Variability of Meteoric Water Isotopes in the Great Lakes Region
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Highlights
- High d-excess values for precipitation collected from two locations in the lower peninsula of Michigan indicate the input of recycled moisture downwind of Lake Michigan
- Analysis of precipitation, river, and lake samples shows seasonal patterns in isotopic composition
- Precipitation samples collected from each sampling location show little variation between sampling sites, demonstrating the pervasiveness of the regional isotopic signal from Lake Michigan
- Combined sampling of precipitation, surface water, and groundwater samples are useful in expanding our understanding of how water moves through hydrologically connected groundwater and surface water systems

Abstract

The hydrological processes that govern water balance in the Great Lakes region are undergoing significant change as shifting climatic conditions continue to impact the area. Meteoric water isotopes ($\delta^{18}O$ and δ^2H) are an efficient tool for studying these changes, but little work has been done to describe the baseline isotopic variability of meteoric waters in the Great Lakes region. Here I analyze precipitation, river, lake, and groundwater samples collected from the University of Michigan Central Campus (UMCC) and University of Michigan Biological Station (UMBS) from April 2017 to February 2020 to understand how their isotopic compositions vary seasonally, between sampling sites, and by water type. The precipitation, river, and lake water samples collected from both the UMCC and UMBS show seasonal patterns in isotopic composition that are consistent with previously established predictions for isotopic seasonality in the mid to high latitudes. Precipitation samples collected from each sampling location show little variation between sampling sites, demonstrating the pervasiveness of the regional isotopic signal produced by Lake Michigan evaporation. $\delta^{18}O$ and d-excess values of the precipitation, lake, and groundwater samples collected from the UMBS indicate hydrologic mixing between each water source and demonstrate the usefulness of sampling multiple water types when studying hydrologically connected groundwater and surface water systems. Precipitation samples from the UMCC and UMBS demonstrated high d-excess values ranging from 3.1 to 25.0‰ and -3.2 to 25.2‰ respectively, which indicates the input of recycled moisture from Lake Michigan. In addition to investigating isotopic variability, I assess the usefulness of downwind precipitation d-excess values as a proxy for tracing changes in evaporation on the Great Lakes with a simple isotopic mixing model and conclude that climate-induced changes in evaporation may be difficult to identify over small time scales. With rapidly changing climatic conditions threatening to alter the hydrologic processes that govern water balance in the Great Lakes region, this work serves as an important baseline for tracing future hydrologic change using meteoric water isotopes.

Introduction

The Great Lakes of North America comprise 20 percent of the world's surface freshwater and make up one of the most intensively used freshwater systems in the world (Hartmann, 1990). The impacts of climate change on the hydrologic processes that govern water balance in the Great Lakes region have become an exceedingly important issue for water management decisions. Over the last two decades, many significant hydrologic changes linked to climate change have been identified including increases in lake water temperature (Austin and Colman, 2007; Austin and Colman, 2008; Schneider and Hook, 2010), lake-effect snowfall amount (Braham and Dungey, 1984; Burnett et al., 2003), and lake water evaporation rates (Assel et al., 2004; Hanrahan et al., 2010). Decreases in seasonal lake levels (Lenters, 2001; Lenters, 2004) and annual maximum ice cover (Assel et al., 2003) have also been observed. With global mean surface temperature warming projected to exceed 1.5°C by the end of the 21st century (IPCC, 2014), many recent climate models have focused on predicting the localized effects future climate warming will have on the Great Lakes region. Zhang et al. (2020) predict that whole basin temperature will increase by as much as 4.0°C during the mid-century and 6.0°C during the late-century. Increases in surface water temperatures across all seasons are predicted by Trumpickas et al. (2009), with summer surface temperatures expected to increase by as much as 6.7°C. Evaporation and precipitation in the Great Lakes region are similarly expected to increase, with climate models estimating increases in annual evaporation and precipitation as high as 204 mm and 140 mm respectively (Mailhot et al., 2019).

The relative abundances of stable oxygen and hydrogen isotopes ($^{18}O/^{16}O$ and $^{2}H/^{1}H$, expressed conventionally as $\delta^{18}O$ and $\delta^{2}H$) are a useful tool for tracing hydrologic change because their distributions within meteoric water samples, which include all waters derived from precipitation, are sensitive to hydrologic processes (Gat, 1996). For example, $\delta^{18}O$ and $\delta^{2}H$ values can serve as conservative tracers of hydrologic mixing between waters with different isotopic compositions. Additionally, the effects of evaporation on bodies of liquid water can be assessed from increases in $\delta^{18}O$ and $\delta^{2}H$, which reflect the enrichment of isotopically heavier isotopes in the liquid phase due to the preferential loss of the more volatile lighter isotopes to the vapor phase.

Methods employed in previous studies to measure evaporation on the Great Lakes include energy balance (Morton, 1967; Croley, 1989; Croley and Assel, 1994), mass balance (Derecki, 1981; Hanrahan et al., 2010), and satellite-based techniques (Lofgren and Zhu, 2000). However, these methods involve indirect calculations of evaporation and require observations of numerous water balance components that can often become complex and expensive. One direct method of studying evaporation is the eddy covariance technique employed by Blanken et al. (2011) and Spence et al. (2011), which uses sophisticated instruments to measure wind speed and humidity at high frequencies. This information is then used to calculate evaporative flux from the Great Lakes. Although the eddy covariance technique is more accurate than previous methods, the necessary instruments must be mounted on tall, stable platforms such as lighthouses and small islands due to their sensitivity to moving platforms such as buoys (Lenters

et al., 2013). These infrastructural requirements limit the locations at which eddy covariance measurements can be made and suitable locations are often remote and difficult to access when available. In contrast, $\delta^{18}O$ and δ^2H measurements can provide direct estimates of evaporation on the Great Lakes while requiring simple methods of precipitation and surface water collection that can be performed by hand at more accessible locations downwind of the Great Lakes. Additionally, this isotope-based method can provide information about the effect of moisture recycling on regional precipitation downwind of the Great Lakes.

The near-linear relationship between $\delta^{18}O$ and δ^2H values of meteoric waters is well established and is described by the Global Meteoric Water Line, often abbreviated as GMWL ($\delta^2H = 8\delta^{18}O + 10$) (Craig, 1961). Rearranging this equation gives the d-excess parameter ($d = \delta^2H - 8\delta^{18}O$), which describes deviations from the slope 8 line defined by the GMWL in δ^2H-$\delta^{18}O$ space (Dansgaard, 1964). The d-excess parameter is an especially useful tool in estimating the effects of moisture recycling from the Great Lakes on atmospheric water content and subsequent regional precipitation (Gat et al., 1994; Machavaram and Krishnamurthy, 1995; Bowen et al., 2012) because it is predominantly controlled by the kinetic fractionation effects associated with the evaporation of surface water into unsaturated air. As shown in **Figure 1**, vapor evaporated from meteoric waters lies to the left of the GMWL and is characterized by high d-excess values. Assuming isotopic equilibrium with the atmosphere during condensation, the subsequent precipitation that forms from this vapor will follow a slope of approximately 8 while remaining high in d-excess. In contrast, the liquid water that the vapor evaporated from is not in isotopic equilibrium with the atmosphere and therefore undergoes kinetic fractionation, resulting in isotopically lighter forms of oxygen and hydrogen preferentially escaping the surface of the liquid water during evaporation. The residual liquid water left behind after evaporation is therefore enriched in heavy isotopologues of water, lies to the right of the GMWL (low d-excess), and follows a $\delta^2H/\delta^{18}O$ slope less than 8.
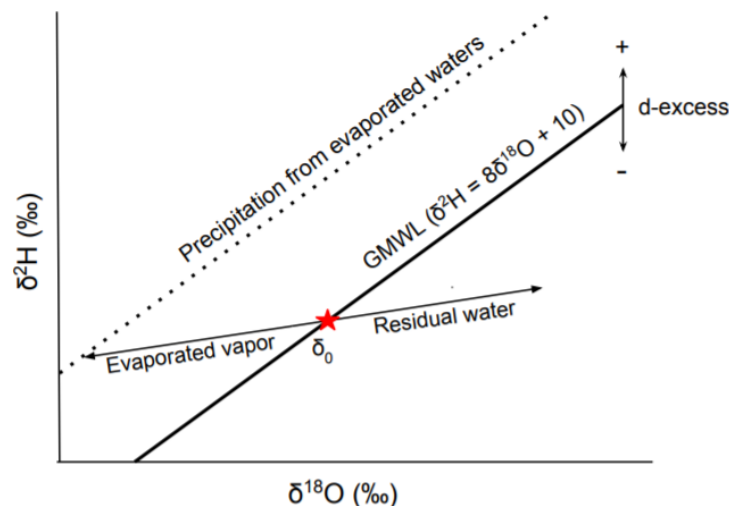

Figure 1. Schematic showing the effects of evaporation and condensation on meteoric waters in δ^2H-$\delta^{18}O$ space. Vapor produced from the evaporation of waters on the GMWL lies to the left of the GMWL and is characterized by high d-excess values. Precipitation produced from the

condensation of this evaporated liquid is similarly high in d-excess and follows a linear relationship with slope 8. The residual liquid water that remains after evaporation lies to the right of the GMWL, is characterized by low d-excess values, and follows a linear relationship with slope < 8.

A baseline understanding of the isotopic variability of meteoric waters in the Great Lakes region is needed to use meteoric water isotopes to trace future hydrologic change. However, previous studies that have employed meteoric water isotopes to understand the hydrologic processes that govern the Great Lakes region have primarily focused on constraining evaporative fluxes (Gat et al., 1994; Machavaram and Krishnamurthy, 1995; Bowen et al., 2012; Jasechko et al., 2014). Bowen et al. (2012) assessed the spatial variability of $\delta^{18}O$ and δ^2H values for a set of groundwater samples in the Great Lakes region, but very little other work has been done to understand seasonal, spatial, and water type variability of meteoric waters downwind of the Great Lakes. Here I analyze precipitation, river, lake, and groundwater samples from two locations in the lower peninsula of Michigan to understand how their isotopic compositions vary seasonally, between sampling sites, and by water type. I then assess the usefulness of downwind precipitation d-excess values as a proxy for tracing changes in evaporation on the Great Lakes with a simple isotopic mixing model. This work is especially important as climate change continues to impact the Great Lakes region and demonstrates the potential of using isotopic measurements (specifically d-excess) of meteoric waters downwind of the Great Lakes as a proxy for tracing future hydrologic change.

Methods

A combined total of 241 precipitation, river, lake, and groundwater samples were collected from two locations east of Lake Michigan in the lower peninsula of the state of Michigan (**Figure 2**). The first location was the University of Michigan Central Campus (UMCC) in Ann Arbor, MI (42.28°N, 83.74°W). The UMCC is located approximately 210 km east of Lake Michigan with mean annual temperature and total annual precipitation values of 9.3°C and 1153 mm (NCDC's Climate Data Online: https://www.ncdc.noaa.gov/cdo-web/). The second location was the University of Michigan Biological Station (UMBS) near Pellston, MI (45.56°N, 84.67°W). The UMBS is located approximately 33 km east of Lake Michigan with mean annual temperature and total annual precipitation values of 5.0°C and 864 mm (NCDC's Climate Data Online: https://www.ncdc.noaa.gov/cdo-web/).
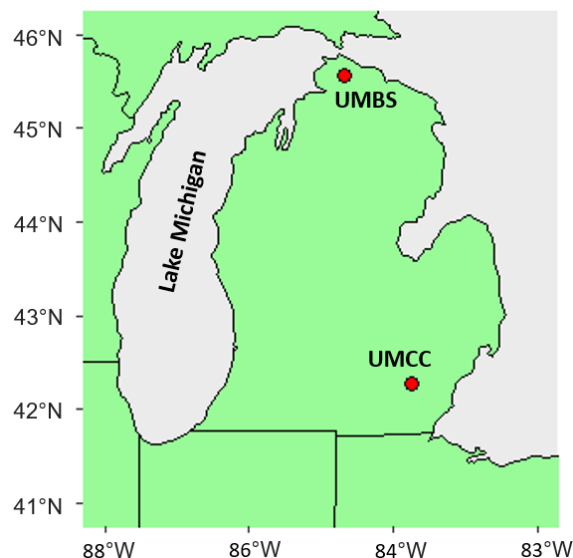
Figure 2. Locations of the University of Michigan Central Campus (UMCC) in Ann Arbor, MI (42.28°N, 83.74°W) and the University of Michigan Biological Station (UMBS) near Pellston, MI (45.56°N, 84.67°W).

      Precipitation and river water samples were collected from the University of Michigan Central Campus (UMCC) in Ann Arbor, MI. Precipitation samples were collected from October 2018 to February 2020 from the roof of the North University Building (**Figure 3**, Precipitation Collector) using an oil-free precipitation collector described by Gröning et al. (2012). A 1.5 L HDPE bottle was fitted with a 3-inch funnel and a narrow HDPE tube (4 mm inner diameter). The narrow tube reached the bottom of the HDPE bottle and was fitted with a small plastic cup attached with stainless steel wire so that the end of the tube was submerged after only a few millimeters of precipitation were collected. The collection bottle was additionally fitted with an open-ended Bev-a-line vent tube (3 mm diameter). This design created a system that allowed pressure change while exposing only the small surface area of water inside the HDPE tube to the atmosphere, which was a negligible fraction of the entire water surface in the bottle. Samples were retrieved from the collector on an approximately weekly interval. Weekly Huron River samples were collected from May 2018 to February 2020 from three locations along the river within Ann Arbor city limits (**Figure 3**). These samples were collected by dipping 20 mL HDPE vials below the water surface and analyzed within a few weeks of collection. The quick turnaround between sample collection and analysis prevented potential fractionation between the sampled water and the plastic HDPE collection vials (Spangenberg, 2012).

Figure 3. Map of the water sample collection sites at the UMCC. Locations are shown for the precipitation collector on the roof of the North University Building and the three collection sites along the Huron River. Map image received from Google Earth.

Precipitation, lake, and groundwater samples were collected from the University of Michigan Biological Station (UMBS) near Pellston, MI. Precipitation samples were collected at the UMBS from April 2017 to September 2019 using oil-based collectors described by Friedman et al. (1992) and Scholl et al. (1996) located at two tower sites within the vicinity of the UMBS (**Figure 4**, FASET and AmeriFlux). Sample collection was run in parallel at the tower sites so that two samples (one from each tower site) were collected for all sample dates listed in the results section. Each collector consisted of a gallon-sized bucket lined with mineral oil to prevent evaporation. A needle-point syringe was used to extract the water samples without transferring any of the oil on an event-scale interval until June 2018, which then changed to an approximately weekly interval. The sampling buckets were cleaned and given a new layer of oil upon each sample retrieval. After September 2018, precipitation collection at the UMBS switched to the oil-free method described above for precipitation collection at the UMCC and was moved from the two tower sites to a single location in an open field at the UMBS (**Figure 4**, Precipitation Collector). Samples were retrieved from the collector on an approximately weekly interval. Monthly lake water and groundwater samples were collected from the edge of Douglas Lake and the mouth of a groundwater spring that originates from a seep in the bottom of Douglas Lake (Hendricks et al., 2016) from April 2017 to October 2017 (**Figure 3**). These samples were collected similarly to the Huron River surface water samples and analyzed within

a few weeks of collection to prevent potential fractionation between the sampled water and the plastic HDPE collection vials (Spangenberg, 2012). The precipitation samples collected at the UMBS from April 2017 to October 2017 and the entirety of the Douglas Lake and groundwater samples were collected and analyzed as part of the work published by Aron et al. (2020). Here I expand upon this dataset by continuing precipitation sample collection at the UMBS through September 2019 and increasing sample collection frequency from an event-based to weekly interval.
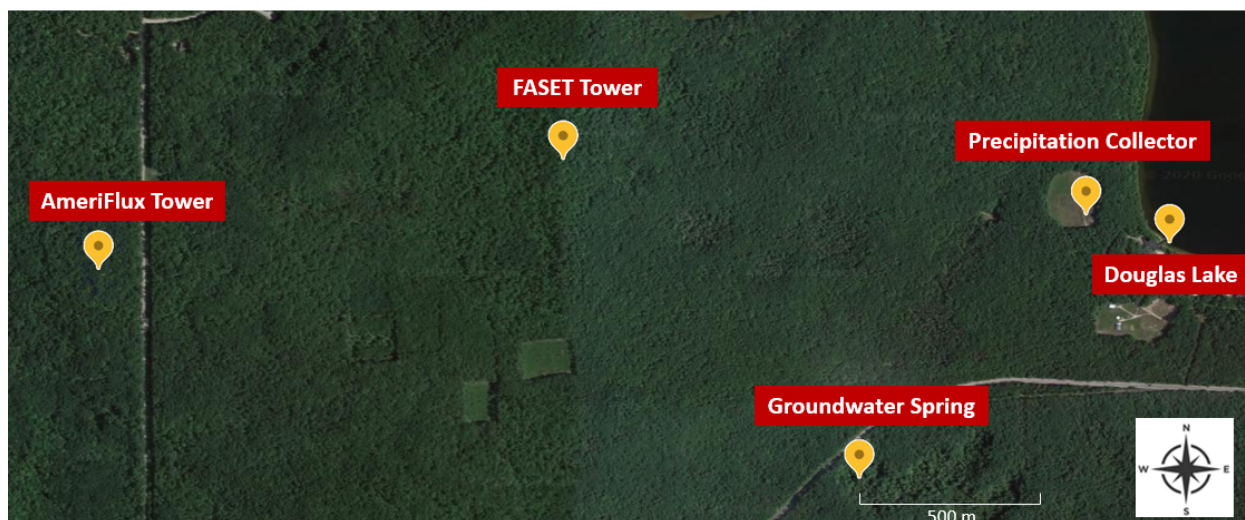

Figure 4. Map of the water sample collection sites at the UMBS. Locations are shown for the two tower sites where precipitation samples were collected using an oil-based method before September 2018 (AmeriFlux and FASET), the oil-free precipitation collector used after September 2018, the groundwater spring, and the Douglas Lake collection point. Map image retrieved from Google Earth.

All water samples collected in this study were placed in 2 mL glass vials with solid caps while awaiting sample analysis. An additional step of filtering the water samples before placing them in the vials was added after June 2018 to ensure sample purity. The vials were filled as close to the top as possible and stored upside down in the dark to minimize fractionation within the vial. The $\delta^{18}O$ and δ^2H values of each water sample were measured using a Picarro L2130-i with a high-precision vaporizer (A0211) and attached autosampler. $\delta^{18}O$ and δ^2H measurements were normalized to the VSMOW-SLAP scale with USGS reference waters (USGS45, 46, 49, and 50) and four in-house liquid standards using the Picarro ChemCorrect software. Additionally, each sample was monitored for organic contamination using the Picarro ChemCorrect software. Average analytical precision was better than 0.1‰ for $\delta^{18}O$ and 0.3‰ for δ^2H based on repeat analyses of deionized water. Isotope results can be found in the supplementary data file attached at the end of this paper.

Results
Isotope Results

The isotopic composition of the UMCC precipitation samples ranged from -21.9 to -2.7‰ for $\delta^{18}O$ (amount weighted average -13.2‰) and from -164.3 to -5.1‰ for δ^2H (amount weighted average -90.5‰). The best-fit local meteoric water line (LMWL) for the UMCC precipitation samples was $\delta^2H = 8.1 \, \delta^{18}O + 15.8$, which is parallel to and offset above the GMWL ($\delta^2H = 8\delta^{18}O + 10$) (**Figure 5**). The high d-excess values of the UMCC precipitation, which range from 3.1 to 25.0‰, indicate the input of recycled moisture.

The isotopic composition for the precipitation samples collected from the UMBS ranged from -23.4 to -3.7‰ for $\delta^{18}O$ (amount weighted average -15.6‰) and from -177.4 to -5.4‰ for δ^2H (amount weighted average -109.0‰). The best-fit LMWL for the UMBS precipitation samples was $\delta^2H = 7.9 \, \delta^{18}O + 14.5$, which is similarly parallel to and offset above the GMWL like the LMWL for the UMCC precipitation samples (**Figure 5**). The high d-excess values of the UMBS precipitation samples ranged from -3.2 to 25.2‰ and similarly indicate the input of recycled moisture.
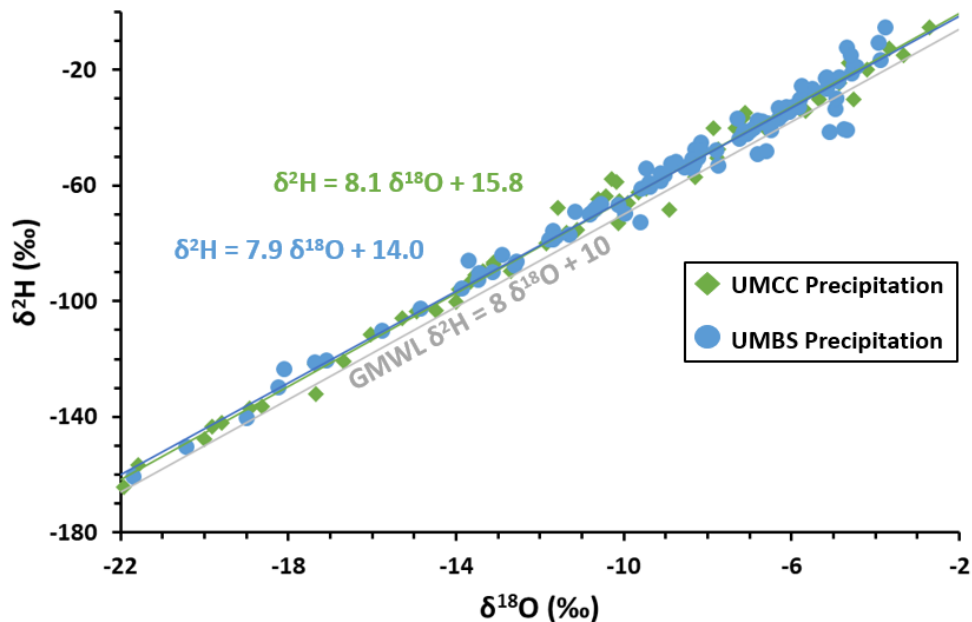

Figure 5. Scatterplot of the $\delta^{18}O$ and δ^2H values of the precipitation samples collected from the UMCC (green) and UMBS (blue). The best-fit local meteoric water lines (LMWLs) are shown for both data sets and closely overlap each other. The Global Meteoric Water Line (GMWL) is shown for reference (gray).

The isotopic composition of the Huron River samples ranged from -10.8 to -5.6‰ for $\delta^{18}O$ and from -77.9 to -29.8‰ for δ^2H. The best-fit regression line for the Huron River samples was $\delta^2H = 6.2 \, \delta^{18}O - 4.5$, which is offset below and follows a shallower slope than the GMWL. The low d-excess values of the Huron River samples, which range from -2.5 to 15.7‰, and this shallower slope indicate the effects of the kinetic fractionation that occurred when the water underwent evaporation. **Figure 6** shows a close-up view of the relative positions of the best-fit regression lines for the Huron River and UMCC precipitation samples. δ_0 describes the starting isotopic composition of the Huron River before undergoing evaporation and is indicated by the

intersection of the best-fit regression lines for the UMCC precipitation and Huron River samples. The amount weighted average $\delta^{18}O$ value for the UMCC precipitation samples was -13.2‰ as mentioned previously, which is similar to the $\delta^{18}O$ value of δ_0 at -11.0‰
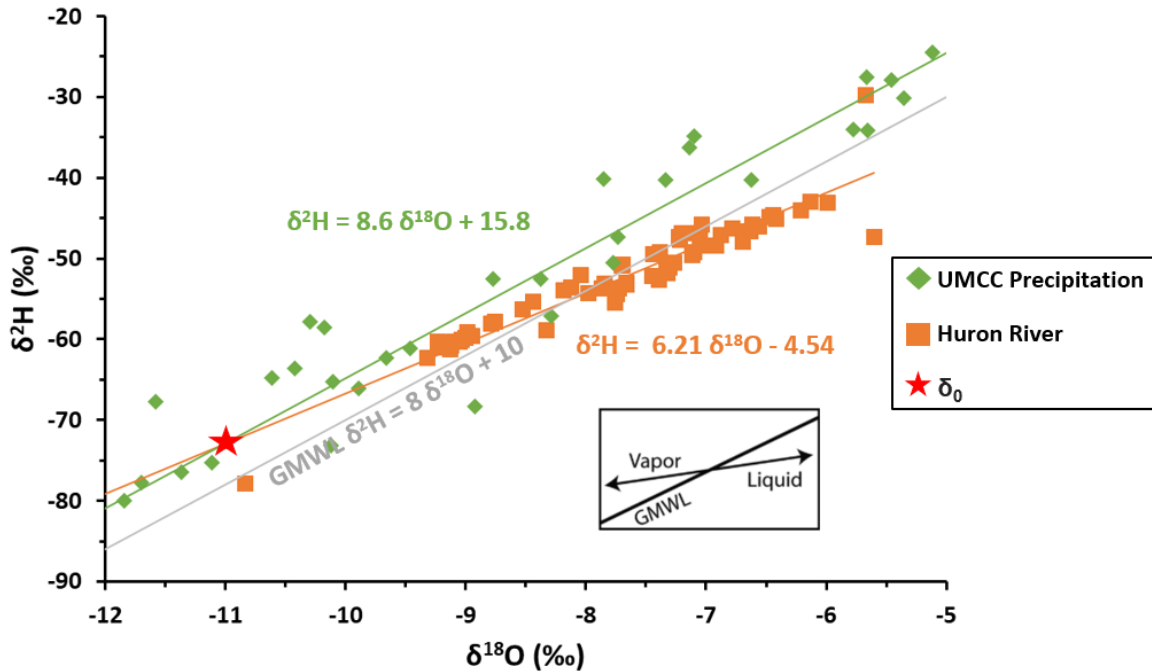

Figure 6. Scatterplot showing the positions of the best-fit regression lines for the UMCC precipitation (green) and Huron River (orange) samples relative to the GMWL in δ^2H-$\delta^{18}O$ space. The UMCC precipitation samples that fall below $\delta^{18}O$ values of -12‰ are not shown to increase the resolution of the best-fit regression lines, but can be seen in Figure 5. δ_0 is indicated with a red star and has a $\delta^{18}O$ value of approximately -11.0‰. The inset shows the expected positions of water vapor that has evaporated from waters that fall along the GMWL and the residual liquid water that remains after evaporation.

Seasonal Variation

Distinct seasonal isotopic variation was observed for the Huron River, UMCC precipitation, and UMBS precipitation samples (**Figure 7**). $\delta^{18}O$ time series data for all three sample types demonstrated higher $\delta^{18}O$ values in the summer months and lower $\delta^{18}O$ values in the winter months (**Figures 7A and 7C**). In contrast, the corresponding d-excess values were lower in the summer months and higher in the winter months (**Figures 7B and 7D**). This seasonal pattern is exceptionally clear and robust in the Huron River dataset, with a few outliers that were most likely a result of sample collection occurring immediately following precipitation events. In contrast, the UMCC and UMBS precipitation samples demonstrate more variability within the overall seasonal pattern, especially during the winter months. The magnitude of the seasonal variation in the Huron River samples was as large as 3.3‰ for $\delta^{18}O$ and 7.5‰ for d-excess.
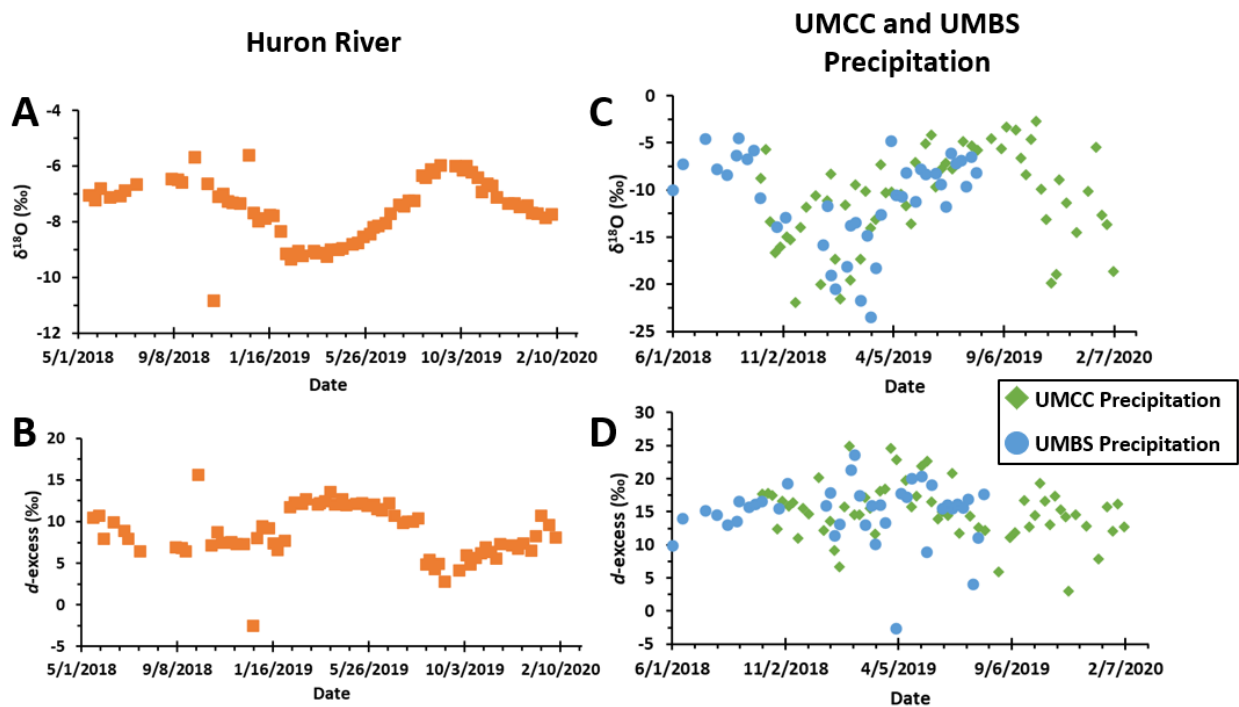
Figure 7. Time-series isotope data for the Huron River samples collected from May 2018 to February 2020 (orange): A) $\delta^{18}O$ values. B) d-excess values. Time-series isotope data for the precipitation samples collected at the UMCC from October 2018 to February 2020 (green) and the UMBS from June 2018 to September 2019 (blue): C) $\delta^{18}O$ values. D) d-excess values.

Water Type Variation

      Figure 8 shows the isotopic composition of the precipitation, lake, and groundwater samples collected from the UMBS. The isotopic composition of the lake water samples ranged from -8.1 to -6.9‰ for $\delta^{18}O$ and from -59.3 to -55.2‰ for δ^2H. These samples were characterized by low d-excess values that ranged from 1.4 to 5.8‰. The best-fit regression line for the lake water samples was $\delta^2H = 4.9\ \delta^{18}O - 19.7$. The isotopic composition of the groundwater samples ranged from -9.1 to -8.5‰ for $\delta^{18}O$ and from -65.2 to -62.1‰ for δ^2H. These samples were characterized by low d-excess values that ranged from 5.8 to 8.3‰. The best-fit regression line for the groundwater samples was $\delta^2H = 4.6\ \delta^{18}O - 23.2$. The $\delta^{18}O$ and d-excess values of the Douglas Lake samples collected at the UMBS demonstrate subtle seasonal trends (**Figure 9**). $\delta^{18}O$ gradually increases by a total of 1.0‰ and d-excess decreases by a total of 2.7‰ from April to October.
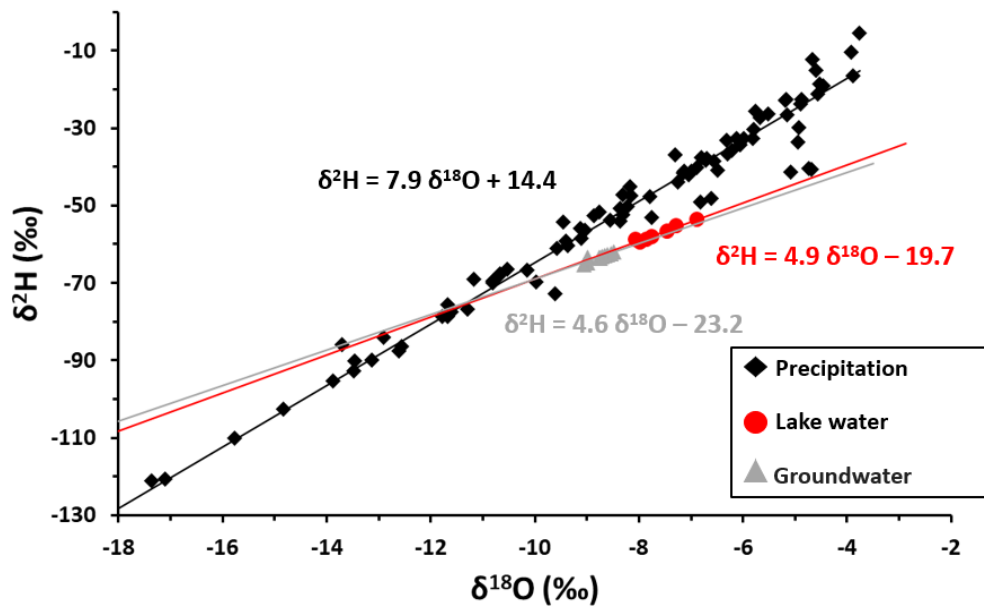
Figure 8. Scatterplot of the $\delta^{18}O$ and δ^2H values of the precipitation (black), Douglas Lake (red), and groundwater (gray) samples collected at the UMBS during 2017. Best-fit regression lines are shown for each water type.
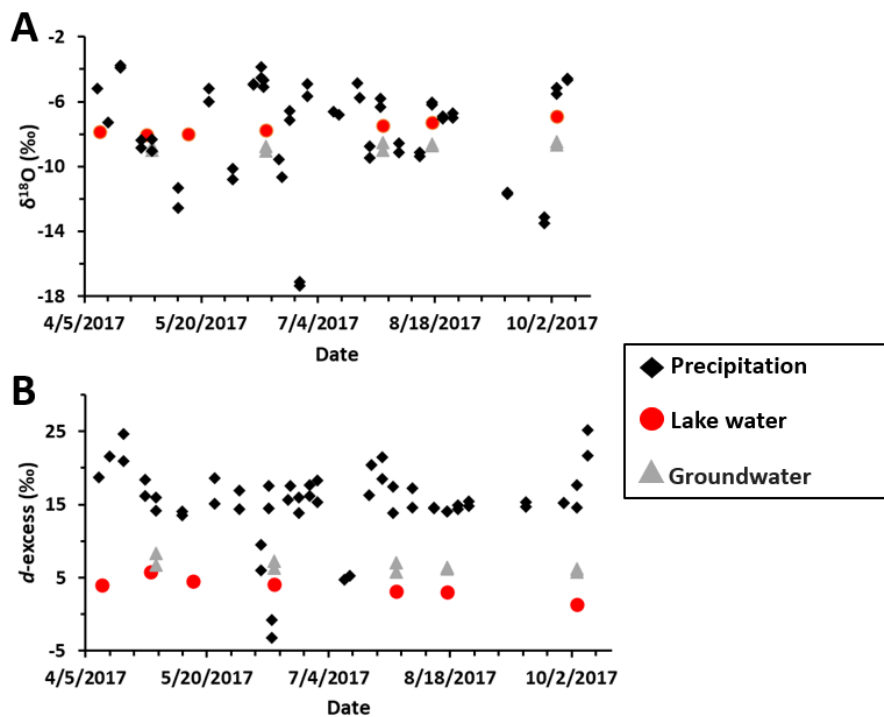

Figure 9. Time-series isotope data for the precipitation (black), Douglas Lake (red), and groundwater (gray) samples collected at the UMBS from April 2017 to October 2017. A) $\delta^{18}O$ values. B) d-excess values.

Spatial Variation

As shown in **Figures 7C** and **7D**, the patterns of seasonal variation demonstrated by the precipitation samples collected from the UMCC and UMBS coincide, with similarly low d-excess (high $\delta^{18}O$) during the summer and high d-excess (low $\delta^{18}O$) during the winter. **Figure 5** also shows that the LMWLs for the UMCC and UMBS precipitation samples are relatively similar to each other ($\delta^2H = 8.1\ \delta^{18}O + 15.8$ and $\delta^2H = 7.9\ \delta^{18}O + 14.5$, respectively). The amount weighted average isotope values of the UMCC precipitation samples ($\delta^{18}O = -13.2‰$, $\delta^2H = -90.5‰$) were slightly higher than the UMBS precipitation samples ($\delta^{18}O = -15.6‰$, $\delta^2H = -109.0‰$).

Discussion

Evaluating d-excess of downwind precipitation as a proxy for upwind evaporative change

The UMCC and UMBS represent hydrologic systems that are expected to be characterized by high d-excess values due to the input of recycled moisture from the evaporation of upwind moisture sources. A significant source of this recycled moisture for the sampling locations included in this study is Lake Michigan, which has been estimated to contribute as much as 16% of the total atmospheric water content during the summer months (Gat et al., 1994; Machavaram & Krishnamurthy, 1995). The significant isotopic impact of contributions from Lake Michigan evaporation on downwind atmospheric moisture suggests that monitoring the d-excess values of precipitation at localities like the UMCC and UMBS could serve as a proxy for identifying future changes in upwind evaporative fluxes on the Great Lakes. However, the effectiveness of using precipitation d-excess values to trace upwind change depends on the magnitude of change occurring on the Great Lakes.

Here I assess whether signals of these evaporative increases are detectable in the d-excess values of downwind precipitation by evaluating a simple mixing model:

$$\delta_A = f_{LME}(\delta_{LME}) + f_E(\delta_E)$$

where δ_A represents the isotopic composition of the downwind atmosphere, δ_{LME} represents the isotopic composition of recycled moisture from Lake Michigan evaporation equilibrated with the atmosphere, and δ_E represents the isotopic composition of atmospheric water that originates from the evaporation of other upwind water sources. *f* represents the contribution of vapor from each water source to the downwind atmosphere as a fraction of total atmospheric vapor (where $f_{LME} + f_E = 1$). The $\delta^{18}O$ and δ^2H values chosen for δ_{LME} were -20.9 and -155.0‰ respectively, which are the annual average δ^2H and $\delta^{18}O$ values listed for the vapor produced from Lake Michigan evaporation in Table 5 of Jasechko et al. (2014). The $\delta^{18}O$ and δ^2H values chosen for δ_E were -10.4 and -74.0‰ respectively, which were retrieved from Table 2 of Bowen et al. (2012) and represent the average $\delta^{18}O$ and δ^2H values of precipitation from four locations located west and north of the Great Lakes. These values were used by Bowen et al. (2012) to represent the isotopic composition of atmospheric water that traverses Lake Michigan before recycled moisture from Lake Michigan is added.

The $\delta^{18}O$ and δ^2H values of the precipitation that would form from the atmospheric vapor calculated above were calculated by rearranging the equation for vapor to liquid fractionation and solving for δ_L:

$$\delta_L = (1000 + \delta_V)/\alpha_{V-L}{}^* - 1000$$

where δ_V represent atmospheric vapor (in this case, δ_A) and $\alpha_{V-L}{}^*$ is a temperature-dependent equilibrium vapor-liquid isotopic fractionation factor. A condensation temperature of 5.0°C, which was the average annual temperature for Ann Arbor, MI in 2019 (NCDC's Climate Data Online: https://www.ncdc.noaa.gov/cdo-web/), was entered into the formulae developed by Majoube (1971) to calculate $\alpha_{V-L}{}^*$ for $\delta^{18}O$ and δ^2H. The δ_L values for $\delta^{18}O$ and δ^2H were then used to calculate δ_L d-excess (d = δ^2H - $8\delta^{18}O$).

Figure 10 shows the relationship between the fraction of downwind atmospheric vapor sourced from Lake Michigan evaporation (f_{LME}) and the d-excess values of downwind precipitation (δ_L). The range of values displayed for f_{LME} (4-33%) represents the highest and lowest estimates for the contribution of recycled moisture from Lake Michigan published in current literature (Gat et al., 1994; Machavaram & Krishnamurthy, 1995; Jasechko et al., 2014). d-excess values range from 9.8 to 12.3‰ and follow a linear relationship with a 1% change in f_{LME} correlating to an approximately 0.1‰ change in d-excess.
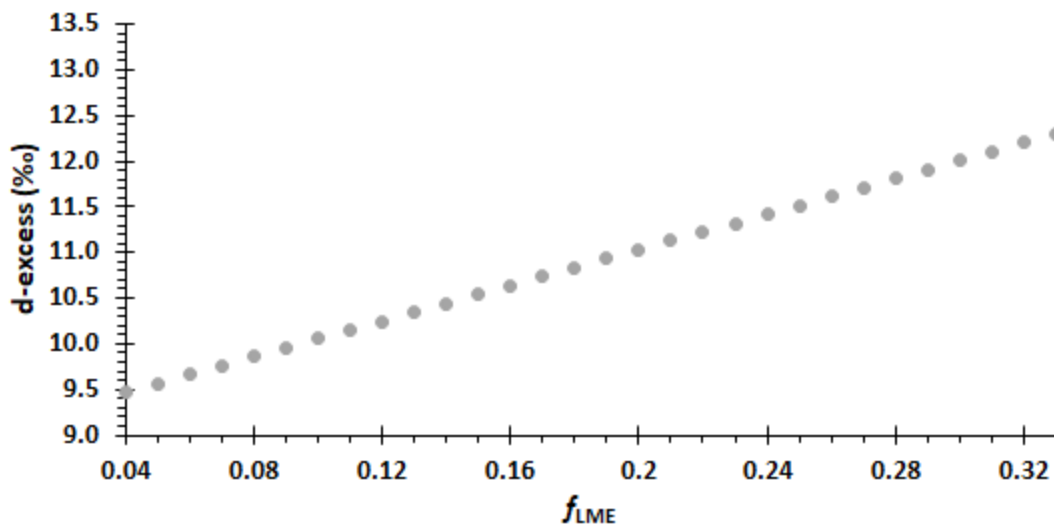

Figure 10. Scatterplot showing the relationship between the fraction of downwind atmospheric vapor sourced from Lake Michigan evaporation (f_{LME}) and the d-excess values of downwind precipitation (δ_L).

Climate models developed by Mailhot et al. (2019) estimate that annual evaporation on the Great Lakes will increase by 204 mm by the year 2100. According to the estimates of current annual evaporation on each of the Great Lakes calculated by Jasechko et al. (2014), a 204 mm total change in annual evaporation from the Great Lakes would equate to a 7.9% overall increase. Based on Figure 10, a 7.9% increase in the evaporative contribution from Lake

Michigan to the total atmospheric water load would amount to an increase of approximately 0.79‰. Such a small change in d-excess occurring over a time scale of almost 80 years would be extremely difficult to capture.

A consideration for this assessment is that the $\delta^{18}O$ and δ^2H values chosen for δ_{LME} and δ_E were average annual values rather than seasonal maxima. This is an important consideration because evaporation and therefore d-excess values of the Great Lakes vary greatly seasonally, with the highest rates of evaporation occurring in the winter. Changes in maximum winter evaporation from year to year may be detectable in the d-excess values of downwind precipitation over relatively short time periods, but little data has been published to show the projected magnitude of change in maximum winter evaporation under future climate conditions.

Seasonal Variation

Seasonal variation in the $\delta^{18}O$ values of precipitation at mid to high latitudes has been primarily attributed to the temperature effect (Dansgaard, 1964). The temperature effect relates seasonal temperature change to the isotopic composition of precipitation through its effect on the saturation vapor pressure of air masses and therefore their degree of rainout. As temperature drops and the degree of rainout from air masses traveling across land increases during the colder winter months, the $\delta^{18}O$ values of precipitation at a given site decrease. The low $\delta^{18}O$ values of the UMCC and UMBS precipitation samples collected during the winter and high $\delta^{18}O$ values of the samples collected during the warmer summer months (**Figure 7C**) suggest that the isotopic seasonality of precipitation in the Great Lakes region is consistent with previously established seasonal patterns in the mid to high latitudes.

Previous studies have determined that d-excess is largely determined by surface water temperature, relative humidity, and wind speed at the site of evaporation (Merlivat & Jouzel, 1979; Petit et al., 1991; Vimeux et al., 1999). Evaporation on Lake Michigan and therefore the d-excess values of the downwind precipitation formed from this recycled moisture are highest during the cold, dry winter months when the temperature difference between the lake water and overlying winter air is greatest (Lenters et al., 2013). The d-excess values of the precipitation collected from the UMBS and UMCC reflect this trend as seen in **Figure 7D**.

Figure 7 shows that the seasonal trends in the $\delta^{18}O$ and d-excess values of the UMCC and UMBS precipitation samples are significantly less clear and robust than the trends demonstrated by the Huron River samples. The variation observed within the seasonal trends demonstrated by the precipitation datasets can be attributed to the impact of single storm events and weekly weather conditions on precipitation $\delta^{18}O$ and d-excess values. Despite significant precipitation inputs to the Huron River, the variability observed in the seasonal trend of the UMCC precipitation samples is not observed in the Huron River dataset. In other words, the Huron River acts as an efficient isotopic integrator of individual precipitation events due to the influence of other water inputs (e.g. groundwater). The similarity between the amount weighted average $\delta^{18}O$ value for the UMCC precipitation samples (-13.2‰) and the calculated δ_0 value for the Huron River samples (-11.0‰) provides additional evidence that the Huron River is an efficient integrator of mean annual precipitation. These findings suggest that using Huron River data as a stand-in for the more difficult process of collecting periodic precipitation samples to track changes in the isotopic composition of precipitation.

Spatial Variation

The amount weighted average isotope values of the UMCC precipitation samples (δ^{18}O= -13.2‰, δ^2H= -90.5‰) were slightly higher than the UMBS precipitation samples (δ^{18}O= -15.6‰, δ^2H= -109.0‰). This spatial variation between the UMBS and UMCC was expected due to the effect of latitude on δ^{18}O and δ^2H values of precipitation (Dansgaard, 1964). However, the overall similarity and small scale of the isotopic differences between the UMCC and UMBS precipitation samples demonstrates the influence of the regional isotopic signal from moisture recycling off Lake Michigan and suggests that regional variability may be more important than variation at the local level when making water management decisions.

Water Type Variation

Douglas Lake and the groundwater spring analyzed in this work have been the subject of multiple studies carried out at the UMBS. Through a tracer test using a concentrated fluorescein dye solution, Hendricks et al. (2016) concluded that the groundwater spring sampled in this study is connected hydrologically to Douglas Lake via a seep at the lake's bottom. Additionally, Aron et al. (2020) reaffirmed this connectivity using δ^{18}O and δ^2H of water samples collected from Douglas Lake, the groundwater spring, precipitation, and multiple shallow groundwater wells. **Figure 8** shows that the Douglas Lake and groundwater samples plot along similar best-fit regression lines in δ^2H-δ^{18}O space, which shows that the groundwater spring is isotopically similar to Douglas Lake. However, the Douglas Lake samples plot further along this line because they have undergone more evaporation than the samples collected from the groundwater spring. Precipitation may also be directly added to the groundwater spring without first undergoing evaporation on the surface, which would also contribute to the lower δ^2H and δ^{18}O of the groundwater spring compared to Douglas Lake (Hendricks et al., 2016).

Figure 9 shows δ^{18}O slightly increasing and d-excess slightly decreasing from April to October for both the Douglas Lake and groundwater samples collected at the UMBS. These trends can be attributed to increased evaporation off Douglas Lake caused by conditions drying out over the summer months. As described by Aron et al. (2020), the evaporative signal of the Douglas Lake samples indicates the input of recycled moisture from Douglas Lake into the atmosphere, which demonstrates that atmospheric vapor and therefore precipitation in the region are influenced by evaporation from local water sources in addition to Lake Michigan. Atmospheric vapor contributions from local water sources complicate the simple mixing model used to assess the usefulness of downwind precipitation d-excess values as a proxy for evaporative change on the Great Lakes because there are more inputs to the atmospheric water load than just the Great Lakes and further upwind moisture sources.

This study demonstrates the usefulness of combining precipitation, surface water, and groundwater sample collection when using isotopes to study hydrologic processes. Compared to traditional methods for tracing hydrologic mixing such as the time-intensive fluorescein dye study carried out by Hendricks et al. (2016), combined water isotopic studies such as the work presented here and by Aron et al. (2020) are more efficient because they can provide immediate, reliable information about the interconnectedness of water in hydrologic systems. Interconnected water sources such as the Douglas Lake-groundwater spring system observed

at the UMBS are prevalent throughout the Great Lakes region due to the abundance of interconnected aquifers with intricate surface water and groundwater flow paths left behind by the retreat of the glaciers (Winter et al., 2001). Although most large public water supplies are obtained from the Great Lakes themselves, groundwater is the primary source of drinking water for about 8.2 million people within the watershed and is becoming an increasingly important water source for many small manufacturing companies (Grannemann et al., 2000). In other words, employing efficient methods for understanding how water moves through hydrologically connected groundwater and surface water systems is especially important for water management in the Great Lakes region.

Future Work

Continued work to understand the effects of climate change on meteoric water isotope variability in the Great Lakes region is critical to expand our knowledge of important water balance processes. This work assesses the baseline variability of meteoric water isotopes from two locations in the lower peninsula of Michigan; additional sample collection at other locations within the Great Lakes basin would expand our understanding of variability within the region. Continuing sample collection to span multiple years at each of the sampling sites included in this study would also improve our understanding of isotopic variation on larger timescales (annual vs interannual variation).

Future research should expand upon my assessment of the usefulness of d-excess values of local precipitation as a proxy for tracing evaporative change on Lake Michigan. One approach would be to consider the impacts climate change may have on the climatic conditions that control the isotopic composition of evaporation from the Great Lakes such as lake temperature, air temperature, and relative humidity. Jasechko et al. (2014) developed an isotope-based evaporation model that incorporates all of the aforementioned climatic conditions and could be used to assess the impact of changing these conditions on the d-excess values of downwind precipitation.

Conclusions

The variability of meteoric water isotopes in the Great Lakes region is assessed from a suite of precipitation, river, lake, and groundwater samples from two sampling locations in the lower peninsula of Michigan. Isotope results indicate seasonal patterns in the isotopic compositions of the precipitation, river, and lake water samples collected from the UMCC and UMBS. Precipitation samples collected from each sampling location show little variation between sampling sites, suggesting the importance of considering regional isotopic signals when assessing trends in local precipitation. Isotope results for the precipitation, lake, and groundwater samples collected from the UMBS demonstrate the usefulness of collecting water samples from multiple sources when studying hydrologic systems. High d-excess values of the precipitation collected from both locations indicate the input of recycled moisture from Lake Michigan, prompting an assessment of the usefulness of monitoring the d-excess values of precipitation downwind of the Great Lakes as a proxy for identifying future changes in upwind evaporative fluxes. I employ a simple isotope mixing model to complete this evaluation and conclude that the magnitude of change expected to occur in the contribution of evaporation from

the Great Lakes to atmosphere water load may not be detectable in the d-excess values of downwind precipitation over short time scales. This work establishes an understanding of the baseline seasonal, spatial, and water type variability of meteoric water isotopes in the Great Lakes region and opens doors for future opportunities to utilize meteoric water isotopes to trace the effects of climate change on the hydrology of the Great Lakes region.

Supplementary data related to this article can be found here:
https://drive.google.com/file/d/1XFc5Di3dLbguzRMQTC7nE_kVzd4BO25F/view?usp=sharing
(filename: Pelletier2020_supplementarydata)

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