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# Identifying the Isotopic Signature of Lake-Effect Precipitation in Shallow Groundwater

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## Abstract

Three different stable isotopes of water occur in nature, with the majority of water on Earth containing the oxygen isotope  $^{16}\text{O}$ . These isotopes have slightly differing physical and chemical properties.  $\text{H}_2\text{O}$  with heavier oxygen isotopes should theoretically precipitate earlier than lighter isotope  $\text{H}_2\text{O}$ , meaning this natural process should allow for the observation of the magnitude of effects of lake-effect precipitation on the basis of water isotope differences. Furthermore, it may allow for better understanding of the significance lake-effect precipitation plays in recharging shallow aquifers. In this study, patterns of lake-effect precipitation from Lake Michigan were observed in a collection of water samples from shallow-depth (<80 ft) aquifers across West Michigan. Difference in isotope concentrations of collected groundwater samples did not appear to vary significantly based on factors such as longitude or well depth. It was concluded that partitioning of water isotopes observed in Lake Michigan sourced precipitation does not have an appreciable effect on groundwater geochemical composition within the region of observation of this study.

## Introduction / Background

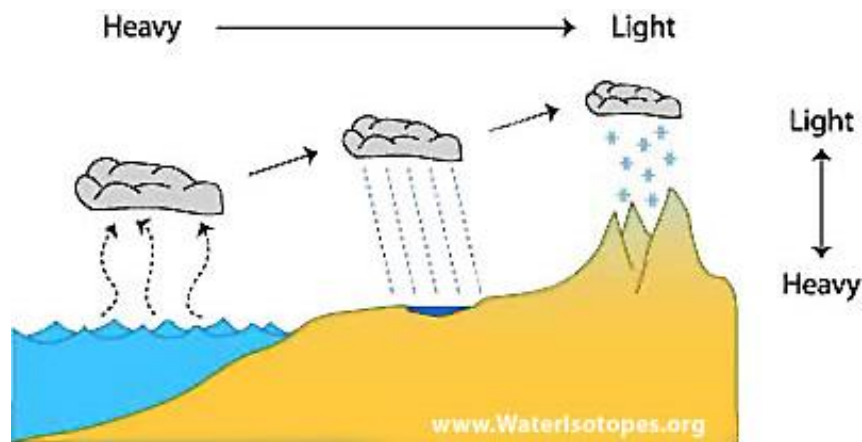
There are three stable isotopes of oxygen and two stable isotopes of hydrogen that occur naturally in water on Earth. Of the three oxygen isotopes,  $^{16}\text{O}$  is the most common, being found in approximately 99.757% of water molecules. The next most common oxygen isotope,  $^{18}\text{O}$ , is found in only 0.205% of water.<sup>1</sup> Hydrogen in water also has two isotope forms, protium ( $^1\text{H}$ ), and deuterium ( $^2\text{H}$ ). Ratios of these oxygen and hydrogen isotope concentrations are widely utilized in Earth science to observe geochemical trends and cycles.<sup>2</sup> In general, the more uncommon isotope of an element displays slightly different physical and chemical properties from their common counterparts. For oxygen and hydrogen, this means their occurrence in a water molecule also thus changes the properties of that molecule. This mass-dependent

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<sup>1</sup> Wright, L. E. Encyclopedia of Geoarchaeology - Oxygen Isotopes. [https://link.springer.com/referenceworkentry/10.1007/978-1-4020-4409-0\\_22#:~:text=Oxygen%20isotope%20species&text=Of%20these%20stable%20isotopes%2C%2016,in%20far%20smaller%20concentrations%20worldwide.](https://link.springer.com/referenceworkentry/10.1007/978-1-4020-4409-0_22#:~:text=Oxygen%20isotope%20species&text=Of%20these%20stable%20isotopes%2C%2016,in%20far%20smaller%20concentrations%20worldwide.) (accessed Apr 9, 2022).

<sup>2</sup> Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468. <https://doi.org/10.3402/tellusa.v16i4.8993>.

behavior difference is important to note because water containing heavier isotopes, namely  $^{18}\text{O}$  and  $^2\text{H}$ , will have a higher preference for liquid and solid phases than water containing lighter isotopes thus affecting their distribution in the hydrologic cycle and its associated processes. For example, during precipitation cycles, the heavier isotope-containing molecules have a greater tendency to precipitate earlier than lighter isotope-containing molecules. As precipitation continues, the ratio of heavy to light isotopes in the precipitation will decrease as the total amount of water precipitated increases (Figure 1). This phenomenon is called partitioning and it is observed in regions where water is evaporated and then precipitated soon after, such as in regions that experience lake-effect precipitation. Partitioning results in a disproportionate concentration (or fractionation) of one isotope over the other in the different hydrologic reservoirs. The cause of this fractionation is due to both non-mass-dependent and mass-dependent effects.<sup>3</sup>



**Figure 1: Partitioning of Water Isotopes in Precipitation.** Note that heavier isotopes have a greater affinity for precipitating earlier.

Because the Great Lakes region of the U.S. has such large quantities of surface water it is also prone to lake-effect precipitation and thus an ideal area to study isotope fractionation effects of water. Lake Michigan is a major perpetuator of lake-effect precipitation. As a result, water isotope partitioning is expressed in precipitation that results from lake-effect precipitation from this lake. However, the relationship between isotope concentrations in precipitation and isotope concentrations in groundwater from the same lake-effect affected

<sup>3</sup> Bao, H., Cao, X., Hayles, J.A., 2016. Triple oxygen isotopes: fundamental relationships and applications. *Annu. Rev. Earth Planet. Sci.* 44, 463–492. <https://doi.org/10.1146/annurev-earth-060115-012340>.

area are not known. Theoretically, groundwater systems closer to Lake Michigan should express higher concentrations of water molecules containing the isotope  $^{18}\text{O}$  relative to  $^{16}\text{O}$  than those further inland, but this pattern has yet to be observed and the extent of this difference is not yet known. Thus, this study sought to observe if a clear isotope footprint of Lake Michigan sourced precipitation could be detected in groundwater, and if so, to evaluate the difference.

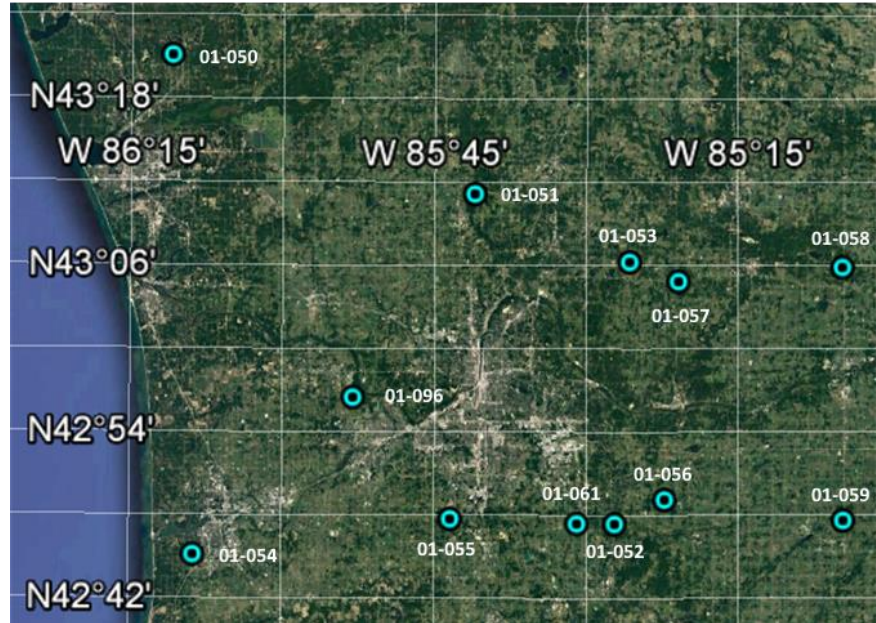
## **Methods**

### *Sample Collection*

Water samples were collected from locations in west to central Michigan during a period between 2/26/22 and 3/7/22. Locations were selected based on two factors, geographic location and well depth. The locations were chosen to obtain an even spread of samples longitudinally with minimal latitudinal variation near similar sites evaluated in Bowen et al. (2012)<sup>5</sup> (Figure 2). Since water from closer to the surface would be more likely to show isotope differences, a well depth limit was set at 80 feet. Samples obtained from deeper than this depth would be unlikely to show precipitation-related geochemical differences, however, two samples were collected from wells with depths of 98 feet and 278 feet to determine if any significant difference would appear. Well depths for locations were obtained using public well records found in the Department of Environmental Quality Wellogic System ([www.egle.state.mi.us/wellogic](http://www.egle.state.mi.us/wellogic)). Water samples were obtained via sampling from outdoor house spickets, so that sampled water would not be affected by any water-softening systems installed in houses. The samples were collected in vials and sent to the Konecky Lab at Washington University for isotope analysis.

**Figure 2: Sample**

**Locations.** This map shows locations from which samples were collected.



*Isotope Analysis*

Several sample metrics were measured in the lab. Isotope concentrations were measured using mass spectrometry, and the results were normalized to isotopic water standards (VSMOW).<sup>4</sup> One reported analytic was a measurement of deuterium excess. Between <sup>18</sup>O and <sup>2</sup>H concentrations and deuterium excess values, a model equation representing the relationship between these three factors could be derived. From there, the source of water in the sample could be determined using a comparison to global averages.

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<sup>4</sup> Sharp, Zachary. "Principles of Stable Isotope Geochemistry, 2nd Edition." (2017). doi:<https://doi.org/10.25844/h9q1-0p82>

## Analysis of Results

Samples were analyzed to determine  $^{18}\text{O}$ ,  $^{17}\text{O}$ ,  $^2\text{H}$ , deuterium excess, and oxygen-17 excess. Shown in Table 1 is the data obtained after sample analysis was completed. All isotope concentrations were reported relative to VSMOW.

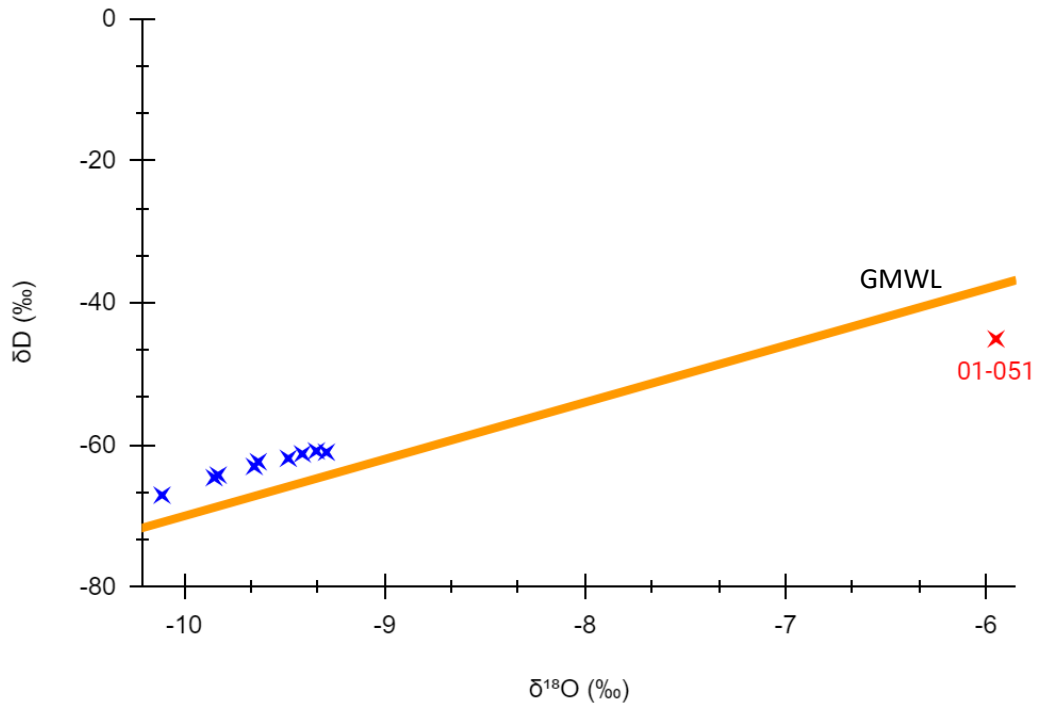
Site ID	Date of Collection	Time of Collection	Longitude	Well Depth (ft)	$\delta^{18}\text{O}$ (‰)	$\delta^{17}\text{O}$ (‰)	$\delta\text{D}$ (‰)	D-Excess (‰)	$^{17}\text{O}$ -Excess ( $10^6 \times \delta$ )
01-051	2/26/22	16:15	-85.682	54.00	-5.95	-3.14	-45.08	2.52	10
01-050	2/26/22	14:27	-86.180	40.00	-10.11	-5.33	-67.06	13.78	21
01-052	3/3/22	12:00	-85.451	32.00	-9.29	-4.89	-61.02	13.26	26
01-054	3/5/22	13:18	-86.142	60.00	-9.63	-5.08	-62.36	14.68	14
01-057	3/5/22	16:16	-85.346	16.00	-9.85	-5.2	-64.6	14.22	14
01-058	3/5/22	16:42	-85.075	52.00	-9.65	-5.07	-63.02	14.16	37
01-059	3/5/22	17:42	-85.075	66.00	-9.83	-5.19	-64.24	14.38	16
01-061	3/7/22	10:15	-85.513	44.00	-9.34	-4.9	-60.85	13.9	46
01-096			-85.881	278.00	-9.48	-4.99	-61.88	13.99	33
01-097			-85.747	98.00	-9.41	-4.97	-61.25	14.06	13

### Global Meteoric Water Line Comparison

Samples were plotted based on  $^{18}\text{O}$  and  $^2\text{H}$  concentrations and compared to a global standard (Figure 3). The orange line represents the Global Meteoric Water Line (GMWL), which is a global average of relationships between concentrations of these two isotopes. The equation for this relationship is expressed as  $d = ^2\text{H} - 8 * ^{18}\text{O}$ , where the deuterium excess value  $d = 10$  ‰ for the GMWL. Generally, values that plotted significantly below the line are usually water left behind after evaporative processes, and values above the line are from water vapor generated from evaporative processes.<sup>5</sup> Notably, all samples had similar isotope ratios, except for one sample (sample X), which had significantly different isotope concentrations than all other samples. Due to this difference and the fact that this sample was significantly below the

<sup>5</sup> Bowen, G. J., C. D. Kennedy, P. D. Henne, and T. Zhang. 2012. Footprint of recycled water subsidies downwind of Lake Michigan. *Ecosphere* 3(6):53. <http://dx.doi.org/10.1890/ES12-00062.1>

GMWL, it was determined to be highly likely that this sample was somehow affected during shipping, and thus its data was disregarded.

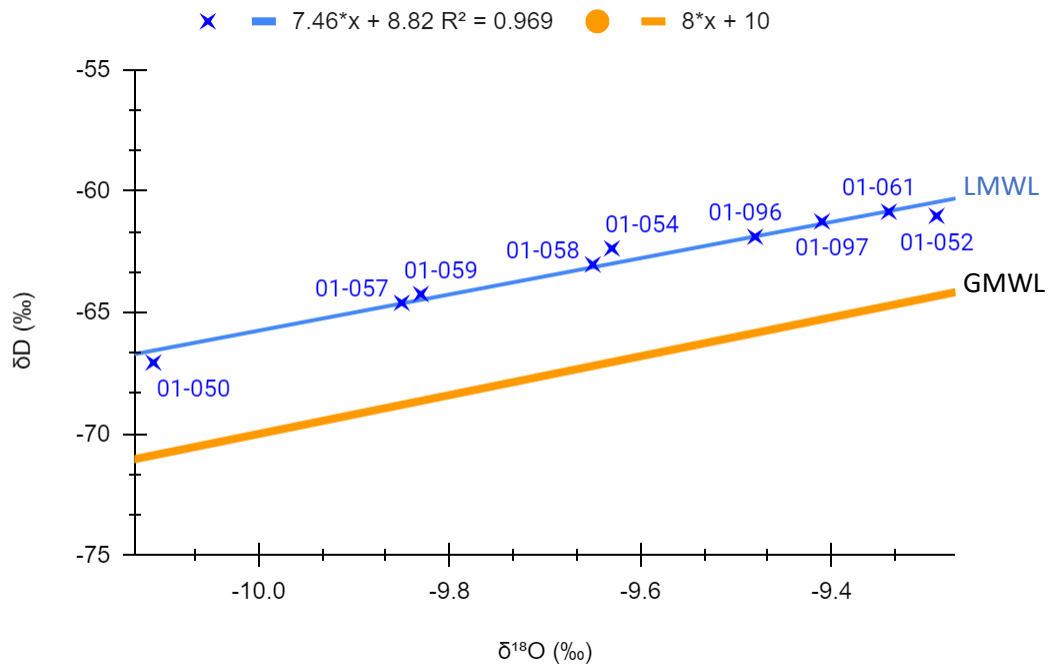


**Figure 3: Comparison of oxygen-18 and deuterium isotope concentrations.** Note that all values are above the GMWL (shown in orange) besides one, marked in red.

The remaining samples were plotted again against the GMWL and a new trendline was observed (Figure 4). This new trendline, called the Local Meteoric Water Line (LMWL), is similar to the GMWL in that both provide guidelines relating deuterium and oxygen-18 isotope concentrations, but whereas the GMWL is a global guideline, the LMWL is more specific and accurate to the region from which samples were collected. In this case, the equation representing the LMWL was determined to be  $d = \delta^2\text{H} - 7.46 * \delta^{18}\text{O}$ , where the deuterium excess value  $d = 8.82$  ‰. Since values above the GMWL tend to be from samples from water vapor, the fact that the LMWL was higher than the GMWL was not surprising, since the studied region experiences a high amount of lake-effect precipitation.



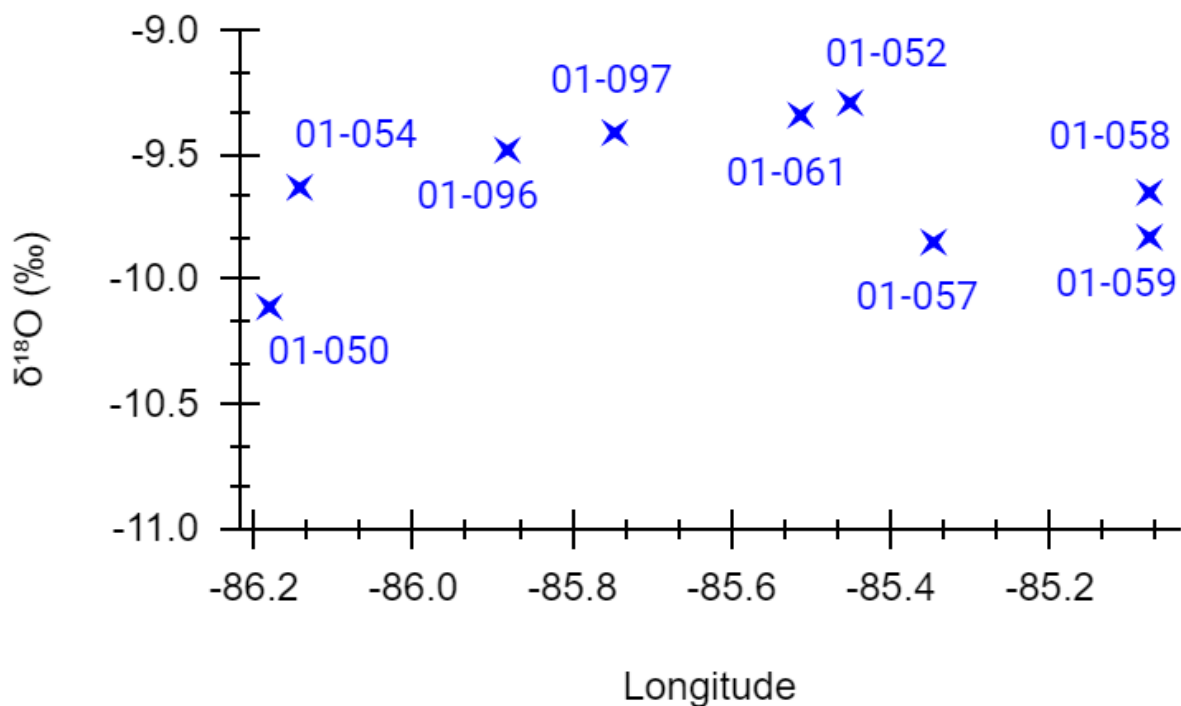
Comparison to isotope data from Bowen et al. 2012 shows that the sample dataset falls within expected bounds for samples collected from the West Michigan region. Most samples from the 2012 study had  $^{18}\text{O}$  and  $^2\text{H}$  concentrations that varied from -9.0 to -12.5 ‰ and -60 to -85 ‰ respectively, normalized to VSMOW. Isotope concentrations from current samples tend to trend towards the higher end of these values but remain proportional to the overall established concentration ratios from this region. The 2012 paper covered a larger area than the current research, so the lack of larger variation is unsurprising for a smaller-scale study. Samples from the older study also trended above the GMWL in a similar pattern to samples from this research.<sup>5</sup>



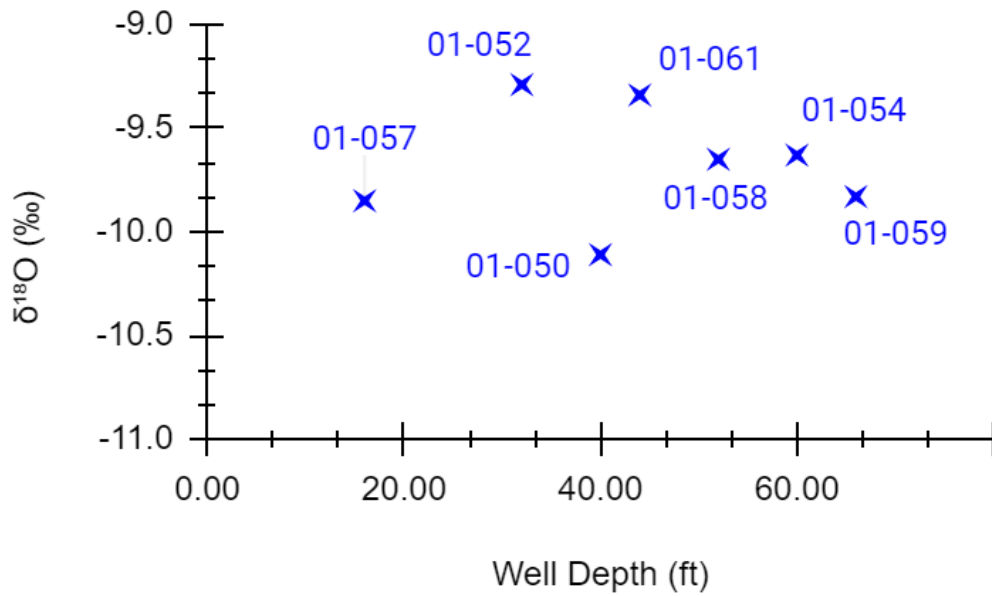
**Figure 4: Comparison of Local Meteoric Water Line to the Global Meteoric Water Line.** The best-fit line for the LMWL is shown in blue and the GMWL is shown in orange. Minus the outlier, the samples closely correlated to the LMWL.

### Well Depth and Longitude Comparison

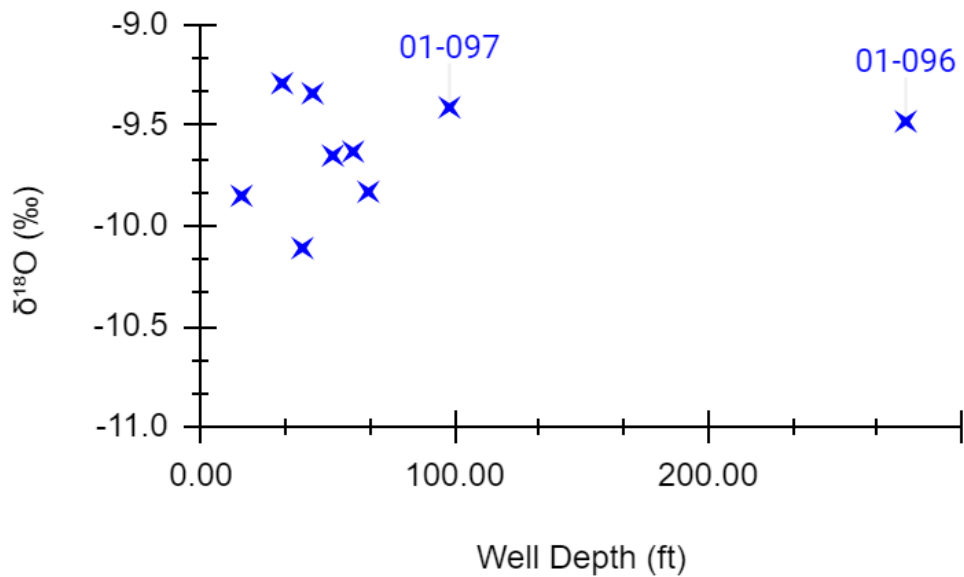
Isotope concentrations were also compared to the variables well depth and longitude (Figures 5 and 6). Neither of these factors appeared to correlate with isotope concentrations. The samples collected from the 98-foot and 278-foot wells did not have significantly different isotopic values than the shallower samples. These samples are shown in the extended graph comparison of longitude to well depth (Figure 7). As a result, it was determined that the effect of lake-effect precipitation on groundwater isotopic composition is negligible within the scope of this study, and as a result it is not possible to track the isotopic signature of lake-effect precipitation in shallow groundwater without more data and data from other possible end member sources.



**Figure 5: Comparison of Oxygen-18 Concentration to Longitude.** No especially strong correlation was observed between these two factors. Thus, these two factors appear to be independent of one another.



**Figure 6: Comparison of Oxygen-18 Concentration to Well Depth.** Similar to the comparison between oxygen-18 concentration and longitude, there was no strong correlation observed between these two factors.



**Figure 7: Extended graph comparison of Oxygen-18 Concentration to Well Depth.** This graph shows the same data as Figure 6 but including the two deeper well data points. Isotope concentrations for these two points did not greatly differ from concentrations obtained from shallower depths.

### Comparison to Non-Lake-Effect Calculations

Using the Online Isotopes in Precipitation Calculator (OIPC),  $^{18}\text{O}$  and  $^2\text{H}$  concentrations for any location can be calculated.<sup>678</sup> However, these values do not take lake-effect precipitation into account and instead follow national trends. By inputting a central location from the study area at the appropriate elevation (~200 meters), a monthly estimation of values for hypothetical isotope values without lake-effect precipitation can be calculated. These values, shown in Table 2, range from vary from -16.3 ‰ to -3.2 ‰ for  $^{18}\text{O}$  and from -118 ‰ to -18 ‰ for  $^2\text{H}$  annually. Since the samples were collected during late February and early March, averaging the oxygen-18 concentration for these two months gives a value of -13.9 ‰. This is lower than the experimental values, which were generally between -9 and -10 ‰. This is significant because it shows that lake-effect precipitation does have a quantifiable effect on precipitation concentrations. If lake-effect precipitation did not occur in this region, precipitation would have a lower oxygen-18 concentration. Additionally, this calculator shows how much these isotopic concentrations change throughout the year as climatological and meteoric conditions change.

**Table 2: OIPC Values for Oxygen-18 and Deuterium Concentrations**

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
$\delta^2\text{H}$ (‰, V-SMOW)	-118	-110	-87	-55	-31	-22	-18	-24	-34	-55	-69	-99
$\delta^{18}\text{O}$ (‰, V-SMOW)	-16.3	-15.4	-12.4	-8.2	-5.0	-3.9	-3.2	-3.9	-5.5	-8.2	-10.3	-14.1

### Conclusion

The main reasoning for why no isotopic footprint of Lake Michigan sourced precipitation could be observed is due to the large variance in hydrologic composition of precipitation throughout the year. This is very apparent when looking at compositional changes by month in Table 2. Even though the OIPC does not account for lake-effect precipitation, the general

<sup>6</sup> Bowen, G. J. (2022) The Online Isotopes in Precipitation Calculator, version 3.1. <http://www.waterisotopes.org>.

<sup>7</sup> Bowen G. J., Wassenaar L. I. and Hobson K. A. (2005) Global application of stable hydrogen and oxygen isotopes to wildlife forensics. *Oecologia* **143**, 337-348, doi:10.1007/s00442-004-1813-y.

<sup>8</sup> Welker J.M., 2000. Isotopic ( $\delta^{18}\text{O}$ ) characteristics of weekly precipitation collected across the USA: An initial analysis with application to water source studies. *Hydrological Processes* **14**, 1449-1464.

pattern is indicative of how much the isotopic concentrations change throughout the year. Additionally, groundwater systems are vast and contain massive amounts of water. To significantly change geochemical composition in these systems, many rain events over a long period of time would be required, since singular and sporadic events would not contain the necessary volume of water to significantly affect these systems.

It may yet be possible to detect a lake-effect precipitation footprint in groundwater, however, within the scope of this study it was not observed. A study conducted over a longer period of time may show more defined trends that shed additional insight into this theoretical pattern. Other possibilities may include conducting the study at a different point in the year or surveying a larger number of locations to provide a wider snapshot of the region.