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RESEARCH AND OBSERVATORY CATCHMENTS: THE LEGACY AND THE FUTURE

WILEY

The stable isotopes of natural waters at the Marcell Experimental Forest

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Abstract

We present a new data set from the Marcell Experimental Forest (MEF) that compiles water isotope measurements from multiple research catchments, some of which have been studied since the 1960s. The MEF is located in northern Minnesota, USA, and is home to heavily studied and monitored forests, streams, bogs, and fens. Peat-forming systems (bogs and fens) are an important component of the MEF landscape and have a profound impact on the water cycle in these catchments. Within the last decade, analysis of stable isotopes of water (expressed as δD and $\delta^{18}O$) has been implemented to characterize the different components of the water budget, and to allow researchers to look at catchment and peatland-specific hydrologic effects in the watershed. This δD and $\delta^{18}O$ data set of natural waters from MEF catchments is primarily composed of measurements from three peatlands (S1, S2, S6) during an 11-year period. More recently collection and analysis were expanded to also include samples from the Spruce and Peatland Responses Under Changing Environments (SPRUCE) project in the S1 bog, peatlands S3, S4, S5, as well as nearby lakes. We establish a local meteoric water line by analyzing the isotopic composition of precipitation, which fills a void in regional meteoric water lines for Minnesota. Furthermore, we establish baseline isotopic composition for bog outlet streams, bog porewater, aquifer groundwater, overland flow, subsurface stormflow, and snowpack, as well as runoff from the SPRUCE experimental chambers. These data are publicly available and will be expanded upon in the future.

KEYWORDS

bog, fen, local meteoric water line (LMWL), peatland, research catchment, stream, water isotopes, $\delta^{18}O$, δD

1 | DATA SET NAME

Marcell Experimental Forest stable isotopes of water, 2008 - ongoing.

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2 | DATA SET IMPORTANCE AND CONTRIBUTION

These data contribute to an improved understanding of hydrological processes by providing a synthesis of timeseries based-, geolocated, baseline, observational, event-based, and experimental data on isotopic signatures of waters collected from peatlands and surrounding catchments in the Marcell Experimental Forest (MEF). Stable isotope ratios of water ($^2H/^1H$ and $^{18}O/^{16}O$) are commonly used tracers in catchment hydrology. First studied for understanding isotopic fractionations associated with the water cycle (Craig et al., 1963; Dansgaard, 1964), stable isotopes are also useful for process understanding in catchment studies (Kendall & McDonnell, 1998). Isotopic geochemical data have been readily used in catchment and peatland study (Kalvāns et al., 2020; Levy et al., 2014, 2016; Sprenger et al., 2017) and these baseline values can be used for modelling catchment and peatland hydrology (Isokangas et al., 2017; Tetzlaff et al., 2015), or in multidisciplinary research such as providing modern values used for paleohydrological interpretations from peat archives (J. Nichols et al., 2010; Stelling & Yu, 2019; Xia et al., 2020).

In this data note, we describe a data set on the natural-abundance isotopic composition of waters from small catchments in the MEF, located in northern Minnesota, USA (Figure 1) and administered by the USDA Forest Service (Kolka et al., 2011). The catchments are headwaters that drain to the Mississippi River and Hudson Bay, making this an important site for study in North America (D. S. Nichols & Verry, 2001; Verry et al., 2011). The MEF watersheds have been studied since 1961, with a long record of data and experimentation on the hydrology and the ecology of these small peat-dominated catchments (Sebestyen et al., 2011). Understanding the isotopic composition at the peatland sources, as well as influent waters, will give greater insight into the water budget and hydrological cycle. Furthermore, one of our study bogs is the site of the Spruce and Peatland Responses Under Changing Environments (SPRUCE) experiment (Hanson et al., 2017), extending the relevance of these data beyond hydrology to diverse scientific disciplines.

Here we outline the isotopic data of water samples collected over 11 years from a suite of locations within peatland-dominated catchments including local precipitation, snowpack, bog and lagg porewaters, outlet stream, overland flow, subsurface stormflow, aquifer groundwater, upland mineral soil, and nearby lakes. Our intention is to provide these isotope data to refine estimates of how water from precipitation partitions into streamflow, evapotranspiration, groundwater recharge, upland runoff, and soil water storage.

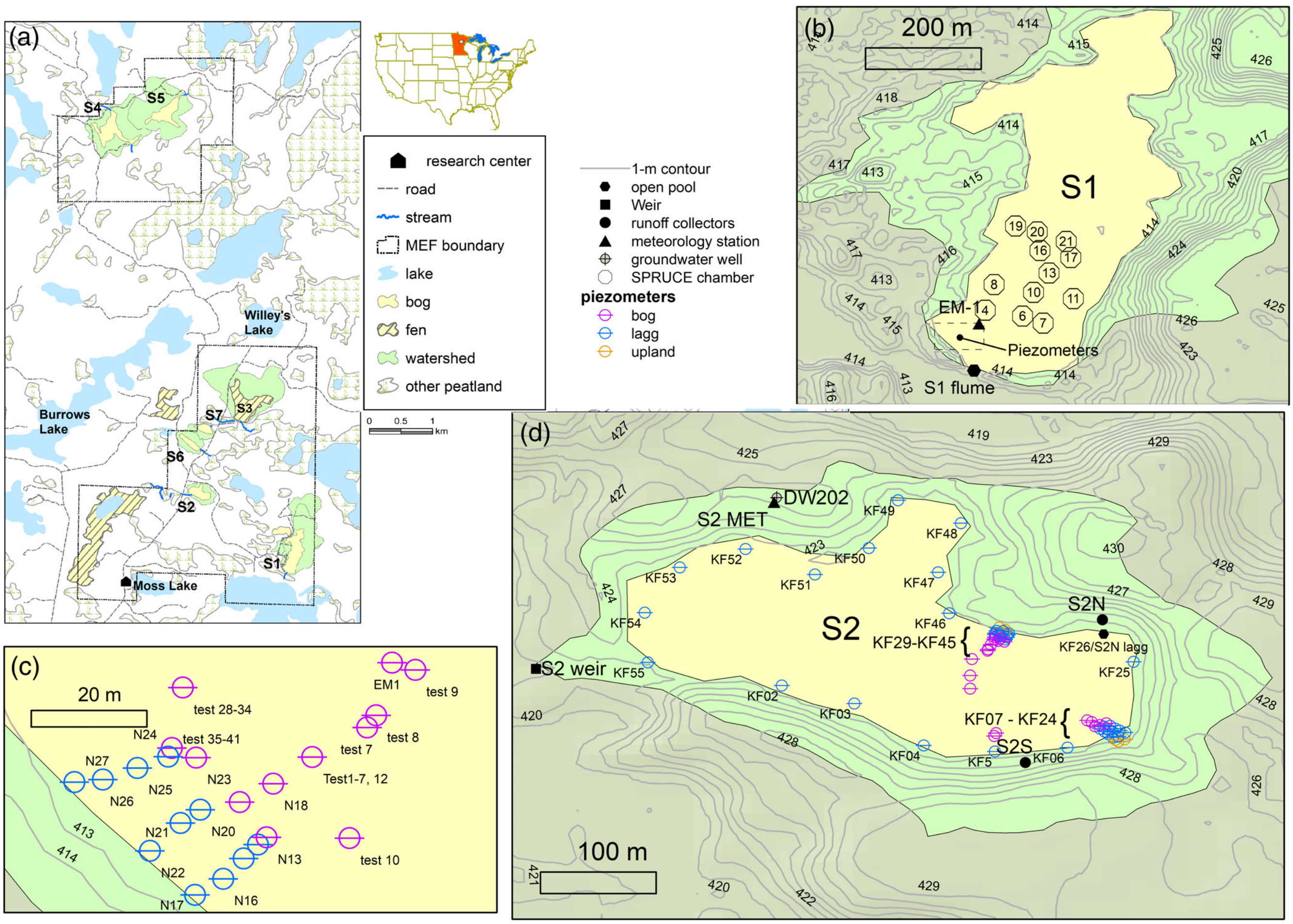

FIGURE 1 Study sites and sampling locations in the Marcell Experimental Forest (MEF). Sampling locations in (a) the peatland study sites of the MEF south unit, Minnesota, USA including S1, S2, S3, S4, S5, S6, and nearby lakes; (b) the S1 bog with the location of the outlet stream (S1 flume), piezometers, and current SPRUCE plot locations (each of which contains a nested set of depth-specific piezometers); (c) detail of S1 piezometer locations in the southern end of the bog; (d) the S2 bog, including S2 MET (precipitation), groundwater well (DW 202), outlet stream (S2 weir), runoff collectors (S2N/S2S), and piezometer nest

3 | STUDY SITE DESCRIPTION AND SAMPLING LOCATIONS

From 1961 to 2019, the MEF (47.51°N, 93.47°W) had a mean air temperature of 3.5°C and mean annual precipitation of 787 mm (Sebestyen, Lany, Roman, et al., 2021). The research catchments within the MEF have a maximum relief of 12 m and contain raised-dome *Sphagnum-Picea* bogs or fens (Sebestyen et al., 2011; Sebestyen, Lany, Roman, et al., 2021). Water sampling for isotopic analysis began in 2008 at three sites (Table 1); the S1 bog (8.1 ha) lies within a 33.2-ha catchment with an outlet elevation at 412 m, the S2 bog (3.2 ha) is in a 9.7 ha catchment with an outlet elevation of 420 m, and the S6 bog (2.0 ha) is in catchment of 8.9 ha with outlet elevation of 423 m (Figure 1). The data set was further expanded to include samples from a greater number of surrounding bogs, fens, and lakes; the S3 fen (18.6 ha), the S4 bog (8.1 ha), the S5 bog (6.1 ha), Willey's lake (20 ha), Sand lake (75 ha), Burrow's Lake (115 ha), Moss Lake (12 ha), and a small pond near S6 named the 'S6 source pond' (1 ha) as this pond was the water source for experimental irrigation of the S6 bog (Coleman Wasik et al., 2012; Jeremiason et al., 2006).

The most extensively studied and sampled sites are the S1 and S2 bog; with the S2 being a reference peatland, and S1 being the site of two experiments over the 60-year history of the MEF including a harvest study, and now being the site of the SPRUCE whole-ecosystem-warming, and increased CO_2 experimental treatments (Hanson et al., 2017).

Most samples taken from the S1 bog (Figure 1b) are focused on the SPRUCE experiment, although some pilot study samples were taken from the southern end of the bog prior to the implementation of the SPRUCE experiment, and longer-term sampling of water from the outlet stream dates back to 2010. The samples from the S1 bog include: aquifer groundwater, bog porewater, including porewater at different depths within the SPRUCE experiment (bog), lagg porewater (lagg), precipitation, outlet stream, and SPRUCE chamber runoff (runoff). Collection of these samples spans from 2010 through 2020, with a subset of the samples from discrete periods completed for isotopic analysis (Table 1).

TABLE 1 Peatland water sampling by site and associated types

Site	Latitude/Longitude	Site type	Sample type	Sampling frequency	Temporal range	*n*=
S1	47.504, −93.454	Bog	Aquifer groundwater	Monthly	Aug 2016 and Aug 2019	16
			Bog	Weekly-bimonthly	Jun 2010–Aug 2019	869
			Lagg	Weekly-bimonthly	Sep 2011–Aug 2013	132
			Precipitation	Post-event	Aug 2016–Nov 2020	70
			Runoff[a]	Post-event	Aug 2016–Nov 2020	230
			Stream	Bi-weekly-monthly	Mar 2010–Nov 2020	85
S2	47.514, −93.473	Bog	Aquifer groundwater	Monthly	Jan 2010–Feb 2020	22
			Bog	Weekly-bimonthly	Jun 2010–Oct 2019	208
			Lagg	Weekly-bimonthly	Mar 2009–Oct 2019	618
			Precipitation	Post-event	Mar 2009–Mar 2020	188
			Snowpack	Monthly	Jan 2010–Mar 2019	52
			Soil water	Bimonthly	Nov 2009–Oct 2019	75
			Stream	Biweekly-monthly	Jul 2008–Jan 2020	281
			Overland flow	Post-event	Apr 2008–Oct 2019	38
			Subsurface stormflow	Post-event	Mar 2009–Mar 2020	250
S3	47.523, −93.475	Fen	Stream	Monthly	Dec 2018, Oct 2019	3
S4	47.558, −93.482	Bog	Stream	Monthly	Dec 2019–Feb 2020	3
S5	47.564, −93.473	Bog	Stream	Monthly	Dec20 19, Feb 2020	2
S6	47.520, −93.470	Bog	Stream	Monthly	Apr 2008–Feb 2020	40
			Subsurface stormflow	Weekly	Oct 2019	3
S6 source pond	47.521, −93.475	Lake	Lake	Weekly	Aug-Oct 2020	15
Burrows	47.520, −93.506	Lake	Lake	Monthly	Aug–Oct 2020	3
Moss	47.503, −93.482	Lake	Lake	Monthly	Aug–Oct 2020	3
Sand	47.488, −93.503	Lake	Lake	Monthly	Aug–Oct 2020	3
Willey's	47.534, −93.461	Lake	Lake	Monthly	Aug–Oct 2020	3

Note: Date range and *n* = correspond to the range of available data at the publication of this manuscript. These data will be increased as research is ongoing.

[a]Runoff from the SPRUCE enclosures (Sebestyen & Griffiths, 2016).

The S2 catchment (Figure 1c) has had no large-scale experiments and only minimal disturbance associated with monitoring and sampling equipment and boardwalks installed for access (Sebestyen et al., 2011). Much of the research has been focused on differentiating how biogeochemical and hydrological processes vary between the lagg (peatland surrounding the bog) and the bog (Mitchell et al., 2008; Richardson et al., 2010). In the uplands, the chemistry and amounts of overland and subsurface stormflow have been quantified (Verry et al., 2011; Verry & Timmons, 1982). The types of samples analyzed from the S2 bog include: aquifer groundwater, porewater (bog and lagg), precipitation, snowpack cores (snow), upland soil water, outlet stream, and overland flow and subsurface stormflow. These waters were sampled from 2008 through 2020, with a subset of the samples from discrete periods completed for isotopic analysis. See Table 1 for specifics on the sample types and sampling frequency and range.

As this data set is a compilation of isotope data from different projects over the last decade, the samples collected from each location and for each type may not be regular over the entire 11-year time span. Sampling of some waters ranges broadly from 2010–2020, others have a shorter period with higher frequency or a greater geographic range represented. We have summarized the waters by sample type, temporal range, and frequency in Table 1.

4 | METHODS AND MATERIALS

4.1 | Sampling methods

While this data set includes a compilation of several different projects, all sampling was done by or supervised by one person (S.D. Sebestyen), ensuring common quality standards to prevent the contamination or post-collection evaporative enrichment prior to analysis. All waters were collected with associated chemistry sampling and aliquots were stored in 16 ml glass vials—without headspace—at room temperature until analysis in various laboratories. Samples of aquifer groundwater were collected from wells drilled to the water table in the surrounding uplands of the S1 and S2 catchments. The wells penetrate 3.4 to 14 m through soil and a glacial till into the aquifer in a deep (∼50 m) outwash sand deposit (Verry et al., 2011). Precipitation was collected with funnel collectors draining through tubing to HDPE (high-density polyethylene) receiving bottles in the S2 uplands, and at three sites in the S1 bog. These samples were collected within 24 hr. of a precipitation event, though collection can be delayed if an event occurs on a weekend or a holiday. Snowpack water was collected by coring the snow with a PVC pipe, both in a forest opening and below the deciduous overstory forest canopy. For snowpack samples, the PVC pipe was driven into the snow until the ground surface was reached. Snow was then excavated from around the pipe and a plastic bag placed underneath to catch the snow as the PVC pipe was lifted. Excess air was removed from the resealable plastic bags, then the snow was allowed to melt, and the water was transferred to glass vials without headspace. Samples from lakes or open pools were taken using a 500-ml dipper.

Stream water was collected from the outlet streams at S1, S2, S3, S4, S5 and S6, with weirs at S2, S4, S5 and S6. Overland flow and subsurface stormflow from the upland surrounding S2 were collected from mineral-soil hillslopes using runoff collectors (Mutchler, 1963) that funnel surface and sub-surface (at the Bt horizon) waters via PVC piping into collection tanks (Sebestyen & Kyllander, 2018). Piezometers were used to sample porewaters and are located in the bog interior (S1 and S2 bog), bog perimeter (S1 and S2 lagg), and upland mineral soil (S2 upland) adjacent to the peatland (Figure 1). The piezometers are screened over 10 cm at the surface (S2 bog, lagg, and upland, and S1 lagg) or nested at different depths from 0 to 3 m (S1 bog).

There are many additional archived samples from these sites and water types on other dates, as well as many other locations within the MEF. These samples represent a vast archive, with water isotope analysis ongoing as time and resources allow. Additionally, each sample has corresponding water chemistry data, some of which are already published (Griffiths & Sebestyen, 2016; Griffiths et al., 2016; Sebestyen, Funke, et al., 2020; Sebestyen, Griffiths, et al., 2020; Sebestyen, Kyllander, et al., 2021; Sebestyen, Lany, Larson, et al., 2021).

4.2 | Water isotope analysis methods

The natural abundance of stable isotopes of hydrogen (H) and oxygen (O) were measured with laser absorption spectroscopy (Lis et al., 2008). As this data set is a composite of several different projects, multiple laboratories have been used for measurements (Table 2). All labs used similar procedures; unfiltered natural waters (6–7 injections of 0.5–1.2 ul sample) were analyzed in the various machines. Isotopic values were scaled relative to the Vienna Standard Mean Ocean Water (VSMOW)-Standard Light Antarctic Precipitation (SLAP) scale. All labs used a series of secondary standards that are calibrated to VSMOW and SLAP. Values for deuterium (D) and oxygen-18 (^{18}O) are reported in delta-notation (δ) in per-mille or permil (‰) relative to VSMOW (Craig, 1961). Isotopic values were quality checked by all laboratories. Each used post-processing software to minimize and correct for machine drift, between-sample memory, and outlier measurements as in Wassenaar et al. (2014).

5 | NEW PRODUCTS FROM THIS DATA SET

The local meteoric water line (LWML) for the MEF (Figure 2) is determined using precipitation samples ($n = 258$) from the S1 and S2 bog. The best fit (using non-volume weighted, ordinary least squares regression) for this line is $\delta D = 7.93\ \delta^{18}O + 9.41$ ‰ (adj. R-squared $= 0.99$), which is relatively similar to the Global Meteoric Water Line (GMWL) $\delta D = 8\ \delta^{18}O + 10$ ‰ (Craig, 1961). A seasonal pattern is found with precipitation in the summer (June, July, August-JJA) being relatively enriched in heavy isotopes. In winter (December, January, February- DJF) the precipitation is relatively depleted. The

TABLE 2 Laboratories for water isotopic analysis

	Lab	Institution	Model	Manufacturer	Machine precision (±)	Sample year
ORNL	Ecosystem Laboratory	Environmental Sciences Division, Oak Ridge National Laboratory	L1102-i	Picarro Inc., Santa Clara, California.	0.5 ‰ δD 0.1 ‰ $\delta^{18}O$	2010–2013
PSU	Center for the Environment Analytical Laboratory	Plymouth State University	DLT-100	Los Gatos Research, Inc, Mountain View, CA, USA	0.8 ‰ δD 0.1 ‰ $\delta^{18}O$	2008–2010
U of T	Integrated watershed hydrology and biogeochemistry research facility	Department of Physical and Environmental Sciences, University of Toronto Scarborough	DLT-100	Los Gatos Research, Inc, Mountain View, CA, USA	0.8 ‰ δD 0.25 ‰ $\delta^{18}O$	2010–2012
UMN	Biometeorology Lab	University of Minnesota-Twin Cities	DLT-100	Los Gatos Research, Inc, Mountain View, CA, USA	1 ‰ δD 0.25 ‰ $\delta^{18}O$	2009 and 2010
FSGR	USDA Forest Service, Northern Research Station	Grand Rapids, Minnesota	T-LWIA-45-EP	Los Gatos Research, Inc, Mountain View, CA, USA	0.5 ‰ δD 0.1 ‰ $\delta^{18}O$	2016 and 2019–2020, ongoing
SIF	Stable Isotope Facility	University of California, Davis	DLT-100	Los Gatos Research, Inc, Mountain View, CA, USA	≤2 ‰ δD ≤0.3 ‰ $\delta^{18}O$	2011

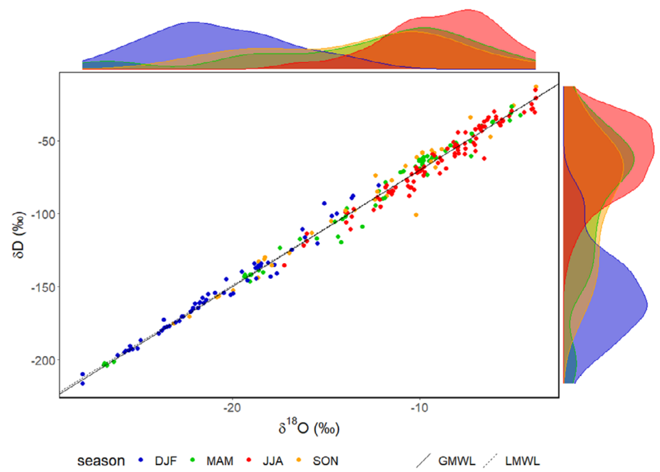

FIGURE 2 Precipitation water stable isotopes from the S2 bog in the MEF. The precipitation data ($n = 258$) are plotted along with a local meteoric water line (solid line: $\delta D = 7.93 \times \delta 18O + 9.41$) and the global meteoric water line (dashed line: $\delta D = 8 \times \delta 18O + 10$). Different symbols correspond to different seasons (DJF = winter; MAM = spring; JJA = summer; SON = fall) and margins displaying density function along each axis

spring and fall both have large overlapping ranges with the other seasons.

A composition time series of precipitation and snowpack from the S2 bog shows the seasonal cycle of $\delta^{18}O$ and δD in precipitation and the snowpack (Figure 3). The time series of water isotope data from the bog waters, upland waters, and outlet streams highlight annual and interannual patterns that we are further investigating in the context of water budgets and catchment processes (Figures 4 and 5).

Beginning in fall 2020 lakes in the nearby region show enriched $\delta^{18}O$ and this appears to be a signal of lake evaporative enrichment, at least in the near-surface waters (Figure 6).

5.1 | Data set contributors

We would like to acknowledge K. Fitzgerald (Michigan Technological University, currently at the National Center for Atmospheric Research) for her early contributions to water isotope studies at the MEF and all who assisted with field sampling: A. Gorham, T. Wojciechowski, J. Prososki, M. Olds, M. Wiley, L. Kastenson, R. Peterson, B. Munson, C. Dorrance, D. Kyllander, and T. Roman (USDA Forest Service), M. Mack, L. Mielke, T. Vang, and A. Gapinski (University of Minnesota). We also thank K. Reynolds, J. Warren, J. Childs, M. Dunham, K. Oleheiser at Oak Ridge National Laboratory and K. King, L. Rosen, and K. Xiao at the University of Minnesota for assistance with sample collection and analysis.

5.2 | Funding and data ownership

This work was a collaborative effort receiving funding and support from multiple organizations: (1) The Northern Research Station of the USDA Forest Service funds the operation of the Marcell Experimental Forest, sample collection, the NRS Grand Rapids laboratory and the contributions of S.D. Sebestyen, K. Fitzgerald, and all other Forest

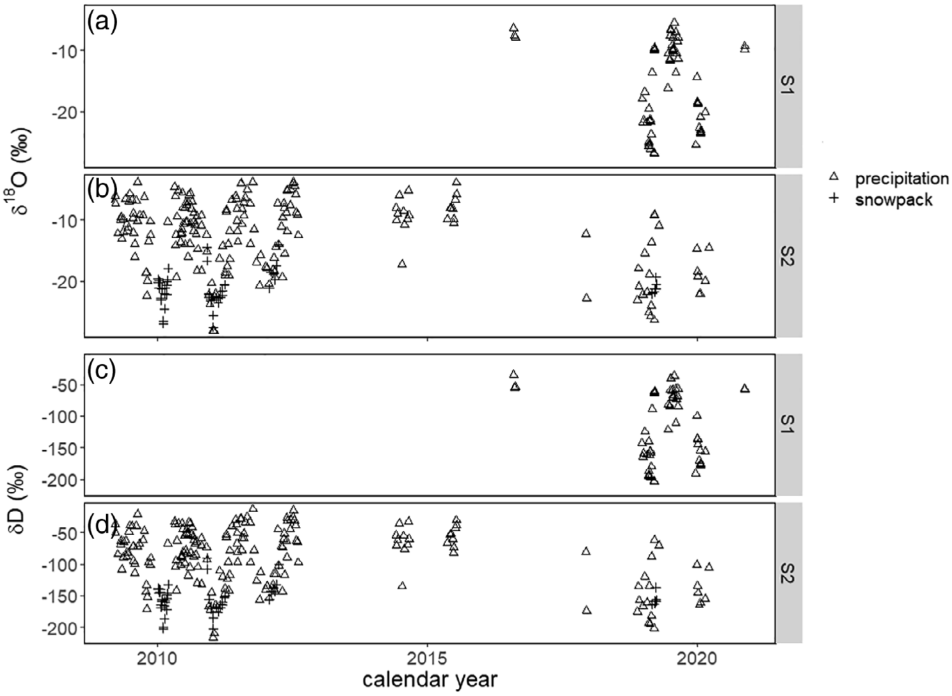

FIGURE 3 Time series of stable isotopes of precipitation and snowpack from the S1 and S2 catchments from 2009–2020 showing both (a) $\delta^{18}O$ from S1 (b) $\delta^{18}O$ from S2 (c) δD from S1 (d) δD from S1. The annual cycle illustrates the seasonal isotopic range for water inputs to the peatland catchments. Data are noncontinuous as analysis has focused on different intervals of time for various projects in the MEF over the 11-year period

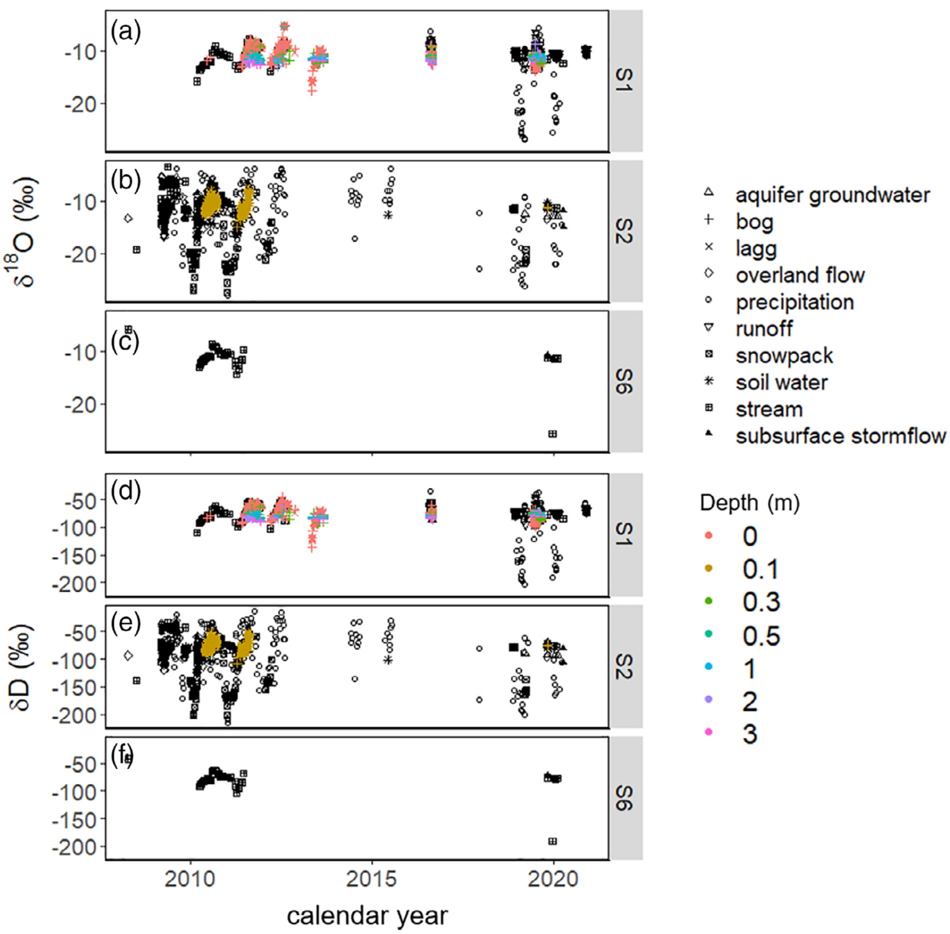

FIGURE 4 Water stable isotope time series of bog-related natural waters from the S1, S2, and S6 bogs in the MEF. (a) $\delta^{18}O$ of S1, (b) $\delta^{18}O$ of S2(c) $\delta^{18}O$ of S6 (d) δD the S1, (e) δD of S2, (f) δD of the S6 waters; all bog and lagg zone porewater, outlet stream water, aquifer groundwater, soil water, overland flow, and subsurface stormflow. Colours represent depths below surface for bog and lagg porewaters

Service employees. (2) Analysis at the University of Toronto was supported by the Natural Sciences and Engineering Research Council, Discovery Grants Program. (3) N. Griffiths was supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under

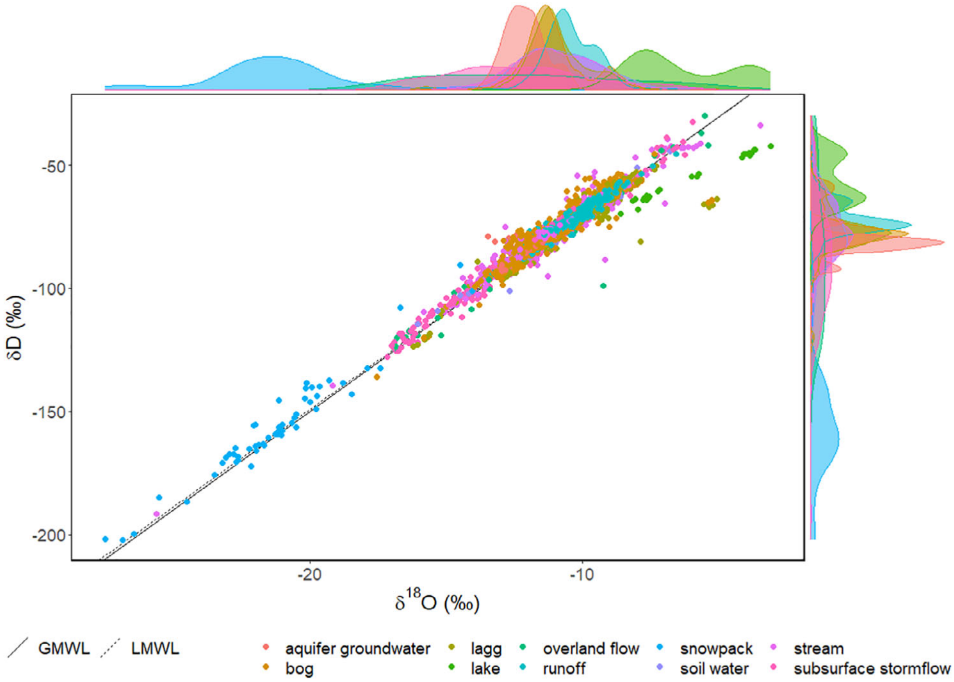

FIGURE 5 Bog related water isotopes from the MEF. Snowpack (blue) is depleted in both heavy isotopes (δD and δ^{18}O), while the rest of the waters are generally more enriched. Lakes (green) lie characteristically to the right of the LWML, while most bog waters lie at or slightly above the meteoric line. Margins display probability density function along each isotope axis

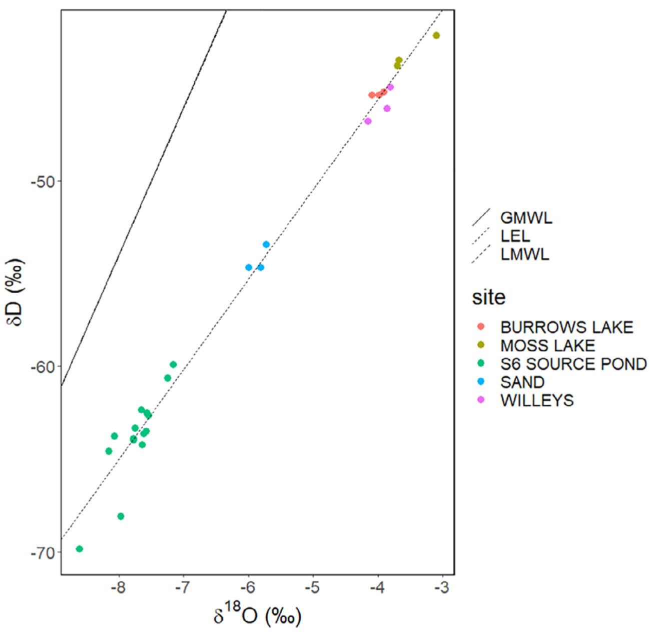

FIGURE 6 Stable isotope composition of lake water surrounding and within the MEF. A clear pattern of enrichment in δ^{18}O more than δD and divergence from the LMWL is evident in samples taken from the surface of nearby lakes. We draw a proposed local evaporation line 'LEL' through these lake points, and intend to improve on this in the future as analysis continues

contract DE-AC05-00OR22725. (4) J.M. Stelling is supported by University of Minnesota via a cooperative agreement with the USDA Forest Service and he has analyzed all the samples at NRS Grand Rapids laboratory. The data are owned by the US Government and can be used without additional permissions or fees. Please do cite appropriately when publishing or presenting.

DATA AVAILABILITY STATEMENT

All data is publicly available through the Environmental Data Initiative (EDI) at the following DOI: https://doi.org/10.6073/pasta/50a287716f80d2b1b602dcceac5a6e5c (Stelling et al., 2021). Data in the repository will be incrementally updated. Downloadable data is in .csv file format with full metadata and supplemental sample locations table.

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REFERENCES

Coleman Wasik, J. K., Mitchell, C. P. J., Engstrom, D. R., Swain, E. B., Monson, B. A., Balogh, S. J., Jeremiason, J. D., Branfireun, B. A., Eggert, S. L., Kolka, R. K., & Almendinger, J. E. (2012). Methylmercury declines in a boreal peatland when experimental sulfate deposition decreases. *Environmental Science & Technology*, *46*(12), 6663–6671. https://doi.org/10.1021/es300865f

Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, *133*(3465), 1702–1703.

Craig, H., Gordon, L., & Horibe, Y. (1963). Isotopic exchange effects in the evaporation of water: 1. Low-temperature experimental results. *Journal of Geophysical Research*, *68*(17), 5079–5087.

Dansgaard, W. (1964). Stable isotopes in precipitation. *Tellus*, *16*(4), 436–468.

Griffiths, N. A., & Sebestyen, S. D. (2016). *SPRUCE S1 bog porewater, groundwater, and stream chemistry data: 2011-2013*. ORNLTESSFA (Oak Ridge National Lab's Terrestrial Ecosystem Science Scientific Focus Area). https://doi.org/10.3334/CDIAC/spruce.018

Griffiths, N. A., Sebestyen, S. D., Oleheiser, K. C., Stelling, J. M., Pierce, C. E., Nater, E. A., Toner, B. M., & Kolka, R. K. (2016). *SPRUCE porewater chemistry data for experimental plots beginning in 2013*. ORNLTESSFA (Oak Ridge National Lab's Terrestrial Ecosystem Science Scientific Focus Area). https://doi.org/10.3334/CDIAC/spruce.028

Hanson, P. J., Riggs, J. S., Nettles, W. R., Phillips, J. R., Krassovski, M. B., Hook, L. A., Gu, L., Richardson, A. D., Aubrecht, D. M., Ricciuto, D. M., Warren, J. M., & Barbier, C. (2017). Attaining whole-ecosystem warming using air and deep-soil heating methods with an elevated CO_2 atmosphere. *Biogeosciences*, *14*(4), 861–883. https://doi.org/10.5194/bg-14-861-2017

Isokangas, E., Rossi, P. M., Ronkanen, A.-K., Marttila, H., Rozanski, K., & Kløve, B. (2017). Quantifying spatial groundwater dependence in peatlands through a distributed isotope mass balance approach. *Water Resources Research*, *53*(3), 2524–2541. https://doi.org/10.1002/2016wr019661

Jeremiason, J. D., Engstrom, D. R., Swain, E. B., Nater, E. A., Johnson, B. M., Almendinger, J. E., Monson, B. A., & Kolka, R. K. (2006). Sulfate addition increases methylmercury production in an experimental wetland. *Environmental Science & Technology*, *40*(12), 3800–3806. https://doi.org/10.1021/es0524144

Kalvāns, A., Dēliņa, A., Babre, A., & Popovs, K. (2020). An insight into water stable isotope signatures in temperate catchment. *Journal of Hydrology*, *582*, 124442. https://doi.org/10.1016/j.jhydrol.2019.124442

Kendall, C., & McDonnell, J. J. (1998). *Isotope tracers in catchment hydrology*. Elsevier.

Kolka, R., Sebestyen, S., Verry, E. S., & Brooks, K. (2011). *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest*. CRC press.

Levy, Z. F., Siegel, D. I., Dasgupta, S. S., Glaser, P. H., & Welker, J. M. (2014). Stable isotopes of water show deep seasonal recharge in northern bogs and fens. *Hydrological Processes*, *28*(18), 4938–4952. https://doi.org/10.1002/hyp.9983

Levy, Z. F., Siegel, D. I., Glaser, P. H., Samson, S. D., & Dasgupta, S. S. (2016). Peat porewaters have contrasting geochemical fingerprints for groundwater recharge and discharge due to matrix diffusion in a large, northern bog-fen complex. *Journal of Hydrology*, *541*, 941–951. https://doi.org/10.1016/j.jhydrol.2016.08.001

Lis, G., Wassenaar, L., & Hendry, M. (2008). High-precision laser spectroscopy D/H and $^{18}O/^{16}O$ measurements of microliter natural water samples. *Analytical Chemistry*, *80*(1), 287–293.

Mitchell, C. P. J., Branfireun, B. A., & Kolka, R. K. (2008). Spatial characteristics of net methylmercury production hot spots in peatlands. *Environmental Science & Technology*, *42*(4), 1010–1016. https://doi.org/10.1021/es0704986

Mutchler, C. (1963). Runoff plot design and installation for soil erosion studies. ARS 41-79. Agricultural Research Service, US Department of Agriculture, National Agricultural Library, Washington DC.

Nichols, D. S., & Verry, E. S. (2001). Stream flow and ground water recharge from small forested watersheds in north central Minnesota. *Journal of Hydrology*, *245*(1-4), 89–103.

Nichols, J., Booth, R. K., Jackson, S. T., Pendall, E. G., & Huang, Y. (2010). Differential hydrogen isotopic ratios of *Sphagnum* and vascular plant biomarkers in ombrotrophic peatlands as a quantitative proxy for precipitation—Evaporation balance. *Geochimica et Cosmochimica Acta*, *74*(4), 1407–1416. https://doi.org/10.1016/j.gca.2009.11.012

Richardson, M. C., Mitchell, C. P. J., Branfireun, B. A., & Kolka, R. K. (2010). Analysis of airborne LiDAR surveys to quantify the characteristic morphologies of northern forested wetlands. *Journal of Geophysical Research*, *115*(G3), 1–16. https://doi.org/10.1029/2009jg000972

Sebestyen, S. D., Dorrance, C., Olson, D. M., Verry, E. S., Kolka, R. K., Elling, A. E., & Kyllander, R. (2011). Long-term monitoring sites and trends at the Marcell Experimental Forest. In *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest* (pp. 15–71). Boca Raton, FL: Taylor and Francis.

Sebestyen, S. D., Funke, M. M., Cotner, J. B., Larson, J. T., & Aspelin, N. A. (2020). *Water chemistry data for studies of the biodegradability of dissolved organic matter in peatland catchments at the Marcell Experimental Forest: 2009-2011*. Forest Service Research Data Archive. https://doi.org/10.2737/RDS-2017-0067-2

Sebestyen, S. D., & Griffiths, N. A. (2016). *SPRUCE enclosure corral and sump system: Description, operation, and calibration*. Climate Change Science Institute, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN. https://doi.org/https://doi.org/10.3334/CDIAC/spruce.030

Sebestyen, S. D., Griffiths, N. A., Oleheiser, K. C., & Stelling, J. M. (2020). *SPRUCE precipitation chemistry and bulk atmospheric deposition beginning in 2013*. Oak Ridge National Laboratory, TES SFA, U.S. Department of Energy, Oak Ridge, TN. https://doi.org/10.25581/spruce.085/1664397

Sebestyen, S. D., & Kyllander, R. (2018). *Event runoff volume data and daily runoff data for the S2 and S6 catchments at the Marcell Experimental Forest*. Forest Service Research Data Archive. https://doi.org/10.2737/RDS-2018-0020

Sebestyen, S. D., Kyllander, R. L., Larson, J. T., Aspelin, N. A., Oleheiser, K. C., Nelson, D. K., Stelling, J. M., Lany, N. K., & Kolka, R. K. (2021). *Marcell Experimental Forest monthly aquifer groundwater chemistry at the S2 catchment, 2007 - ongoing*. https://doi.org/10.6073/pasta/73f3053d71454f2b935c12bb8f0b6412

Sebestyen, S. D., Lany, N. K., Larson, J. T., Aspelin, N. A., Oleheiser, K. C., Nelson, D. K., Hall, S. J., & Curtinrich, H. J. (2021). *Marcell Experimental Forest porewater chemistry at the S2 catchment, 2009 - ongoing*. https://doi.org/10.6073/pasta/d7d5a29015ede8f226166064bc41cb87

Sebestyen, S. D., Lany, N. K., Roman, D. T., Burdick, J. M., Kyllander, R. L., Verry, E. S., & Kolka, R. K. (2021). Hydrological and meteorological data from research catchments at the Marcell Experimental Forest, Minnesota, USA. *Hydrological Processes*, *35*(3), 1–9. https://doi.org/10.1002/hyp.14092

Sprenger, M., Tetzlaff, D., Tunaley, C., Dick, J., & Soulsby, C. (2017). Evaporation fractionation in a peatland drainage network affects stream water isotope composition. *Water Resources Research*, *53*(1), 851–866. https://doi.org/10.1002/2016wr019258

Stelling, J. M., Sebestyen, S. D., Griffiths, N. A., Mitchell, C., Green, M. B., & Lany, N. K. (2021). *Marcell Experimental Forest stable isotopes of water, 2008 - ongoing*. https://portal.edirepository.org/nis/mapbrowse?packageid=edi.747.1

Stelling, J. M., & Yu, Z. (2019). Regional climate change recorded in moss oxygen and carbon isotopes from a late Holocene peat archive in the western Antarctic Peninsula. *Geosciences*, *9*(7), 1–14. https://doi.org/10.3390/geosciences9070282

Tetzlaff, D., Buttle, J., Carey, S. K., van Huijgevoort, M. H., Laudon, H., McNamara, J. P., Mitchell, C. P. J., Spence, C., Gabor, R. S., & Soulsby, C. (2015). A preliminary assessment of water partitioning and ecohydrological coupling in northern headwaters using stable isotopes and conceptual runoff models. *Hydrological Processes*, *29*(25), 5153–5173. https://doi.org/10.1002/hyp.10515

Verry, E. S., Brooks, K., Nichols, D., Ferris, D., & Sebestyen, S. (2011). Watershed hydrology. In *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest* (pp. 193–212). CRC Press.

Verry, E. S., & Timmons, D. R. (1982). Waterborne nutrient flow through an upland-peatland watershed in Minnesota. *Ecology*, *63*(5), 1456–1467. https://doi.org/10.2307/1938872

Wassenaar, L. I., Coplen, T. B., & Aggarwal, P. K. (2014). Approaches for achieving long-term accuracy and precision of $\delta^{18}O$ and $\delta^{2}H$ for waters analyzed using laser absorption spectrometers. *Environmental Science & Technology*, *48*(2), 1123–1131. https://doi.org/10.1021/es403354n

Xia, Z., Zheng, Y., Stelling, J. M., Loisel, J., Huang, Y., & Yu, Z. (2020). Environmental controls on the carbon and water (H and O) isotopes in peatland Sphagnum mosses. *Geochimica et Cosmochimica Acta*, *277*, 265–284. https://doi.org/10.1016/j.gca.2020.03.034

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