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

**May through December 2012**

**Latest Update:** June 10, 2021

**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 2012 data set.

**Shon Schooler, Research Coordinator**

**14 Marina Drive, Superior, WI 54880**

**715-392-3141**

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

**Kim Duernberger, 2012 Interim Monitoring Coordinator**

**Tracey Ledder, Monitoring Coordinator (SWMP)**

**14 Marina Drive, Superior, WI 54880**

**715-392-3141**[**tracey.ledder@ces.uwex.edu**](mailto:tracey.ledder@ces.uwex.edu)

**SWMP Technicians – Joseph Ripley, Seth Bliss, Jesse Carlson**

**Analytical Lab – Thomas Pevan, Masters student in Water Resources Science, University of Minnesota at Duluth, Large Lakes Observatory, Duluth, MN 55812**

**2) Research objectives** –

The Lake Superior NERR 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 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 Freshwater Estuary and Lake Superior coastal habitats.

Implementation of the NERR System-Wide Monitoring Program (SWMP) began in 2012. Three continuous water quality monitoring stations with monthly nutrient and chlorophyll *a* grab sampling were operational, with one additional nutrient site that did not have continuous water quality monitoring. Ultimately the fourth continuous water quality monitoring station will be brought online, diel sampling will also occur at one of these four primary SWMP stations, and a meteorological station will be added.

* 1. Monthly grab sampling program – The principal objective of the monthly grab sampling is to collect data relevant to the understanding of the ecological functioning of the St. Loius River Estuary, on a river-to-lake gradient. The system is complex, with many smaller tributaries on the red clay plain, as well as large influences of Lake seiche.
  2. Diel sampling program – (Not implemented in 2012) Diel sampling (autosampler taking samples every two hours) will be important to the overall monthly grab sampling program as it will be informative in the understanding of the aquatic system and seiche influences. Seiche is related to barometric pressure changes and winds across Lake Superior, which can push Lake water up river as far as the dam 23 miles upstream.

**3) Research methods** – This section includes information on the collection and handling of samples to be sent for nutrient and chlorophyll *a* analyses. All sample bottles were acid washed at the Large Lakes Observatory, and subsequently rinsed with sample water prior to sample collection. The one-liter samples were filtered through a 0.45 micron disposafilter for nutrients and GF/F filter for chlorophyll (as required by each analytical method) and the unfiltered portion was frozen. All samples were driven to the Large Lakes Observatory (University of Minnesota - Duluth) for analyses. Samples were collected in replicate in the field. Each sample was split in the lab and analyzed in duplicate, the average value of the lab duplicate was reported.

1. Monthly Grab Sampling Program – Subsequent (replicate) grab samples were collected from a boat at the depth of sonde deployment (1.5 meters beneath the surface) using a horizontal sampler. A depth profile was taken each time at this location as well, utilizing a datasonde prior to its deployment and recording data on a data sheet. Secchi depth was also recorded and is available by request from the Reserve. Depth profiles indicate that the St. Louis River was not stratified at the time of sampling. Depth profile data is available from the Reserve by request. Analyses of all samples were done in duplicate in the LLO Aquatic Ecology Lab.
2. Diel Sampling Program – not implemented in 2012.

**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. 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) 46.65685, -92.20166

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) pollutants: approximately 12 miles downstream of the Fond du Lac dam

h) fhis 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.

*Blatnick Bridge site* (BL)

a) 46.748649, -92.10027

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) pollutants: site is located within the urban area of Superior, WI/Duluth, MN. Site is immediately downstream of the Western Lake Superior Sanitary District wastewater treatment plant (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)

a) 46.721772, -92.06352

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) pollutants: 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.

*Bong Bridge site* (BO) – *nutrient grab samples were collected at this site in 2012, but it was since discontinued and was never associated with a water quality data sonde or designated as a SWMP station. These limited data points are available by contacting the Reserve directly*

1. -92.14257, 46.73169
2. this site is located at the Bong Bridge in the lower estuary and therefore is influenced to some extent by Lake seiche
3. salinity range thought to be similar, 0.08 – 0.2 ppt
4. freshwater estuary site, receives flow of the St. Louis River and tributaries to the estuary (urban)
5. water approximately 7 m depth, 1286 meters across
6. bottom habitat or type undocumented
7. pollutants: site is located within the urban area of Superior, WI/ Duluth, MN
8. this site is within the St. Louis River estuary.

**5) Coded variable definitions** – Standardized station code names and monitoring program codes are utilized to differentiate the Reserve, station, and nutrient dataset. For example:

lksbanut = Lake Superior NERR Barker’s Island nutrients

lksolnut = Lake Superior NERR Oliver Bridge nutrients

lksblnut = Lake Superior NERR Blatnick Bridge nutrients

Monitoring programs:

monthly grab sample program = 1

diel grab sample program = 2

**6) Data collection period** – Date and time the first grab sample was collected, replicate samples were generally collected within a few minutes. In 2012, this information was compiled from depth profile data sheets.

|  |  |  |
| --- | --- | --- |
| **Site** | **Date** | **Time** |
| ol | 5/8/2012 | 10:35 |
|  | 6/13/2012 | 14:23 |
|  | 6/27/2012 | 15:22 |
|  | 7/10/2012 | 10:14 |
|  | 8/6/2012 | 11:06 |
|  | 9/4/2012 | 13:30 |
|  | 10/2/2012 | 10:45 |
|  | 11/7/2012 | 11:56 |
| bl | 5/8/2012 | 12:10 |
|  | 6/13/2012 | 16:00 |
|  | 6/27/2012 | 16:32 |
|  | 7/12/2012 | 10:56 |
|  | 8/6/2012 | 10:25 |
|  | 9/4/2012 | 12:09 |
|  | 10/2/2012 | 9:24 |
|  | 11/7/2012 | 10:34 |
| ba | 5/8/2012 | 9:10 |
|  | 6/13/2012 | 16:19 |
|  | 6/27/2012 | 17:15 |
|  | 7/12/2012 | 10:40 |
|  | 8/6/2012 | 9:14 |
|  | 9/4/2012 | 11:45 |
|  | 10/2/2012 | 9:00 |
|  | 11/7/2012 | 10:10 |

**7) Associated researchers and projects –**

Samples were taken monthly at these four sites (ol, , bl, ba) for nutrient and chlorophyll *a* analyses from May through November, 2012. The System-wide Monitoring Program datasonde deployments (water quality monitoring dataset) occurred at three of these sites (ol, bl, ba). 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. Water quality data may be found at [www.nerrsdata.org](http://www.nerrsdata.org).

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 2012 included the biological control of purple loosestrife, a study of the microbial communities related to mercury methylation in sediment, geospatial analyses of stressor gradients and stakeholder participation patterns in the estuary.

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** –

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:

National Estuarine Research Reserve System (NERRS). 2012.  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](http://cfcdmo.baruch.sc.edu/). 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.

The results of the nutrient data were received from LLO in Microsoft Excel worksheets. Nutrient data were entered into a Microsoft Excel worksheet by the SWMP Technician, Joe Ripley, and double-checked by the Monitoring Coordinator, Tracey Ledder. Tracey Ledder processed the data using the NutrientQAQC Excel macro and performed secondary QAQC.

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.

Conversion documentation: The Large Lakes Observatory of University of Minnesota at Duluth calculated and reported results in µM and either ug/L or mg/L, depending on the analyses. For purposes of consistency in the NERR System, NERRs normally calculate the concentrations as mg/L based on atomic weights of 14.01, 30.97, 28.09, and 12.01 for N, P, Si, and C respectively. For the 2012 NUTCHLa data, LLO staff multiplied the uM concentrations reported by 0.0140067 and 0.06001 to yield concentrations in mg/L as N and Si, respectively (Si was analyzed as SiO4F, silicate). The phosphorus results were all a calculated as ug/L directly from the standard curves, and LS NERR staff divided these results by 1000 to yield mg/L as P.

**10) Parameter titles and variable names by category –**

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

**Data Category Parameter Variable Name Units of Measure**

Phosphorus and Nitrogen:

\*Orthophosphate PO4F mg/L as P

\*Ammonium, Filtered NH4F mg/L as N

\*Nitrite, Filtered NO2F mg/L as N

\*Nitrate, Filtered NO3F mg/L as N

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

Total Phosphorus TP mg/L as P

Total Nitrogen TN mg/L as N

Plant Pigments:

\*Chlorophyll a CHLA\_N µg/L

Phaeophytin PHEA µg/L

Other Lab Parameters:

Silicate, Filtered SiO4F mg/L as SI

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.

3. Ammonium, Nitrite, and Nitrate were not reported in this introductory year, see Other Remarks section.

**11) Measured or calculated laboratory parameters** – This section lists all measured and calculated variables. See Table 2 in the “Nutrient and Chlorophyll Monitoring Program and Database Design” SOP version 1.5 (January 2011) document for a full list of directly measured and computed variables.

1. **Parameters measured directly**

Nitrogen species: NH4F, NO2F, NO3F, NO23F, TN

Phosphorus species: PO4F, TP

Other: CHLA\_N, PHEA, SiO4F

1. **Calculated parameters**

NO3F NO23F – NO2F

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

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 by the LLO Aquatic Ecology Lab.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Start Date | End Date | MDL |
| TP | 05/08/2012 | 12/15/2012 | 0.00035 |
| TN | 05/08/2012 | 12/15/2012 | 0.0006 |
| PO4F | 05/08/2012 | 12/15/2012 | 0.00035 |
| NO23F | 05/08/2012 | 12/15/2012 | 0.0006 |
| NO2F | 05/08/2012 | 12/15/2012 | 0.0006 |
| SiO4F | 05/08/2012 | 12/15/2012 | 0.012 |
| CHLA\_N | 05/08/2012 | 12/15/2012 | 0.05 |
| PHEA | 05/08/2012 | 12/15/2012 | 0.05 |

**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. All analyses were performed at the Large Lakes Observatory, University of Minnesota – Duluth. Each sample submitted to the lab was analyzed in duplicate (both field samples and field replicates) and the results averaged for reporting each field replicate sample result.

1. **Parameter: CHLA\_N**

*LLO Method*: Determination of chlorophyll a with acidification in water samples (Flourometric Method)

*Reference Method*: Stainton, M.P. 1977. The chemical analysis of freshwater. Fisheries and Oceans Canada. Special Publication No. 25. Winnipeg, MB

*Principle*: Particulate matter collected on a glass fiber filter is extracted in acetone. After extraction, fluorescence of extract is measured before and after acidification. Chlorophyll a, with excitation between 430-450 nm, gives an emission maximum between 650-675nm. The output is in arbitrary units, and therefore must be calibrated using a chlorophyll solution of known concentration.

*Preservation Method*: Filters with particulate matter are stored frozen in the dark.

1. **Parameter: PO4F**

*LLO Method*: Determination of Soluble Reactive Phosphorous in Water Samples

*Reference Method*: Standard Methods for the Examination of Water and Wastewater. 18th Edition, 1992

*Principle*: Samples for SRP analysis were filtered through a 0.45 um filter. Ammonium molybdate and potassium antimony tartrate react in acid medium with orthophosphate to form phosphomolybdic acid, which is reduced to intensely colored molybdenum blue by ascorbic acid. Using the appropriate acid and molybdate strength, reducing with ascorbic acid, and with antimony as a color enhancing species, an intense blue complex will form, with maximum absorbance at 885nm. The absorbancies of sample blanks are also read and utilized in background correction for colored waters.

*Preservation Method*: Filtered samples are kept in screw capped polyethylene bottles, without acidification at -10° C. Frozen samples may be stored for up to 3 months. Unfrozen samples should be analyzed within 48 hours.

*Quality Control*:

1. Method Blank: MB is analyzed after the calibration, after every batch, and at the end of the analysis.
2. Duplicate Sample: DS is analyzed for the first sample of every batch. The difference between the duplicate results must be within acceptable limits. (To be determined.)
3. Method Blank Spike: MBS is analyzed after calibration, after every batch of the run, as well as at the end of the analysis. MBS should be within acceptable control limits. Plot every first MBS value in a control chart.

Precision and Accuracy: Calculations based on the analysis of blanks and standards between the periods of new SOP implementation.

1. **Parameter: TP**

*LLO Method*: Determination of Total Phosphorus and Total Dissolved Phosphorus in Water Samples.

*Reference Method*: Standard Methods for the Examination of Water and Wastewater. 18th Edition, 1992.

*Principle*: Unfiltered samples are used for total phosphorus. Organic phosphorus is converted to orthophosphate in the presence of potassium persulphate. Orthophosphate is determined by soluble reactive phosphorus method.

*Preservation Method*: All samples (filtered and unfiltered) are kept frozen in 60 mL polycarbonate containers.

*Quality Control*:

1. Blank: Blank analyzed after calibration, after every batch, and at the end of the analysis. Blank must be < MDL.

2. Duplicate Sample: DS is analyzed for the first sample of every batch. The difference must be within a predetermined amount.

3. Method Blank Spike: Analyzed after the calibration, after every batch, and at the end of the analysis. MBS should be within acceptable limits. Every first MBS value of analysis should be plotted in a control chart.

1. **Parameter: SiO4F**

*LLO Method* : Determination of Silicate in Brackish or Seawater by Flow Injection Analysis ( QuikChem Method 31-114-27-1-A)

*Reference Method*: Grasshoff,K. “Methods of Seawater Analysis”, Verlag Chemie, Second Edition, 1976.

*Principle*: Soluble silica species react with molybdate at 37°C and a pH of 1.2 to form a yellow silicamolybdate complex. This complex is subsequently reduced with stannous chloride to form a heteropoly blue complex which has an absorbance maximum at 820 nm. The absorbance is proportional to the concentration of “molybdate reactive” silica. Though the method is written for Brackish water and Seawater, it is also applicable to non-saline sample matrixes. The method is calibrated using standards prepared in deionized water. Once calibrated, samples of varying salinities may be analyzed. The determination of background absorbance is necessary only for samples which have color absorbing at 820 nm.

*Preservation Method*: Samples are collected in screw cap polyethylene bottles, and filtered through a 0.45 um filter. Samples may be frozen at -20°C, but some loss of silicate may occur at high concentrations. In high diatom blooms, some regeneration of soluble silicate can occur if plankton is not removed by filtration. Ideally, analysis should be done within 24 hours of sample collection.

*Quality Control*: An external check standard is analyzed after calibration. Field blanks and laboratory blanks are analyzed within the analytical run and must be below the MDL.

1. **Parameter: TN/NO23F**

*LLO Method*: Determination of Nitrate + Nitrite in brackish or seawater by flow injection analysis colorimetry (QuikChem Method 31-107-04-1-C)

*Reference Method*: Zimmerman, Carl F. and Keefe, Carolyn W., EPA Method 353.4, Determination of Nitrate + Nitrite in Estuarine and Coastal Waters by Automated Colorimetric Analysis in An Interim Manual of Methods for the Determination of Nutrients in Estuarine and Coastal Waters., Revision 1.1, June 1991.

*Principle*: Samples for nitrate+nitrite were filtered through 0.45 um filter. Unfiltered samples are used for total nitrogen. These samples are digested and then analyzed according to the NO2/NO3 method. A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that was originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-napthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Though this method is written for Seawater and Brackish water, it is also applicable to non-saline sample matrixes. The determination for background is only necessary for samples which have color absorbing at 520 nm.

*Preservation Method*: Samples should be analyzed as soon as possible after collection. If storage is required, preserved samples are maintained at 4°C and may be held for up to 28 days.

*Quality Control*: The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method. Linear Calibration Range (LCR) the LCR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected. Quality Control Sample (QCS) when beginning to use this method, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS.

**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.

* 1. **Precision**
     1. **Field variability** – A field replicate (successive grab sample) was taken at every site for every sampling event. In general, the field replicate results were well within ±20% for all NO23 and TN analyses. Most TP and PO4 field replicate results were well within a ±20% RPD with the exception of the following, which ranged from 21% to over 100% RPD;

TP– ba 9/4

PO4 – ol 10/2, 11/7; bo 6/27, 8/6, 9/4, 10/2, 11/7; bl 10/2, 11/7; ba 5/8, 11/7

These samples were flagged SRD in the dataset.

* + 1. **Laboratory variability** – With the exception of the May sampling round, all analyses were performed in duplicate for all samples (field samples and field replicates).
    2. **Inter-organizational splits** – None in 2012
  1. **Accuracy**
     1. **Sample spikes** – none reported in 2012
     2. **Standard reference material analysis –**  external, manufacturer-purchased standards were utilized as calibration checks for some analyses. The table below summarizes percent error of the analyzed standards, columns denote sample batches analyzed with the same standard curve.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Percent Error from known concentration | | | | |
| Analysis | May 8 | June 13 | June 27 Jul 10 | Aug 6 | Sept - Nov |
| Chl a/Pheo | NA | NA | NA | NA | NA |
| NO23 | -8.0% | -3.8% | 2.8% | 4.4% | -4.7% |
| TN | 4.2% | -7.3% | -8.1% | 9.7% | 8.4% |
| PO4 & TP | NA | NA | NA | NA | NA |
| Si | 0.04% | 1.7% | 2.8% | -2.2% | 8.7% |

NA= not analyzed

* + 1. **Cross calibration exercises** – none in 2012

**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 –** This section further documents the research data set. Included are 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.

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 2012 data set is missing ammonium data. Samples were collected and submitted to LLO for analysis of ammonium. Mechanical problems with the analytical equipment meant that the analyst had no confidence in the results and ultimately stopped running monthly ammonium samples.

All data for individual analyses of nitrite and nitrate are missing for 2012. Limited samples were processed as part of an EPA project and are available by contacting the Reserve directly. Individual analyses will be conducted by the Reserve in the future.

All data for orthophosphate, total phosphorus and dissolved phosphorus were flagged as “Suspect” due to QA/QC reviews that revealed incomplete quality control data, inability to re-calculate results from reported analytical data due to a difference in decimal places between what was reported to the LSNERR and what was utilized by the analyst to calculate concentrations, rounding different from that of NERR method, inconsistent calculation methods from month to month.

Several of the phosphorus analyses also had replicate values that differed significantly, as described in Section 14, under Field Variability. Specifically the following grab replicates reported in the data set differed significantly:

BL 10/2/12 PO4F

OL 11/7/12 PO4F

BA 11/7/12 PO4F

June and July total nitrogen and dissolved nitrogen data were flagged as “suspect” as the laboratory reported greater concentrations of dissolved nitrogen than total nitrogen. The cause, while unknown, could have been incomplete digestion, or a simple mistaken labeling of results.

June nitrite/nitrate data were flagged as “suspect” as the laboratory reagent water and field blanks for that batch were either missing or detected the analyte at greater than 10% of the sample results.

Most of these inconsistencies were apparently a result of the fact that there was a staff vacancy at the LS NERR (Monitoring Coordinator) as this program is in the developmental phases. Since there is a new Monitoring Coordinator in 2013, we anticipate that with the use of the training in NERR procedures received at the Technicians Training Workshops and NERR guidance, better documentation of sampling and analysis activities will occur in the future.

June 2012 FLOOD – The western Lake Superior area experienced an extreme flood event in late June of 2012. Up to 8 inches of rain in one day were reported from several places in the Duluth/Superior area. The USGS stream gage on the St. Louis River at Scanlon (upstream of the estuary) documented a river flow of 40,000 cfs in late June (peak was approximately 45,300 cfs on June 21), whereas the average was approximately 500 cfs in September and October (long-term yearly median is 2278 cfs). This rain event caused heavy flooding in the Duluth and Superior areas, with road and dam failures, river bank slumping and changes in upper estuary bathimetry. A set of NUTCHLa samples were taken on June 27, 2012 when the river discharge as Scanlon was recorded as 19,700 cfs.