples were within criteria as were laboratory duplicates, however, only two laboratory duplicates were analyzed within the overall study that included SWMP sites, and filter blanks were only run for the first two months of grab samples from all sites. The only chlorophyll *a* samples flagged were those below MDLs.