TITLE

Marcell Experimental Forest chemistry of surface water draining the S2 catchment, 1986 - ongoing

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Abstract:

This data set is a record of chemistry for surface water draining the S2 catchment at the Marcell Experimental Forest (MEF) in Itasca County, Minnesota since 1986. Unfiltered water is usually collected every one or two weeks since the 1970s as part of the long-term monitoring program of the S2 catchment. Some samples were collected more often for various other studies and are included in this data set. Samples are measured for pH, specific conductivity, anions (chloride, sulfate), cations (calcium, magnesium, potassium, sodium, aluminum, iron, manganese, strontium), silicon, nutrients (ammonium, nitrate+nitrite, soluble reactive phosphorus, total nitrogen, total phosphorus), and total organic carbon. Some solute concentration measurements were interrupted for periods and some others were initiated after 1986. We lack adequate metadata for some solutes prior to 1992 and only report a subset of analytes from 1986 to 1992. Occasionally, stable water isotopes as well as concentrations of dissolved organic carbon, ferrous and ferric iron, total mercury (filtered or unfiltered), methylmercury (filtered or unfiltered), and lead were measured. More solutes and values will be added as additional metadata are documented (1986 to 1992), water samples are collected and analyzed (concentrations and isotopes), or archived water samples are analyzed for stable water isotopes. The MEF is operated and maintained by the USDA Forest Service, Northern Research Station.

Methods and protocols used in the collection of this data package

Description:

This data set is a report of chemistry for surface waters draining the S2 peatland and surrounding uplands (the S2 catchment) at the Marcell Experimental Forest (MEF) in Itasca County, Minnesota. Surface water was collected every two weeks, week, or more often, starting during the 1970s. We lack adequate metadata for some solutes prior to 1992 and only report a subset of analytes from 1986 to 1992. Metadata are more complete and a broader suite of analytes is reported after 1992. As metadata are better described and more data become available through ongoing sampling and analysis efforts, we will update this data product.

Samples are measured for a core suite of pH, specific conductivity, anions (chloride, sulfate), cations (calcium, magnesium, potassium, sodium, aluminum, iron, manganese, strontium), silicon, nutrients (ammonium, nitrate+nitrite, soluble reactive phosphorus, total nitrogen, total phosphorus), and total organic carbon (TOC). Some solute concentration measurements were interrupted for periods, and some others were initiated some year after 1986. Occasionally, stable water isotopes as well as concentrations of dissolved organic carbon (DOC), ferrous and ferric iron, total mercury (filtered or unfiltered), methylmercury (filtered or unfiltered), and lead were measured.

The MEF is operated and maintained by the USDA Forest Service, Northern Research Station. The S2 catchment is located on US federal government land that is part of the Chippewa National Forest.

SITE DESCRIPTION:

The S2 catchment has a 6.5-ha deciduous upland forest and a natural, undrained 3.2-ha peatland (raised-dome bog with a surrounding lagg). A stream forms in the lagg and flow is intermittent throughout the year (Verry et al. 2011). A lagg is the transitional peatland area between a bog and surrounding mineral soil uplands. Streamflow occurs during and after snowmelt and rainfall events. In some years, there is streamflow from snowmelt to freeze-up during the following winter. In most years, there is a period of no streamflow during summer that may extend into fall or winter, and in most years, streamflow does not persist through winter.

Surface elevation ranges from 420 m a.s.l at the outlet to 430 m a.s.l. in the uplands. In the uplands, a Warba sandy clay loam developed in glacial till atop 50-m deep outwash sand deposits. The Warba soil series is a fine-loamy, mixed, superactive, frigid Haplic Glossudalfs; Alfisol (Nyberg 1987). Peat depth has been surveyed across the bog (Verry and Janssens 2011). Peat is less than 1 m deep around the perimeter of the bog to about 7 m at the deepest location. The Loxley peat (Dysic, frigid Typic Haplosaprists; a Histosol; Nyberg 1987) has accumulated in the last 10,000 yr since Wisconsin glaciation (Verry and Janssens 2011). The peatland surface has hummock and hollow microtopography. Hummocks are uneven, elevated areas that rise various heights, up to about 50 cm, above the adjacent hollows. Hollows have a relatively uniform elevation within a localized area, with an overall raised-dome profile across the entire bog surface. The peatland water table fluctuates from about 0.10 m above the surface to as much as 0.30 m below during a typical year.

The upland forest is dominated by aspen (Populus tremuloides), white birch (Betula papyrifera), red maple (Acer rubrum), and balsam fir (Abies balsamea), with some red oak (Quercus rubra), basswood (Tilia americana), and jack pine (Pinus banksiana). The upland forest was last harvested during the 1910s.

The peatland has a black spruce (Picea mariana)-tamarack (Larix laricina)-Sphagnum community. Below the overstory tree canopy, there is variable coverage of ericaceous shrubs (primarily Rhododendron groenlandicum, Chamaedaphne calyculata, and Vaccinium angustifolium), cotton grass (Eriophorum spissum), Sphagnum moss, or haircap moss (Polytrichum spp.) across the bog. Three-leaved false Solomon’s seal (Maianthemum trifolium) and common pitcher plant (Sarracenia purpurea) are found throughout the bog. The lagg has most of the same species but is richer in species than the bog (Verry and Janssens 2011). The more noticeable additional species include speckled alder (Alnus incana), paper birch (Betula papyrifera), and various Carex species.

The climate is continental with warm summers, cold winters, and a mean annual air temperature since 1961 of 3.5 deg C (1961 to 2019, Sebestyen et al. 2021b). Air temperature ranges from -46 to 38 degrees Celsius. Mean annual precipitation since 1961 is 787 mm. Most precipitation occurs as rainfall during summer and a winter snowpack starts to accumulate around December and fully melts in March or April. Air temperatures are below freezing with limited days of mid-winter thaw and snow typically accumulates from November or December to March or April.

At the S2 catchment, snow depth, snow water equivalent, precipitation, ground frost, upland runoff volume, streamflow, and water levels have been monitored, with some measurements as early as 1960 (Sebestyen et al. 2021b). Some chemistry (mostly unpublished) was measured as early as 1966. Surface water draining the S2 peatland is acidic (mean pH = 3.7 at the S2 LAGG POOL from 1992 to 2021) with low concentrations of ions and nutrients, and high concentrations of dissolved organic matter (mean TOC concentration = 71.8 mg/L at S2 LAGG POOL from 1992 to 2021).

LOCATIONS OF WATER SAMPLING:

The water chemistry reported in this data release began during 1992. Water has been repeatedly sampled from two locations. Streamflow is intermittent. Although the protocol is to only sample when the stream flows, samples were rarely, but sometimes collected from the weir pool when there was no streamflow over the v-notch weir. While the long-term sampling occurs every two weeks, some samples were collected for separate projects and multiple samples may have been collected on the same day or throughout a week.

Samples have been collected for the longest period (starting 1986 in this data release) from a location about 100 m upstream of a weir. These samples are named S2 LAGG POOL, which is located upstream of a discernable stream channel in the general area where the lagg coalesces into the stream. The lagg pool was excavated sometime before 19##. The pool has probably infilled over the years as dead biomass has accumulated. It is currently about 30 cm deep. Because the peatland has a compressible, organic soil that is prone to disturbance, and there are extended periods of standing water on the approach to and surrounding the pool, an elevated boardwalk was constructed during 2011 to access the lagg pool for sampling. Prior to that, the lagg pool was approached by walking on the lagg surface. The area is surrounded by black spruce, tamarack, ericaceous shrubs, Sphagnum, and other lagg plant species. The lagg has hummock and hollow microtopography, the area extending around the lagg pool is relatively flat and low lying. Samples from the S2 LAGG POOL have occasionally been supplemented with grab samples of stream water at the S2 weir to maintain long-term biweekly sampling when the stream was flowing but the S2 LAGG POOL was ice covered.

Beyond those occasional samples during ice cover at the S2 LAGG POOL, stream water at the v-notch weir has been collected for various studies and routinely each week since 2008 for the core suite of analytes. The weir is used to measure stream stage and calculate streamflow for the S2 catchment and represents the outlet of the entire S2 catchment. Samples from the weir are named S2 WEIR and are collected when the stream flows. These samples are either grab samples of water falling over the v-notch (2001 to ongoing) or were autosampled (2008 to 2013) from the weir pool. From about October or November until high flow during snowmelt, an insulated cover was placed over the weir. This shelter was heated with a propane lamp to avoid ice accumulation in the v-notch and to allow sampling during freezing conditions.

From April 2001 to June 2011, grab samples were collected about every two weeks (though there were some years with few or no samples during December) to document reference conditions in the S2 catchment relative to a sulfate and mercury cycling experiment at the S6 catchment (Jeremiason et al. 2006, Coleman Wasik et al. 2012, Coleman Wasik et al. 2015). Samples were collected at higher frequency (one to several days between samples) corresponding to three times each year (2001-2008) when sulfate was added to the S6 bog to mimic atmospheric deposition levels of the late 1970s. These filtered samples were only analyzed for total mercury and methylmercury concentrations from 2001 to 2011, chloride and sulfate concentrations from 2006 to 2011, and the core suite of analytes from 2009 to 2011).

Starting during October 2007, grab samples were collected during some stormflow events and starting April 2008 weekly grab samples were collected for the core suite of analytes. Dissolved organic carbon, total mercury (filtered or unfiltered), methylmercury (filtered or unfiltered), lead (filtered), ferric and ferrous iron concentrations and water isotopes have been measured for select samples. Many of the weekly S2 WEIR grab samples are paired within five to ten minutes of a grab sample being collected from the S2 LAGG POOL, which allows chemistry comparisons between those particular samples.

Stormflow samples were collected from water pooled behind the V-notch using an Isco 3700 portable sampler (Teledyne Isco, Lincoln, Nebraska, USA) from April 2008 to August 2013. From April to June of 2008, automated sample collection was triggered every two hours on some days when stormflow was expected based on precipitation forecasts. From July 2008 to July 2013, automated sample collection was triggered by threshold changes in absolute stream stage. The threshold value was changed over time, but the general goal was to collect several samples over the rise and fall of stream stage. For example, during 2010, a change in stage from 0 to 8 cm resulted in the actuation of sampling six times as stream stage was rising. Samples may have been collected anywhere from minutes to days apart depending on the magnitude of stormflow and rate of change in streamflow. Not every sample was kept. While the streamflow record (Verry et al. 2018) was derived from stage measured with a Type A-35 stripchart recorder (0.3-cm precision), the Isco sampler was triggered by a Campbell Scientific (Logan, Utah, USA) CR1000 datalogger with a float-tape-counterweight driven shaft encoder (Handar, 436b encoder, 100 measurements per rotation of a 30.5 cm diameter pulley). A 5:1 reduction gear was used to increase the precision of stage measurements to 0.06 cm. Stage was measured every 10 seconds. These samples were analyzed for the core suite of analytes and occasional samples were analyzed for water isotopes.

Sampling location, whether at the S2 LAGG POOL or at the WEIR, is important to consider, especially for some solutes, as will be discussed later. Sample location, temporal resolution, and the period of sampling all need to weighed relative to the research questions that are being asked. While not at the catchment outlet, for research that requires the longest and most complete record, it is logical to use samples from the S2 LAGG POOL and to include occasional samples from the S2 WEIR when the S2 LAGG POOL was ice covered. Accordingly, a chemistry value will be available when the stream was flowing despite the inaccessibility of the S2 LAGG POOL. However, dates and times of samples need to be assessed by data users to identify samples that are relevant to any particular research objective. It is otherwise not likely advisable to mix samples from the LAGG POOL and WEIR for research on temporal trends. Differences in some solute concentrations between the LAGG POOL and WEIR could lead to a false assessment of patterns and trends. The record of chemistry from the S2 WEIR should likely be used for research that is focused on periods that begin after weekly sampling started during 2008. The 2008 to 2013 period also deserves consideration relative to what level of temporal resolution is most appropriate to address particular research questions. For example, emphasis was placed on sampling during storm events using grab sampling up to several times a week and higher temporal resolution of stormflow with autosampling. Comparing periods with only weekly sampling to periods with autosampling may limit direct comparisons of those periods if the chemistry was skewed by additional representation of the chemistry during stormflow. Since storm samples have not been collected at other MEF catchments, sub-weekly samples should likely be excluded from direct comparisons of chemistry to other catchments. Given these considerations, the chemistry values are presented in three separate comma separated value (CSV) tables: one table for the S2 LAGG POOL, one for grab samples from the S2 WEIR, and another for autosampled waters from the S2 WEIR. Regardless of intended data use, it is advisable to only use a subset of values that are directly relevant to specific research objectives. Since each sample receives a unique serial identifier (ID), we also advocate that data users specify in a list that accompanies a research publication the serial IDs of samples that were used in any particular data analysis.

WATER SAMPLING AND ANALYTICAL METHODS:

Unfiltered water was used for most chemistry analyses. If an aliquot was filtered for analysis of a particular solute, the sample may have been filtered later in a laboratory.

At the S2 LAGG POOL, samples were dipped with a plastic kitchen ladle and poured into bottles. After about April 2010, the ladle or a polyethylene dipper (CXBA00, Global Water Instrumentation, Phoenix, Arizona) with an approximately 0.5-m handle was used. The ladle or dipper was rinsed with 18 megaohm deionized water before the start of sampling, including sampling at other sites in S2 as well as other MEF catchments. At the S2 LAGG POOL, the ladle was rinsed three times with water from the pool before sampling. The rinse water was discarded outside of and away from the sampling pool.

For S2 WEIR grab samples, stream water flowing over the v-notch was collected in sample bottles.

The autosampler was placed on a wooden platform that was about 2 m higher in elevation than the weir pool surface. A standard Isco weighted polypropylene strainer on the end of the suction line (1-cm or 3/8 inch internal diameter reinforced vinyl tubing) was suspended from a float in the pool about 30 cm behind the v-notch and about 10 cm beneath the water surface. Suction was drawn along an approximately 60-cm section of Silastic (medical-grade silicon rubber) tubing, connected to a 5-6-m long vinyl suction line, by the Isco peristaltic pump. The silicon and vinyl tubing were connected with an approximately 5-cm stainless steel adaptor (0.6 cm diameter). The base of the Isco held twenty-four 1000-mL polypropylene bottles (standard wedge shaped Isco 3700 bottles that fit inside the perimeter of the circular base). At the start of a sampling sequence, air was backflushed through the line to purge any water. A sample of about 800 mL was then pumped into a bottle, followed by another backflush and purge cycle to clear water out of the tube. During sampling, the light environment was similar to or less than exposure in the weir pond because about 2 m of suction line was underwater in the weir pool before passing underground through schedule 80 PVC for about 3 m before entering the Isco. Pump tubing was changed as needed if dirty or worn from use. The Isco bottles were replaced with clean, acid-washed bottles every two to three months, or if noticeably dirty. Water was poured from an Isco bottle into a sample bottle upon retrieval. Usually six or fewer bottles filled between retrievals, and the used bottles were sometimes replaced with other unused bottles in the base before all bottles were retrieved and washed. Samples were typically retrieved every weekday during snowmelt (March or April) or from May to August (when summer field technicians visited the MEF daily). Samples usually remained in a sampler if collected after business hours on Friday or over a weekend or holiday until the next business day. Samples were typically transferred from Isco bottles to sample bottles in the field. Samples that froze inside the autosampler were returned to the Forestry Sciences Laboratory in Grand Rapids to thaw.

Unfiltered water was used for most laboratory analyses. It is important to keep in mind that surface waters in peatlands are free of inorganic particulates due to flowpaths through peat and slow transit times due to low hydraulic gradients that allow for deposition of particulates. For that reason, we have considered unfiltered water samples of surface and peatland porewaters to be dissolved. The samples are likely to include colloids, but no inorganic particulates and rarely peat particles. Attempts are made to avoid or eliminate aquatic organisms (mostly mosquito larvae during late spring when abundant) or plant leaves and needles.

Occasionally, a field duplicate was collected. These duplicates can be identified by two consecutive serial ID values that have the same timestamp (date, hour and minute).

Unless otherwise noted, samples were placed inside chilled coolers within minutes of collection. When returned to the Marcell Field Laboratory (before 2006), Marcell Research Center (after 2006), or the Forestry Sciences Laboratory in Grand Rapids, samples were chilled to 4 degrees Celsius in a refrigerator until analyzed, unless otherwise noted.

When collected, date/time of retrieval, sample location, and associated notes were recorded on field data sheets. A unique serial ID number was assigned to all aliquots of the same sample for tracking purposes in the laboratory and data reporting. The serial ID, date/time, and sample location were also written on label tape on each sample bottle or vial.

Time was recorded as hour (Central Standard Time) and minute. Minutes were oftentimes recorded to the closest 5 minute interval (e.g., 0, 5, 10, 15, etc. minutes after the hour) for grab samples. Sampling and recording on field data sheets generally took several minutes, but no longer than 5 minutes to complete. Occasionally, time was not recorded which results in a 0:00 timestamp even though grab samples were never collected at midnight. The autosampler occasionally collected a sample with a legitimate 0:00 timestamp. Otherwise, 0:00 timestamps should be disregarded and treated as if the time is unknown.

Sample ID numbers are five-digit or six-digit integers. Samples IDs are not necessarily consecutive because water from other sites at the MEF are interspersed in the numbering series. Since samples were sometimes collected for multiple research projects, several samples may have been collected on the same day.

In general, the long-term grab sampling of the S2 LAGG POOL and the S2 WEIR by the Forest Service was every two weeks and samples were in six-digit ID series. From 1992 to 2018, a new ID series was started each year and the value was usually 1000 plus the first ID value of the previous year. For example, samples 164000 to 164458 were sequentially collected during 1992, and the first sample of 1993 was assigned the ID 165000. Incrementing by 1000 continued each year from 1992 to 2003 (i.e., series 164 to 175). During 2004, the series jumped to 213 (i.e., first sample 213000 to last sample 213308) and continued from there (series 213 during 2014 to 227 during 2018). When weekly and automated samples were added during 2008, a separate series (346) was started. During 2009, samples were added in the 347 series (347000 to 347395). Since 2010, samples have been consecutively numbered from 348000 without starting a new series at the beginning of each calendar year. By 2018, these consecutively numbered samples had reached into the 354 series. During 2018, we merged all sample IDs into the consecutively numbered 354 series to avoid redundant weekly sampling and IDs no longer advance to a new series each year.

For long-term sampling at the S2 LAGG POOL, stream stage at the weir is usually (but not always) recorded prior to or after collection. These measurements are usually read from a manual point gage that is made within about 5 minutes of the recorded sample collection time. When both S2 LAGG POOL and S2 WEIR samples are collected, stream stage is usually reported with the S2 WEIR sample. Stream stage is not measured with the point gage if the weir pool is ice covered.

For most grab samples, water temperature is measured after water sampling, but at about the same time. Alcohol or perhaps mercury thermometers were used exclusively before 2011 and read to the closest degree. Extech (Model 39240, Nashua, New Hampshire, USA) waterproof digital stem thermometers have oftentimes been used since 2011 and temperature is read to 1 decimal place.

Forestry Sciences Laboratory in Grand Rapids, Minnesota:

For each type of laboratory measurement (except water isotopes), every tenth to twentieth sample is run in duplicate (analytical duplicate) followed by two references. References are chosen to be within the range of calibration standards and optimized for particular solutes or suites of solutes to be within the range typically observed for waters at the MEF. For anion, cation, silicon, nutrient, and TOC analyses, standard solutions were made in volumetric flasks with deionized water (18.0 megaohm/cm). Some references and reagents were made in-house from stock solutions or anhydrous reagents. Over time, references for ions have been transitioned from in-house preparation to purchase of commercially prepared solutions. Commercially prepared solutions are not altered (e.g., diluted or mixed) before analysis. The vendors and concentrations have changed over time and that information is maintained in unpublished laboratory records for each batch of samples. For each instrument and sample, we record the date and time of analysis and that information is stored in our unpublished laboratory records. The location of some records before 1992 are not currently known.

Several criteria need to be met or the laboratory reanalyzes samples. For concentration values, analytical duplicates and the preceding samples are acceptable for reporting when the relative error is less than 10 percent between duplicates. When certified references differ by more than 5 percent from actual values, a batch of samples is reanalyzed. When a particular sample is higher in concentration than the highest calibration standard, that sample is diluted and re-run until within the range of the calibration standards.

While the methods and quality assessment/quality control procedures are largely consistent over time in the Forestry Sciences Laboratory, the instruments have been updated, sometimes several times, and the method detection limits have changed. New analytes have been added over time. When new instruments were acquired, there was oftentimes little effort to directly compare samples run on both old and new instruments, and sometimes failure of a critical instrument component hindered further analysis on a previous instrument. Nonetheless, references spanned the transition periods and provided evidence of consistent results with a previous instrument. Whenever possible, transitions were timed to occur so that an entire year of samples was analyzed by one instrument. When transitions were known to occur sometime during the calendar year, that information is provided.

Instruments are operated in accordance with Standard Methods (APHA 2017). However, holding times of samples sometimes do not meet those standards (as described below).

During partial US Federal Government shutdowns lasting more than several days, field sampling was maintained, but laboratory analyses were interrupted until Government operation resumed. During these periods, holding times would have been prolonged. The three government shutdowns that affect laboratory operation occurred from December 6, 1996 to January 1, 1996; October 1 to October 17, 2013; and December 22, 2019 to January 25, 2019.

Typically within two years of analysis completion, refrigerated samples are discarded. For the foreseeable future, there is plenty of space to store frozen aliquots if any sample is left and we have no discarded frozen aliquots.

Specific Conductivity, pH, and Ion Concentrations:

Unfiltered water was collected in 250-mL low density polyethylene (LDPE) sample bottles after rinsing 3x with sample water. Samples were refrigerated until analysis.

In the Forestry Sciences Laboratory in Grand Rapids, aliquots were poured from the 250-mL sample bottle at the time of any particular analysis.

Specific conductivity:

Conductivity was measured on a Yellow Springs Instruments (YSI; Yellow Spring, Ohio, USA) Model 35 meter for samples collected from 1987 to 1991 and 1994 to May 14, 2010. Information on the conductivity probe is unknown. On each day of operation, the instrument was calibrated with a standard. After verifying instrument response with a blank and a reference, samples were measured. After about every 15 to 20 samples or at the end of a smaller batch, a reference was measured. An analytical duplicate was measured after about every 10 to 20 samples, or at the end of a smaller batch.

Specific conductivity was measured in the University of Minnesota Research Analytical Laboratory (St. Paul, Minnesota, USA) for samples collected from 1992 to 1994. We have no other metadata.

For samples collected from May 17, 2010 to 2019, conductivity was measured on a YSI Model 3100 meter. A YSI 3403 probe (cell constant = 1.0/cm) was used until March 2017 and a YSI 3253 probe (cell constant = 1.0/cm) thereafter. After verifying instrument response with a blank and a reference, samples were measured. After about every 10 samples, an analytical duplicate was measured.

For both YSI instruments, the manually loaded cell of the conductivity probe was twice rinsed with sample water and then conductivity was measured on the third poured aliquot (1 cubic cm). Conductivity values were recorded on paper. More than 100 samples could be measured each day, but smaller batches of samples were oftentimes measured within several days of collection. Specific conductivity (conductivity at 25 degree Celsius) was calculated from conductivity measured at 21 degree Celsius when values were transferred to spreadsheets.

For samples collected since 2020, conductivity is measured with a Mettler Toledo Inlab 710 conductivity probe connected to a T7 Titration Excellence titrator. The Inlab 710 is a 4 platinum poles conductivity cell with a chemical resistant glass body and integrated probe. Once a day, the measurements are calibrated with a 46.7 microSiemen/cm standard, and periodically checked with 23.8, 84.0, or 150 microSiemen/cm references. Eighty mL of sample is poured into a sample beaker (polypropylene; pre-rinsed with deionized water) in an InMotion Pro Autosampler. With this instrument, specific conductivity, pH, and acid neutralizing capacity (ANC; not reported) are sequentially measured from the same aliquot of water. For specific conductivity measurement, the probe is dipped into a sample beaker in the autosampler tray before water is withdrawn for pH measurement. Samples, the standard, and references are measured in a laboratory maintained at 21 degrees C. Specific conductivity is calculated and reported by the T7 instrument.

Samples typically are analyzed within days of collection. Although ucommon, samples sometimes are held for weeks to several months while awaiting maintenance on the meter, for a replacement probe, or full instrument replacement.

pH:

We have inadequate metadata to report values prior to 1992.

For samples collected from 1992 to 1994, pH was measured in the University of Minnesota Research Analytical Laboratory. We have no other metadata on these analyses.

After that 1992 to 1994 period, all samples have been analyzed at the Forestry Sciences Laboratory in Grand Rapids. Autotitrators have been used to measure pH according to Standard Method 4500-H+ B (APHA 2017). A sodium carbonate reference (prepared in-house) was run after at least every ten samples. Samples were only analyzed if reference values were accurate to within 10 percent and pH is reported to the nearest tenth decimal place.

Sample beakers are pre-rinsed before filling with sample and rinsed before reuse with deionized water. When samples were pipetted (DL20 and DL53 titrators), a new disposable pipette tip was used for each sample.

Samples, standards, and references are measured at room temperature in a laboratory maintained at 21 degree C. Commercial buffer solutions are used for daily pH calibration.

A Mettler Instruments (Hightstown, New Jersey, USA) DL20 CompactTitrator with a ST20 Sample Changer, DV401 1-mL burette, ME-23955 Data Interface, and DL20 Controller software was used for samples collected from 1995 to 2001. A two-point calibration (pH 4.00 and 7.00 buffer solutions) was performed on each day of operation. A 40-mL aliquot of each sample was manually pipetted into a sample beaker (polypropylene) in the autosampler, which held up to 14 sample beakers. Up to three batches of samples were loaded and analyzed each day.

A Mettler Toledo (Columbus, Ohio, USA) DL53 Autotitrator with ROND060 autosampler, 10 mL burette, and LABX PC titration software was used for samples collected from 2001 to 2019. A four-point (pH = 4.0, 6.0, 7.0, and 10.0) calibration was performed and four sodium carbonate references (prepared in-house) were run on each day of operation. When check standards were accurate to within 10 percent, samples were then analyzed. Each sample was manually pipetted into a sample beaker (polypropylene) in the autosampler, which held 15 sample beakers. Each sample batch included 10 samples, a duplicate sample, and four more samples for 14 total unique samples per batch. Up to three batches of samples were loaded and analyzed each day.

A Mettler Toledo T7 Titration Excellence titrator with an InMotion Pro Autosampler, DGi11-SC combined glass pH electrode, and DV1010 interchangeable 10-mL burette is used for samples collected since 2020. An 80-mL aliquot of a sample is poured into a sample beaker (pre-rinsed with deionized water) that is placed into an InMotion Pro Autosampler that holds 69 beakers (standards, samples and reference solutions). A four-point calibration (pH = 4.0, 6.0, 7.0, and 10.0) is performed each day of operation. Between samples, tubing and the flow-through cell are rinsed with deionized water and then 30 mL of deionized water followed by 20 mL of sample to rinse tubing. The titrator then meters 50-mL of a sample into the cell for initial pH measurement and then tittering of acid for ANC measurement (not reported). Throughput per batch (50 samples plus five duplicates) is higher than the previous DL53 titrator, and checks are run after every 10 samples.

Samples for pH analysis typically were analyzed within days of collection. Although rare, samples sometimes were held for weeks to several months while awaiting maintenance on the meter, a replacement pH probe, or full instrument replacement.

Anions:

Anion (chloride and sulfate) concentrations are measured using suppressed conductivity and conductimetric detection on ion chromatographs. The methods are consistent with Standard Method 4110-C (APHA 2017).

At the Forestry Sciences Laboratory in Grand Rapids, standards were made in-house from separate chloride and sulfate certified stock solutions for samples collected through 2020. Starting with samples collected during 2021, commercially prepared certified analytical standards will be used. Commercial, certified references are analyzed with each batch of samples.

A Dionex (Sunnyvale, California, USA) 2000i/SP Ion Chromatograph with an ASM-2 autosampler, AMMS Micromembrane Suppressor, a Spectra Physics integrator (model unknown), and automation interface (unknown manufacturer and model) was used for samples collected from 1986 to 1991 and 1995 to July 1999. Dionex IonPac AG1 guard columns and AS4A columns were used for isocratic separation of anions. The detection limits are 0.1 mg chlorine/L and 0.14 mg sulfate/L.

Anion concentrations were measured in the University of Minnesota Research Analytical Laboratory for samples collected from 1992 to 1994. We have little metadata, but samples were analyzed on an ion chromatograph. Samples were shipped several times each year. The detection limits are 0.2 mg chlorine/L and 0.3 mg sulfate/L.

A Dionex DX-500 with an AS40 Autosampler, LC10-2 load module, CD20-1 conductivity detector, IP25 isocratic pump, and PeakNet Software was used for samples collected from August 1999 to 2011. IonPac AG14 pre-columns and AS14 columns (DX500) were used for isocratic separation of anions. The detection limits are 0.01 mg chlorine/L and 0.02 mg sulfate/L.

A Thermo Scientific Dionex (Sunnyvale, California) ICS-2100 with an AS-DV autosampler and Chromeleon Chromatography Data System Software was used for samples collected from 2012 to 2019. IonPac AG22 pre-columns and AS22 columns were used for isocratic separation of anions. The detection limits are 0.01 mg chlorine/L and 0.02 mg sulfate/L.

A Thermo Scientific Dionex (San Jose, California) Aquion with an AS-DV autosampler and Chromeleon Chromatography Data System Software was used for samples collected 2020 and after. IonPac AG22 pre-columns and AS22 columns are used for isocratic separation of anions. The detection limits are 0.01 mg chlorine/L and 0.02 mg sulfate/L.

Samples are poured from 250-mL LDPE sample bottles into 5-mL PolyVials (new, not rinsed). Samples are injected through 20 micrometer filter caps (Dionex 038009) into 5-mL PolyVials (038008).

In the past 10 or so years, an ion chromatograph was typically operated every business day. Daily throughput of samples was lower than the rate at which samples were sometimes collected. For that reason, samples for anion measurement were sometimes analyzed within several days of collection, but sometimes held for months to a year before analysis. Due to higher throughput on the Aquion instrument, hold times have decreased to only several weeks after an initial backlog of samples was analyzed.

Concentrations of nitrate were analyzed by ion chromatography on samples collected since 1992. However, samples for nitrate analyses were refrigerated from 1992 to 2019, not frozen. Because we now know that nitrate concentrations were unstable during refrigerated storage, we do not report nitrate concentration values. Some of the refrigerated samples may have been analyzed with short enough holding times to provide environmentally relevant and valid concentrations. However, at this time, we are not reporting any nitrate values from ion chromatography. Past assessments of MEF data should be considered with caution unless short-holding times, freezing, or validation were specified in any particular publication. We no longer determine nitrate concentrations using ion chromatography because the detection limit of 0.05 mg/L is much greater than the 0.002 mg/L detection limit of nitrate+nitrite measured using flow injection analysis.

Finally, nitrite was not separately measured using ion chromatography or flow injection analysis and nitrite standards have not been included in calibration standards. Nonetheless, nitrite peaks would appear in sample chromatograms and it has been rare in our experience to observe nitrite in MEF water samples, even when holding times were reasonable.

Cations and silicon:

Cation concentrations were analyzed by atomic absorption spectroscopy or inductively coupled plasma optical emission spectroscopy (ICP-OES). Standard method 3120 was used (APHA 2017). Concentrations of calcium, magnesium, potassium, sodium, and iron were always measured. Concentrations of aluminum and manganese were measured from 1992 to 1996 and onwards from 2009. Concentrations of silicon and strontium were added during 2009. Sampling and concentration measurement for trace constituents mercury and lead are separately described.

For samples collected from 1986 to 1991 and after July 26, 1995, samples have been analyzed at the Forestry Sciences Laboratory in Grand Rapids. Standards were made in-house from individual cation certified stock solutions for samples collected through 2020. Starting with samples collected during 2021, we will use commercially prepared certified analytical standards. Commercial, certified references were analyzed with each batch of samples. Samples are poured from 250-mL LDPE sample bottles into borosilicate or polypropylene test tubes (new, not rinsed) that are placed in autosampler racks.

A Perkin-Elmer (Norwalk, Connecticut) Model 5000 Atomic Absorption Spectrometer with a Model 3600 Data Station and an auto sampler (no product info available) was used for samples collected 1986 to 1991 and from July 26, 1995 to 2002. Samples were analyzed for calcium, magnesium, potassium, sodium, and iron. Detection limits are not specified in laboratory data reports, except for potassium (some values were reported as “<0.03” mg potassium/L). For calcium, magnesium, and sodium, we presume that all reported values are greater than detection limits, but have found no records to refute or verify that supposition.

Cation concentrations were measured at the University of Minnesota Research Analytical Laboratory for samples collected from 1992 to 1995. We have little metadata. An Applied Research Laboratories (Bausch and Lomb, Sunland, California) 3560 Simultaneous ICP was used. Samples were acidified to 1 percent nitric acid for analysis. Samples were analyzed for calcium, magnesium, potassium, sodium, aluminum, iron, and manganese concentrations. Detection limits are 0.05 mg calcium/L, 0.2 mg magnesium/L, 0.8 mg potassium/L, 0.2 mg sodium/L, 0.2 mg aluminum/L, 0.03 mg iron/L, and 0.003 mg manganese/L. Samples were shipped several times each year. Holding times were two weeks to four months before analysis.

A Thermo Electron Corporation (Waltham, Massachusetts) Iris Intrepid ICP-OES with a Thermo Elemental Timberline IIL Autosampler and iTEVA iCAP software was used for all samples collected from 2003 to 2015. Samples were analyzed for calcium, magnesium, potassium, sodium, and iron. Concentrations of silicon and strontium were measured for samples collected starting 2009. Measurements of aluminum and manganese concentrations resumed for samples collected that year and onward. Detection limits are 0.05 mg calcium/L, 0.05 mg magnesium/L, 0.5 mg potassium/L, 0.1 mg sodium/L, 0.01 mg aluminum/L, 0.05 mg iron/L, 0.01 mg manganese/L, 0.05 mg silicon/L, and 0.01 mg strontium/L.

A Thermo Scientific (Waltham, Massachusetts) ICAP 7600 Duo with an ASX-520 Autosampler and Qtegra Intelligent Scientific Data Solution Software is used for samples collected during and after 2016. Analytes are the same as the Iris Intrepid instrument. Starting 2022, radial and axial. Detection limits are 0.05 mg calcium/L, 0.05 mg magnesium/L, 0.5 mg potassium/L, 0.1 mg sodium/L, 0.01 mg aluminum/L, 0.05 mg iron/L, 0.05 mg silicon/L, and 0.01 mg strontium/L.

Samples were typically run one to four times a year in large batches of samples. Analysis occurred within several days of collection for some samples to a year from collection for those that were held longest.

Nutrients:

Prior to 2019, unfiltered samples were collected in 250-mL LDPE sample bottles after rinsing 3x with surface water. Samples were refrigerated until analyzed.

Since 2019, unfiltered water has been collected in a 60-mL high-density polyethylene bottle (HDPE) after 3x rinsing. Samples are frozen until thawed for each successive nutrient analysis. Samples were refrozen between analyses.

In the Forestry Sciences Laboratory, samples from either bottle type are poured into borosilicate (new, unrinsed) test tubes that are placed into autosampler racks. Samples for nitrogen and phosphorus chemistry are typically run once or twice a year in large batches of samples. Analysis occurs within several days of collection for some samples to a year from collection for those that are held longest.

Commercial, certified references are analyzed with each batch of nutrient samples.

Ammonium and nitrate+nitrite:

Concentrations of ammonium and nitrate+nitrite have been analyzed on samples collected since 1992. However, samples for ammonium and nitrate+nitrite analyses were refrigerated from 1992 to 2019, not frozen. Because we now know that ammonium and nitrate+nitrite concentrations were not stable during refrigerated storage, we only report ammonium and nitrate+nitrite methods and concentration values for frozen samples. Some of the refrigerated samples may have been analyzed with short enough holding times to provide environmentally relevant and valid concentrations. However, at this time, we are not reporting any pre-2019 values. Past assessments of S2 surface water based on pre-2019 values should be considered with caution unless short-holding times, freezing, or validation were specified in any particular publication.

Ammonium and nitrate+nitrite concentrations are measured on the same instrument: a QuickChem (Hach Company, Loveland, Colorado) 8500 Flow Injection Analysis System with ASX-260 Series XYZ AutoSampler, Ismatec SM933 IPC High Precision Multichannel Pump, A85132 Heater Apparatus including 175CM and 650CM Inserts, and Omnion software.

Ammonium is measured according to the Lachat QuikChem 10-107-06-1-F method. The Lachat methods are equivalent to the flow injection analysis method to form indephenol blue for colorimetric analysis (Standard Method 4500-NH3 H; APHA 2017). Ammonium is reported as the amount of nitrogen in ammonium. The detection limit is 0.01 mg nitrogen/L for ammonium.

Nitrate+nitrite is measured according to Lachat QuikChem 10-107-04-1-B. Nitrate is reduced to nitrite using the flow injection analysis (cadmium reduction) method and concentration is colorimetrically determined as the amount of nitrogen in the resulting nitrite (Standard Method 4500-NO3- I; APHA 2017). The detection limit is 0.002 mg nitrogen/L for nitrate+nitrite.

Total nitrogen, total phosphorus, and soluble reactive phosphorus:

Concentrations of these three solutes were usually analyzed using flow injection analysis (FIA). Analysis of total nitrogen started during 1997. Prior to that concentration of total Kjeldahl nitrogen (TKN; not reported) was measured. Total phosphorus concentration has been measured since 1986. Though sometimes measured before 1992, we report soluble reactive phosphorus concentration starting 1992.

Metadata are incomplete, but a Technicon AutoAnalyzer II was used for total phosphorus concentration measurement from 1986 to 1991. This instrument was at the Forestry Sciences Laboratory in Grand Rapids. Though details are incomplete, the Technicon Autonalyzer II system included a data handler, integrator, recorder, autovalve, pumps, autosampler, cartridges, and flow cells. Throughput was 50 samples per day and the detection limit was 0.01 mg phosphorus/L.

At the University of Minnesota Research Analytical Laboratory, total phosphorus concentration was measured for samples collected from 1992 to July 1997 and soluble reactive phosphorus (ortho-phosphate) concentration was measured for samples collected from 1992 to July 1997. Total phosphorus was measured by ICP (same ARL 3560 ICP that is listed for cation measurement) for samples collected from 1992 to July 20, 1995. Soluble reactive phosphorus was measured by flow injection analysis, as was total phosphorus for samples collected on and after July 25, 1995. The total phosphorus detection limits are 0.04 mg phosphorus/L for samples collected from 1992 to July 20, 1995 (when ICP was used) and 0.02 mg phosphorus/L for samples collected from July 25, 1995 to July 1997. Otherwise, we have little metadata. The SRP detection limits are 0.2 mg SRP/L for samples collected during March and April 1992 and 0.01 mg SRP/L from May 1992 to July 1997.

In the Forestry Sciences Laboratory, concentrations of the three analytes were measured using:

\* A Lachat (Milwaukee, Wisconsin) QuickChem 8000 with RAS Sampler, A82000 12 Channel Pump, A85100 Heating Unit, and Omnion FIA Software (RAS) for samples collected from September 1997 to 2014.

\* A QuickChem 8500 Flow Injection Analysis System with ASX-280 Series XYZ AutoSampler, Lachat RP-150 Series Reagent Pump, A30111 Lange Lachat QuikChem In-Line Module with heater block and ultraviolet lamp (total nitrogen), A30000 Lachat In-Line Sample Prep Module with heater block and ultraviolet lamp (total phosphorus), and Omnion software for samples collected since 2015.

Total nitrogen (TN) concentration is measured colorimetrically after in-line automated persulfate oxidation catalyzed by ultraviolet irradiation to nitrate (Standard Method 4500-N B; APHA 2017). Concentrations were measured according to the Lachat QuikChem 10-107-04-1-P method for samples collected before 2016 and Lachat QuikChem E10-107-04-3-D method thereafter. The Lange Lachat QuikChem In-Line Module with heater block and ultraviolet lamp is used in conversion of organic nitrogen to inorganic nitrogen. The detection limit is 0.05 mg nitrogen/L.

Total phosphorus (TP) concentration is measured using automated persulfate oxidation catalyzed by ultraviolet irradiation and flow injection analysis with ascorbic acid reduction for colorimetric detection (Standard Method 4500-PI; APHA 2017). Concentrations were measured according to the Lachat QuikChem 10-115-01-3-A method for samples collected from September 1997 to 2015. Lachat QuikChem E10-115-01-3-A method was used thereafter. The Lachat In-Line Sample Prep Module with heater block and ultraviolet lamp is used to convert organic phosphorus to inorganic phosphorus. The detection limit is 0.02 mg phosphorus/L for samples collected from July 1997 to July 10, 2003 and is 0.05 mg phosphorus/L for samples collected since then.

Soluble reactive phosphorus concentration (referred to as ortho-phosphate in all laboratory records) was measured according to the Lachat QuikChem 10-115-01-1-B method for samples collected from September 1997 to 2012. The Lachat methods are equivalent to the flow injection analysis method with ascorbic acid reduction and colorimetric detection (Standard Method 4500-P F; APHA 2017). The detection limit is 0.001 mg phosphorus/L.

Total organic carbon (TOC):

Total organic carbon was first measured during 1992.

At the Forestry Sciences Laboratory, unfiltered sample water was poured from a 250-mL LDPE sample bottle into a 20-mL or 40-mL vial after rinsing 3x with sample water. Samples were refrigerated until analyzed.

Concentration of TOC has been measured by sodium persulfate wet oxidation catalyzed by:

* platinum with high-temperature combustion (a Dohrmann instrument) and non-dispersive infrared (NDIR) detection (Standard Method 5310 B, APHA 2017).
* high-temperature combustion with ultraviolet irradiation (several Shimadzu instruments) and NDIR detection (Standard Method 5310 C, APHA 2017).

Concentration of TOC was measured at the University of Minnesota Research Analytical Laboratory for samples collected from 1992 to October 1995. We have little metadata other than the method detection limit (0.5 mg carbon/L) on these analyses.

After that 1992 to 1995 period, all samples have been analyzed at the Forestry Sciences Laboratory in Grand Rapids.

A Dohrmann (Rosemount Analytical, Santa Clara, California) DC-190 High-Temperature TOC Analyzer was used for samples collected from November 1995 to 2004. Concentrations were measured as total carbon minus inorganic carbon (TOC by difference, TC-IC). The instrument was calibrated using a deionized water blank and a 100-ppm sucrose standard (prepared in-house).

A Shimadzu TOC-V CPH with External Sparge Kit and ASI-V Auto-Sampler and TOC Control-V Software was used for samples collected from 2005 to 2012. Concentration was measured as TC-IC before June 2010 for samples in the 219 and 348 series, January 2011 for the 311 series. Concentration was measured as non-purgeable organic carbon (NPOC) after those specified dates.

A Shimadzu (Columbia, Maryland) TOC-L with ASI-L Auto-Sampler and TOC Control-L Software is used for samples collected from 2013 onward. Concentration was measured as NPOC on all samples. To compare the NPOC and TC-IC analyses, TOC was measured as TC-IC on a subset of samples during 2012, 2016, 2017, 2018, and 2019 for both the S2 LAGG POOL and S2 WEIR locations.

For both Shimadzu instruments, samples were poured from 250-mL LDPE bottles into 40-mL glass vials that fit an autosampler carousel that held 68 vials or into 20-mL vials that fit an autosampler carousel that held 94 vials. The instruments were calibrated using a deionized water blank and a potassium hydrogen phthalate (KHP) analytical standard (prepared in-house). The detection limit is 1 mg carbon/L for the TC-IC method and 0.5 mg carbon/L for the NPOC method of TOC analysis, regardless of instrument.

For the Dohrmann and Shimadzu instruments, A certified reference was analyzed at the beginning and end of a daily batch. Results were acceptable when references were within 10 percent of the actual value. Every tenth sample was followed by a duplicate, a deionized water blank, a sucrose reference, and perhaps an additional certified reference. Sucrose references were prepared in-house. The sucrose reference was 20 mg carbon per L for the Dohrmann instrument and rotated among 2, 5, 10, 25, 50, or 100 mg carbon per L within a batch of samples for the Shimadzu.

Sebestyen et al. (2020) show that the TC-IC and NPOC are comparable to within 10 percent relative error as a measure of TOC concentration (linear regression, p << 0.001, Pearson correlation coefficient = 0.98, n = 62, and plotting along a 1:1 relationship). We consider the two instruments and methods to be equivalent for our sites.

Samples were typically measured within days of sample collection. Rarely, samples were held for weeks or months when an instrument needed maintenance, consumables such as compressed gas, or full replacement.

Dissolved Organic Carbon (DOC):

Samples for DOC analysis are not routinely collected. When DOC concentration was measured, there was oftentimes a corresponding sample for TOC concentration measurement at the Forestry Sciences Laboratory.

Concentration of DOC has been measured by sodium persulfate wet oxidation catalyzed by:

* ultraviolet irradiation (a Dohrmann instrument) and NDIR detection (Standard Method 5310 B, APHA 2017).
* platinum with high-temperature combustion (an Oceanography International Analytical instrument) and NDIR detection (Standard Method 5310 B, APHA 2017).
* high-temperature combustion with ultraviolet irradiation (several Shimadzu instruments) and NDIR detection(Standard Method 5310 C, APHA 2017.

Additional aliquots of the biweekly samples of the S2 LAGG POOL were collected from 1993 to 1998 as part of mercury source and transport studies (Kolka et al. 1992, 2001; Fleck 1998; Grigal et al. 2000). Samples were collected in acid-washed 250-mL polyethylene sample bottles. Shipped? Samples were frozen upon arrival at the University of Minnesota Carbon Laboratory. After thawing and before analysis, samples were filtered through 0.7 micrometer glass fiber filters. The filters were precombusted. A Dohrmann DC-80 Total Organic C Analyzer. WHAT METHOD (TC-IC or NPOC?). Comparisons before and after freezing have shown that DOC concentrations can significantly decrease after sample freezing (Fellman et al. 2008). For that reason, and there being greater differences between TOC and DOC concentrations during the period when samples were frozen than any subsequent periods, we caution on the use of the 1993 to 1998 DOC concentration values. We provide those values in this data release because they have been used in past studies and we have not verified the effect of freezing on DOC concentration for S2 samples.

Aliquots of many samples from the S2 WEIR in the 348 to 351 series were collected from 2009 to 2013 as part of a study of dissolved organic matter sources, transport, and biodegradability (Sebestyen et al. 2021a). Samples were collected in 1-L acid-washed HDPE bottles or collected in new 250-mL LDPE bottles. Either bottle type was first 3x rinsed with sample water before being filled. Samples were chilled on ice, transported, and received one day after sampling at the Aquatic Ecology Laboratory at the University of Minnesota, St. Paul. Samples were filtered after receipt in the laboratory through Whatman (now Cytiva/Global Life Sciences, Marlborough, Massachusetts, USA) GF/F 0.7 micrometer glass fiber filters (precombusted) using vacuum filtration. Filters were pre-rinsed with sample water before filtration. Filtered samples were acidified to pH = 2 and stored in pre-combusted and pre-rinsed glass vials until analysis. A Shimadzu TOC-V CPH with External Sparge Kit and ASI-V Auto-Sampler was used and concentrations were measured as NPOC. Potassium hydrogen phthalate was used as an analytical standard. In addition to the research described in Jacobson (2012) and Sebestyen et al. (2021a), correlation between DOC concentration measured at the Aquatic Ecology Laboratory and TOC concentration measured at the Forestry Sciences Laboratory were used to provide evidence (linear regression, p << 0.0001, Pearson correlation coefficient = 0.87, and n = 53, and plotting along a 1:1 relationship) that TOC and DOC are equivalent (Sebestyen et al. 2020).

Some samples were collected at the S2 WEIR during 2011, 2016 and 2017 as part of a study of lead transport (Jeremiason et al. 2018) and analyzed at Gustavus Adophus College. While these samples have an accompanying sample with an identical time stamp in the 350 series (2011), 352 or 353 series (2016), or 353 series (2017) for the core suite of measurements, all of the samples have six-digit serial identification numbers that start with 399 or 400. These samples were collected into 125-mL polyethylene terephthalate glycol (PETG) sample bottles. Samples were shipped overnight. Upon receipt, the samples were filtered through 45-mm diameter Whatman 0.7 micrometer glass fiber filters in BRAND (CITY, STATE) MODEL filter holders and acidified by adding 0.5% (volume/volume) 12 molar hydrochloric acid. Filters were precombusted at 450 degrees Celsius for 4 hr. An aliquot was poured from a PETG bottle into a borosilicate vial to measure TOC using the NPOC method on a Shimadzu TOC-V with ASI-V autosampler. The auto dilution feature of the TOC analyzer was used to calibrate using three different concentrations from a KHP reference standard. A sucrose and OTHER SOLUTION reference were run after every 10 samples. Samples may have been held for up to 3 months after acidification.

Three samples (serial identifiers 352011, 352020, 352033) were collected during 2014 and sent to the US Geological Survey Organic Carbon Laboratory in Boulder, Colorado. Samples were pumped with a peristaltic pump (Global Water Instrumentation, Phoenix, Arizona, USA, SP100 Water Sampler with silicon pump tubing). Samples were field-filtered through GeoTech (Geotech Environmental Equipment, Inc, Denver, Colorado, USA) 0.45 micrometer High Capacity Disposable Filters and collected in 1-L amber glass bottles with PTFE lined caps. Filters were first rinsed with at least 10 mL of surface water and bottles were 3x rinsed with filtered water prior to filling. Concentration of DOC was measured using an Oceanography International Analytical Model 700 Carbon Analyzer (Aiken 1992).

Some samples from 2014, 2015, and 2018 were analyzed at the Forestry Sciences Laboratory in Grand Rapids. Samples were either field collected in Norm-Ject 60-mL Luer Lock Syringes (polypropylene barrel and polyethylene plunger; Henke Sass Wolf, Tuttlingen, Germany) or poured from 250-mL LDPE sample bottles into the syringe barrel in the laboratory. For field filtration, a syringe was 3x rinsed with deionized water before a day of sampling and 3x rinsed in between samples with water that was to be collected. In the laboratory, a syringe was 3x rinsed with deionized water between samples, then 3x rinsed with sample water. Samples were filtered through Whatman (Cytiva/Global Life Sciences, Marlborough, Massachusetts, USA) Puradisc 25 GF/F 0.7 micrometer disposable (polypropylene housing) glass fiber filters. A filter was rinsed with about 5 mL or more of stream water prior to 3x rinsing of a vial with filtered water. Filtered water was then collected into a 40-mL glass vial with a cap (PTFE lined silicone septa) that fit into a Shimadzu autosampler rack (same instrument and methods as listed above for TOC analyses on the TOC-L instrument).

Liquid Water Isotopes:

The natural abundances of water stable isotopes (deuterium and oxygen-18) were measured using laser absorption spectroscopy (Lis et al. 2008).

An aliquot of some samples during 2007, and most samples thereafter, was collected in a 16-ml scintillation vial with a Wheaton (DWK Life Sciences, Millville, New Jersey) Polyseal cap (phenolic with polyethylene cone line) for liquid water isotope analysis. Vials for water isotope samples were completely filled, with no headspace or bubbles. Water isotopes samples are stored at room temperature in the Grand Rapids Forestry Sciences Laboratory before being analyzed there or shipped to other laboratories for analysis.

The glass scintillation vials for water isotope measurement are stored in a sample archive and are available for eventual analysis. Some samples have been analyzed on Los Gatos Research (Mountain View, California) DLT-100 Water Isotope Analyzers at Plymouth State University (Center for the Environment Analytical Laboratory), the University of California (Stable Isotope Facility, Davis), the University of Minnesota (Biometeorology Laboratory, St. Paul), or the University of Toronto (Integrated Watershed Hydrology and Biogeochemistry Research Facility, Scarborough, Ontario, Canada); a Picarro Inc (Santa Clara, California) L11102-I at Oak Ridge National Laboratory; or a Los Gatos Research T-LWIA-45-EP liquid water isotope analyzer at the Grand Rapids chemistry laboratory. Further information can be found in Stelling et al. (2021a, b).

All laboratories used similar procedures and certified water isotope standards. Six or seven injections (0.5-1.2 microliter) of a sample were analyzed. Isotopic values are reported relative to the Vienna Standard Mean Ocean Water (VSMOW)-Standard Light Antarctic Precipitation (SLAP) scale. In each laboratory, a series of secondary standards were calibrated to VSMOW and SLAP. Machine raw data post-processed to account for machine drift and between-sample memory (Wassenaar et al., 2014). Values for deuterium (D) and oxygen-18 (O-18) are reported in delta-notation (permil or per mil relative to VSMOW; Craig 1961). All laboratories used similar procedures to operate the instruments and post-process the isotopic ratios (Stelling et al. 2021). Each laboratory had slightly different analytical precisions for delta deuterium and delta oxygen-18 values:

\* 0.8 permil for delta-D and 0.1 permil for delta-O-18 at Plymouth State University,

\* 2 permil for delta-D and 0.25 permil for delta-O-18 at the University of California,

\* 1 perml for delta-D and 0.25 permil for delta-O-18 at the University of Minnesota,

\* 0.8 permil for delta-D and 0.25 permil for delta-O-18 at the University of Toronto,

\* 0.5 permil for delta-D and 0.1 permil for delta-O-18 at Oak Ridge National Laboratory

\* 0.5 permil for delta-D and 0.1 permil for delta-O-18 at the Grand Rapids Forestry Sciences Laboratory.

Samples have holding times of more than a decade before some samples have been analyzed, which is not a concern as long as the vials remain sealed. Samples are disposed after analysis and quality assurance/quality control checks.

Ferrous and Ferric Iron:

An aliquot of a weekly sample from September 2016 to November 2020 was collected for determination of ferric and ferrous iron concentration. Samples were collected at both the S2 LAGG POOL and S2 WEIR for a study of iron mediated carbon cycling. These samples had IDs in the 353, 354, and 355 series.

Samples bottles for ferrous and ferric iron analysis were not rinsed because each bottle received 0.5 ml (30-ml bottle) or 1 ml (60-ml) of 12 mol/L high-purity trace-metal grade hydrochloric acid in advance of sampling to preserve iron speciation in samples. Bottles for ferric/ferrous iron analysis were either refrigerated or stored at room temperature, and later shipped (up to several times a year) to Iowa State University for analysis.

Total iron and ferrous iron concentrations were colorimetrically measured using the high-throughput ferrozine method (Huang and Hall 2017) on a microplate spectrophotometer (Biotek Synergy HT, Winooski VT). Ferric iron concentration was calculated as the difference between total iron and ferrous iron concentrations (Huang and Hall 2017). The calculation of ferric iron concentration sometimes resulted in small negative values for samples with extremely low ferric iron concentrations. The median absolute value of these negative numbers was used as the detection limit for ferric iron concentration (0.07 mg/L) and positive ferric iron concentration values within this range are reported as zeroes. The detection limit is 0.04 mg/L for ferrous iron.

When a particular sample was higher in concentration than the highest calibration standard, that sample was diluted and re-run until within the range of the calibration standards.

The sum of ferrous and ferric iron concentrations from colorimetric analysis occasionally exceeded the total iron values measured by ICP-OES at the Grand Rapids Forestry Sciences Laboratory. This discrepancy is likely a result of dissolution of particulate iron from occasional peat fragments in the acidified (pH < 2) samples used for ferrous and ferric iron analysis. Samples for colorimetric analysis were collected in pre-acidified bottles to inhibit oxidation of ferrous iron to ferric iron during sample storage. Samples for ICP-OES analysis were not similarly acidified for storage and analysis.

Acidified samples were held for weeks or months to several years before analysis. Samples were analyzed between 2016 and 2021.

Total mercury, methylmercury, and lead:

For various studies since 1993, an aliquot for total mercury (THg) and methylmercury (MeHg) determination was collected for select samples and various research projects. From 1993 to 1998, samples were only analyzed for THg. During 1999 and 2000, there were no samples. Sampling every 1 to 2 weeks resumed during 2001 and both THg and methylmercury (MeHg) concentration were measured. Both unfiltered and filtered samples have been analyzed, though rarely on the same sample except for weekly samples from 2017.

Sampling techniques have been fairly consistent among studies. All samples were collected using US EPA method 1669 (US EPA 1996) for trace metal sampling of ambient waters, though the method was modified to oftentimes allow collection by a single person. Ultra-clean trace metal protocols were used during sampling and for sample processing equipment.

Since 2008, many samples collected using ultra-clean sampling techniques were also analyzed for lead to assess long-term ecosystem responses to this legacy pollutant (Jeremiason et al. 2018).

Numerous laboratories have been used to analyze samples with various instruments. Methods for THg were fairly similar and concentration was most often measured using cold vapor atomic fluorescence spectroscopy (CVAFS). One laboratory used isotope dilution and detection by inductively-coupled plasma mass spectrometry (ICP-MS; e.g., Hintelmann and Ogrinc 2002).

MeHg was measured using distillation, aqueous ethylation, purge and trap, and CVAFS (US EPA 1998; Method 1630).

From 1993 to 1998, an aliquot of a sample from the S2 LAGG POOL was collected, except one sample from March 27, 1996 that was collected at the S2 WEIR when S2 LAGG POOL was inaccessible due to ice. A mercury analysis aliquot was collected in an acid-washed 30-mL or 125-mL Teflon (PTFE, polytetrafluoroethylene) bottle that was rinsed three times with surface water before being filled. Unfiltered samples were collected from April 1993 to June 1998. Samples were acidified to 0.5 percent (volume per volume) with trace metal grade nitric or hydrochloric acid within hours of collection and then transported to the University of Minnesota (St. Paul). Samples were either stored in a dark refrigerator or frozen prior to analysis. Total mercury was measured using a Brooks-Rand Model III cold vapor atomic fluorescence spectrometer with Mercury Guru 2.0 Software (Seattle, Washington, USA). More details on the field sampling, laboratory, and analysis are provided by Kolka (1996). These data were used in studies of THg transport (Kolka et al. 2001; Grigal et al. 2000). The detection limit is #.## ng THg/L.

After that first period, most samples were collected at the S2 weir. Total mercury was analyzed according to US Environmental Protection Agency method 1631 Revision E (US EPA 2002).

From 2001 to 2008, samples were collected at the S2 WEIR to serve as a reference for experiment to assess mercury cycling and transport responses to sulfate pollution at the S6 catchment (Jeremiason et al. 2006). These samples were labelled with seven-digit 2001, 2002, 2003, and 2004 series, and six-digit 295, 296, 307, 308, 309, and 310 ID series. MOST NO TIME. Samples were pumped from the weir pool using a Geopump Peristaltic Pump (Geotech Environmental Equipment) with Teflon tubing. Stream water was pumped through the entire length of tubing as a rinse. Then, a Teflon filter holder (Savillex MODEL, Eden Prairie, Minnesota) with 47-mm diameter 0.7-micrometer glass fiber filter (GF/F) was attached and rinsed for 3 seconds Two new 125-mL polyethylene terephthalate glycol (PETG) sample bottles were then filled after 3x rinsing with filtered sample water. Prior to filtration, filters were combusted for 4 hours at 500 degrees Celsius. Samples were acidified to 0.5 percent (volume per volume) with trace metal grade hydrochloric acid (HCl) within 1 hour. Field duplicates and equipment blanks were collected every 10 samples. While several laboratories were used for THg and MeHg analysis, procedures were similar among those laboratories. Instruments were calibrated daily and deionized water blanks, sample duplicates, and matrix spikes were included with each analytical run. Results were acceptable when references were within 15 percent of the actual value for both THg and MeHg concentrations.

2001 - 2003 Nater lab. THg was measured using a Tekran 2400 (Toronto, Ontario, Canada). #.## ng THg/L and #.## ng MeHg/L.

2005 Branfireun lab MeHg and THg 2005-2008. Class 100 cleanroom at the University of Toronto (US EPA 1998, 2001; methods 1630 and 1631). MeHg aqueous phase ethylation MeHg Tekran 2500. THg Tekran model 2600 Automated Sample Analysis System CVAFS. DL = 0.06 ng Hg / L. #.## ng THg/L and #.## ng MeHg/L.

2006 Jeremiason laboratory MeHg. Agilent 7700. #.## ng THg/L and #.## ng MeHg/L. Lead ICP-MS. Dilute sample (100-fold dilution). Check standard, analytical standard, 15 samples then standards and check. THg CVAFS Brooks Rand Merc/T Mercury Analysis System. MeHg Standard dual amalgamation method.

2007 - 2008 Balogh lab MeHg. #.## ng THg/L and #.## ng MeHg/L.

2009 - 2011 Mitchell UT lab. #.## ng THg/L and #.## ng MeHg/L.

2008 – onward Tsui, Nater S2 WEIR sampling: From 2008 to 2010, a weekly sample was collected in a 0.5-L, 1-L, or 2-L Teflon sample bottle, shipped overnight to the University of Minnesota (St. Paul). #.## ng THg/L and #.## ng MeHg/L.

2008 –Jeremiason S2 WEIR sampling: ICP-MS (Agilent 7700 series). Water samples were diluted with 0.32 M nitric acid (HNO3) prior to addition of internal standard (Inorganic Ventures ICPMS-71D) followed by analysis. Recovery of Pb from

standard reference materials (MESS-3 (marine sediment; 21.1 ± 0.7 μg/g) and SLRS-5 (riverine water; 0.081 ± 0.066 μg/L), National Research Council Canada) were always within the range of certified values. #.## ng THg/L and #.## ng MeHg/L.

Samples for mercury studies were in seven-digit serial identification series that started with the year of sampling followed three decimal places from 2001 to 2004, with several samples in 2005 identified that way. For example, 2001.001 for the first sample collected in 2001. Most samples during and after 2005 were labelled with a six-digit serial identifier that started with 296 during 2005, 295 during 2006, 307 during 2007, and 308 and 309 during 2008. Three samples had an eight-digit identifier with 1 decimal place (i.e., 307309.1, 308007.1 and 308657.1). Samples during 2009 were labelled in the 310 and 311 series when two samples were collected: one for Hg analyses (310 series) and another the core suite of analytes (311 series).

REPORTED VALUES:

To document when a sample was collected, we include a laboratory ID, sample name, and date/time of collection. Sometimes chemistry values are assigned -9999 for individual solutes or for all analytes (i.e., pH, specific conductivity, and solute concentrations), which may have resulted from insufficient sample volume to complete all analyses, contamination that affected individual solutes or suites of analytes that were simultaneously measured on a single instrument for a particular sample, or contamination that affected all solutes for a particular sample. Samples pending analysis are also assigned a value of -9999.

Concentrations of ammonium and nitrate+nitrite are only reported onward from 2019 when aliquots were frozen for analysis (see above). Values are reported as -9999 prior to preservation with freezing.

Concentrations of ferrous and ferric iron are only reported between September 2016 to October 2020. Select samples were analyzed.

Data values below the detection limit are reported in the data file and are not flagged. Detection limits, as listed above, must be considered when using these data.

MARCELL EXPERIMENTAL FOREST sites and data collection are described in further detail in:

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