Correlation of seasonal precipitation isotopic profile with the modern climatological data: a case study from the western Newfoundland region of Canada

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Abstract: The measurement of stable water isotopes (i.e. δ18O and δ2H) in precipitation is a powerful tool for detecting changes in climate patterns, assessing groundwater movements and studying the hydrological budget. In this study, daily precipitation was collected and δ18O and δ2H were analysed in Corner Brook, western Newfoundland, and Labrador, for 2015. The study provides the first background data of any kind related to liquid water isotopes in western Newfoundland. More than 130 samples were analysed using a state-of-the-art cavity ring-down spectrometer, the Picarro Liquid Water Isotope Analyzer L2130-i, with a minimal instrumental error. The data suggest seasonal variations in which the δ18O varies from −33.4 to −0.03‰ (± 0.023‰) and δ2H ranges from −253.4 to 15.1‰ (± 0.148‰). Our data are compared with modern meteorological data and publicly available δ18O and δ2H data from greater Atlantic Canada, which suggests that the atmospheric circulation patterns, spatial features and other climate factors are distinct in Corner Brook. Isotopes in meteorological precipitation data referenced and collected in this study reflect the cool, wet climate and air-mass fluctuations unique to the geographical region and thus, this baseline is fundamental to understanding the modern isotope hydrological/climatic studies for this region.

Supplementary material: Oxygen and hydrogen isotopes and modern climatological data (Appendices 1 and 2) used in the paper are available at https://doi.org/10.6084/m9.figshare.c.5122096

Understanding the relationship between precipitation (snow, rain, storms, etc.) and isotopes in high and low latitudes and high spatial and temporal frequency requires sophisticated approaches and instrumentation (IPCC 2013; Fiorella et al. 2018). Historically one of the most important proxies for investigating the hydrological cycle has been the use of stable (Craig 1961; Dansgaard 1964; Bowen 2010) hydrogen and oxygen isotopes (i.e. δ2H and δ18O). Water reflects changes in hydrological processes as these isotopes undergo measurable and systematic fractionations (Sigenthal and Oeschger 1980) between phases in the water cycle (Birks and Gibson 2009). This makes these isotopes a useful tool in examining the hydrological cycle with respect to changes in climatic and geographic conditions from which modern precipitation is formed, such as latitude, temperature, altitude and humidity (Rozanski et al. 1993; Bowen 2010; Delavau et al. 2011; Jasechko 2019). The variation of stable isotope abundances of hydrogen and oxygen in meteoric precipitation has been documented by the Global Network of Isotopes in Precipitation of the International Atomic Energy Agency (IAEA) for over 50 years (Rozanski et al. 1993; Gat 2010).

The measurement of stable water isotopes (i.e. δ18O and δ2H) in precipitation is a powerful tool for detecting changes in climate patterns, assessing groundwater movements and studying the hydrological budget. In this study, daily precipitation was collected and δ18O and δ2H were analysed in Corner Brook, western Newfoundland, and Labrador, for 2015. The study provides the first background data of any kind related to liquid water isotopes in western Newfoundland. More than 130 samples were analysed using a state-of-the-art cavity ring-down spectrometer, the Picarro Liquid Water Isotope Analyzer L2130-i, with a minimal instrumental error. The data suggest seasonal variations in which the δ18O varies from −33.4 to −0.03‰ (± 0.023‰) and δ2H ranges from −253.4 to 15.1‰ (± 0.148‰). Our data are compared with modern meteorological data and publicly available δ18O and δ2H data from greater Atlantic Canada, which suggests that the atmospheric circulation patterns, spatial features and other climate factors are distinct in Corner Brook. Isotopes in meteorological precipitation data referenced and collected in this study reflect the cool, wet climate and air-mass fluctuations unique to the geographical region and thus, this baseline is fundamental to understanding the modern isotope hydrological/climatic studies for this region.

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The origin and dynamics of air masses which affect a certain area dictate the patterns measured in the isotopic composition of precipitation, especially when these patterns change with seasonality (Araguás-Araguás et al. 2000; Gat 2010).

The δ18O and δ2H values of meteoric water are strongly linked as both hydrogen and oxygen isotopes experience the same sequence of events as water molecules during the migration of air masses (Dansgaard 1964; Rozanski et al. 1993; van der Veer et al. 2009; Bowen 2010; Delavau et al. 2011). On a regional level, this correlation is expressed as a linear equation, obtained by plotting the δ18O along the δ2H on the y-axis for a group of samples from a certain geographic area, known as a local meteoric water line (LMWL) (Rozanski et al. 1993; Darling et al. 2006):

$$\delta^2H = m(\delta^{18}O) + d$$

(1)

Quantitative calculation suggests that the slope (m) is close to 8, as determined by the ratio of equilibrium isotope enrichments for 2H and 18O, which is the result of relating the liquid–vapour fractionation factors for 2H and 18O at 25°C (Merlivant and Jouzel 1979; Darling et al. 2006). The intercept of the

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LMWL, known as the ‘deuterium excess’ ($d$), is mainly controlled by parameters of the evaporation processes in major source areas for atmospheric moisture (Rozanski et al. 1993; Darling et al. 2006).

**Meteorological drivers of isotopic fractionation in water**

The $\delta^{18}$O and $\delta^2$H in water molecules vary widely because of isotopic fractionation during the phase changes throughout the hydrological cycle (Sklash et al. 1976; Sharp 2007). The extent of isotope fractionation of meteoric water is generally related to several environmental parameters, namely the surface air temperature, latitude, altitude, distance to the coast and amount of precipitation that characterizes a given sampling site (Dansgaard 1964; Jouzel et al. 2008). The most depleted $\delta^{18}$O and $\delta^2$H usually occur during the period of most intense rain (Good et al. 2014). It has also been observed that convective cloud types (Bony et al. 2008) produce precipitation with higher $\delta$-values than clouds formed in the stratosphere. Thus, the $\delta^{18}$O and $\delta^2$H of precipitation from a given rain event depends heavily on the meteorological history of the air mass from where the precipitation is formed. Rain and snow (or hail) can differ in their $\delta^{18}$O and $\delta^2$H because raindrops may undergo evaporation and isotopic exchange with residual atmospheric vapour while falling to the Earth’s surface (Jouzel and Merlivat 1984; Burnett et al. 2004). Measurements of the water isotopes collected in single rainout events have revealed that in-storm variations can be relatively large, reaching in some cases >21‰ in $\delta^{18}$O and >160‰ in $\delta^2$H (Good et al. 2014; Darling et al. 2006).

Raindrops leaving a cloud base continuously isotopically re-equilibrate with the surrounding moisture on their way to the surface. The degree of this re-equilibration is controlled by the size of the raindrops, the actual height of the cloud base and the relative humidity of the atmosphere beneath the cloud (Darling et al. 2006). This causes the isotopic composition of rainfall collected at the ground surface to be close to isotopic equilibrium with near-ground water vapour (Darling et al. 2006). Solid precipitation (snow or hail) is usually more depleted in heavy isotopes, reflecting equilibrium conditions at much lower in-cloud temperatures (Jouzel and Merlivat 1984; Darling et al. 2006). The isotopic composition of precipitation samples, representing a certain rainfall event in whole or part, therefore, depends strongly on the meteorological history of the air mass and specific conditions in which the precipitation is formed, as well as the isotopic composition of humid air through which it falls (Rozanski et al. 1993; Darling et al. 2006). Regular seasonal variations of isotopes in precipitation are observed at mid and high latitudes where seasonal variations of temperature are well developed (Darling et al. 2006; Bowen 2010; Delavau et al. 2011).

**Regional weather and circulation in western Newfoundland**

The two distinct seasons in the western Newfoundland are dominated by excessive snow and heavy rain and accompanying fluctuations in surface air temperature (SAT). In the winter months (defined as November–March for the study), monthly precipitation can vary from 93.3 to 149.2 mm (of which snowfall amounts range from 36.7 to 105.5 cm), whereas the SAT ranges from $-10.6$ to $5^\circ{C}$ (Fig. 1). In contrast to the winter season, summer (spring and autumn are nearly non-existent) averages 80.4–112.2 mm of precipitation (of which snowfall amounts range from 0 to 23.4 mm) and SAT varies from $-1.2$ to $22^\circ{C}$. In addition to the seasonal precipitation (i.e. snow and rainfall), western Newfoundland also receives occasional rain storms, hurricanes and snow owing to winter storms. The distinct differences in seasonal climatic conditions in the precipitation-laden area of western Newfoundland (e.g. Corner Brook) and the abundance of rain and snow throughout the year present an opportunity to study the process of isotopic fractionation in precipitation over a range of weather patterns. Therefore, the objectives of the study were to: (1) collect and determine the isotopic composition of snow and rain; (2) compare these data with the meteorological data; and (3) assess the characteristics of the seasonal trends in the region of western Newfoundland within the wider Atlantic Canada using publicly available data.

**Materials and methods**

Precipitation samples were collected from 12 January 2015 until 19 December 2015 using a large plastic container on the ground at Grenfell Campus, MUN, Corner Brook, western Newfoundland (Fig. 2). The location of the sample collection site is far from major walkways and was sheltered from the wind, which is thought to improve the representativeness of the sample as well as preventing fallen snow from blowing into the container. On 25 April, 12 May, 20–22 May, 6 June, 13 June, 8–22 July, 1–12 September, 20 September, 19 October, 14–15 November and 17–19 December the container was moved to Meadows, Bay of Islands, NL (Fig. 2). The method of water collection was to leave the container outside anywhere from 30 min to several hours, depending on the time required to collect an adequate amount of precipitation (no less than 200 ml). Once a
sufficient amount of precipitation was collected, the container was brought inside the laboratory (Thompson and Mosley-Thompson 1981).

Snow samples were allowed to melt at room temperature and then processed, whereas rain was processed immediately. Processing consisted of the transfer of precipitation from the container using a large funnel into a 2000 ml plastic graduated cylinder. The liquid sample was then filtered (using Whatman no. 4 filter paper) to remove solid particle impurities in the sample. The 200 ml water sample was filtered directly into two clear plastic 75 ml bottles and sealed to prevent (Leslie et al. 2017) air bubbles. The sample bottles were labelled with the date and times the container was set and retrieved, and stored in a refrigerator at c. 2.0°C until instrumental analysis. One of the two 75 ml portions of filtered water was used to estimate salinity and conductivity using an Orion Model 105 conductivity meter with the factory supplied 1413 µS/cm (692 ppm as NaCl) standard solution when sample contamination appeared to be a possibility. The other 75 ml portion of the sample was used in the isotopic analysis. In total, 134 precipitation samples were collected from 12 January to 19 December 2015, which are listed in Appendix 1.

Several surface water samples within the region were collected as well. Samples include Tipping’s Pond (16 February 2015), Big Bonne Bay Pond (4 September 2015), Meadows Water Supply Pond (6 September 2105) and an unknown named pond (6 September 2015) (Fig. 2). To collect the sample, a 500 ml plastic bottle was completely submerged in the water vertically to allow the dispersal of air, and the bottle was sealed underwater to prevent the trapping of air bubbles. The sample was then filtered and stored in the same manner as the precipitation samples, and subsequently analysed for possible use in future research. The results of surface water sample analysis are not discussed further in this publication.

**Method**

The measurement of δ¹⁸O and δ²H is traditionally carried out using isotope ratio mass spectrometry; however, in the last 20 years, it has most often been carried out using cavity ring-down spectroscopy (CRDS), which is a very sensitive laser absorption technique (Zalicki and Zare 1995; Romanini et al. 1997; Wheeler et al. 1998). CRDS has several advantages when compared with traditional absorption techniques; it is virtually immune to shot-to-shot fluctuations in laser intensity and utilizes ultra-high-reflectivity mirrors to create very long effective path lengths that allow for trace detection of isotopomers (Wheeler et al. 1998; Bailey et al. 2015).

A state-of-the-art CRDS, the Picarro L2130-i Liquid Water Isotope Analyzer with an autosampler, was utilized in this study. The instrument automatically and continuously calculates and compares the ring-
The map shows the regional topography of the western Newfoundland and two locations at which precipitation samples and four locations at which surface water samples were collected during this study. Inset depicts the generalized geography of Atlantic Canada and the sites of collection of precipitation and water isotopic data, namely Corner Brook, Goose Bay, Bay D’Espoir and Truro, discussed in the text.
down the time of the cavity with and without absorption owing to the target gas species (Picarro Technology 2015). This accounts for any losses of absorption present in the optical cavity that could be changing over time or due to non-uniformity of reflection in the mirrors (Picarro Technology 2015). The laser is tuned to several locations across the spectral absorption line of the target gas (and ring-down measurements are conducted at all these points) and direct numerical output of $\delta^{18}O$ and $\delta^2H$ is recorded once the calibration has been completed.

In isotope geochemistry, the isotopic composition is conventionally expressed as a delta value ($\delta$) as follows:

$$\delta^{18}O_{\text{VSMOW-SLAP2}} = \frac{R^{\text{sample}}(18O/16O) - R^{\text{VSMOW-SLAP2}}(18O/16O)}{R^{\text{VSMOW-SLAP2}}(18O/16O)} \times 1000$$

$$\delta^2H_{\text{VSMOW-SLAP2}} = \frac{R^{\text{sample}}(2H/1H) - R^{\text{VSMOW-SLAP2}}(2H/1H)}{R^{\text{VSMOW-SLAP2}}(2H/1H)} \times 1000$$

where $R$ is the relative abundance of heavy and light isotopes of oxygen/hydrogen for the measured sample and standard (Craig 1961; Dansgaard 1964). Isotopic $\delta$-values are presented as per mille (parts per thousand, %$e$) deviations from an appropriate standard. For liquid water, isotope ratios are compared with the internationally accepted standard United States Geological Survey (USGS) Vienna Standard Mean Oceanic Water or IAEA Standard Light Antarctic Precipitation.

Initial drift testing and the development of a consistency standard were carried out using USGS Vienna Standard Mean Oceanic Water ($\delta^{18}O = 0.00\%e$, $\delta^2H = 0.00\%e$) and IAEA Standard Light Antarctic Precipitation 2 ($\delta^{18}O = -55.50\%e$, $\delta^2H = -427.50\%e$) (USGS 2012; IAEA 2015). One of the two previously described 75 ml sample water bottles were used for analysis. A clean and dry Pasteur pipette was used to transfer $c. 2$ ml of each of the water samples into vials which had caps with a septum appropriate for use with the autosampler syringe. The autosampler was set to rinse the syringe once in 2 µl of $n$-methyl-2-pyrrolidone wash solvent (as recommended in the Picarro user instruction manual), once in 2 µl deionized water and once in 2 µl of the sample to be analysed, before taking active measurements of each vial. After rinsing, six separate 2 µl injections of the sample in the vial were analysed (as per recommendations in the Picarro instrument user manual). The data for the first three injections were discarded to reduce any possibility of contamination from prior samples, resulting in three isotope measurements for every sample vial. The sampling method used groups of 25 vials (one vial per sample) plus a consistency standard in the middle, bracketed by the international standards as well as the consistency standard, to produce three-point calibration lines. Sample measurements were fitted to the corresponding line for each group of 25 samples, one for each of the $\delta^{18}O$ and $\delta^2H$ measurements, providing the calibrated measurements. Several samples were re-measured to test the veracity of analytical confidence and assess variance. Statistical analyses include standard deviation ($\sigma$) for each triplicate analysis and outlier analysis was evaluated using the standard Dixon $Q$-test with a 90% confidence level (CL90%) (Rorabacher 1991).

**Modern meteorological data**

Modern meteorological data were collected from the weather station housed in the Grenfell Campus of Memorial University of Newfoundland, which automatically records every 30 min. The data include outside air temperature, wind speed and direction, wind chill, heat index, atmospheric pressure, solar radiation and rain amounts, among others. Meteorological data for 1 January 2015 (12:30 a.m.) to 31 December 2015 (11:30 p.m.) (Appendix 2) were used for the calculation of daily and monthly averages of temperature.

**Results**

In total, 134 samples were analysed and the data are plotted in Figure 3. Two samples were discarded after performing the standard statistical $Q$-test for each triplicate measurement and were suspected of contamination by salts during sample collection. Two calibration plots (one for $\delta^{18}O$ and one for $\delta^2H$) were constructed for every group of 25 samples. Calibration curves obtained for the data gave good linearity, with $R^2$ values of greater than 0.999. The calibration curves were used to obtain calibrated $\delta$-values, which were then used to construct an LMWL from the raw data for Corner Brook as presented in Figure 3a. Average instrumental error ($1\sigma$) across all samples was $\delta^{18}O$ ($\%e$) = $\pm 0.023$, and $\delta^2H$ ($\%e$) = $\pm 0.148$, indicating excellent precision.

**Discussion**

**Validation of correlation between the isotopes and modern meteorological data**

Seasonal variation in snow and rain and the surface air temperature plays a dominant role in influencing
the liquid water $\delta^{18}O$ and $\delta^2H$ in western Newfoundland. The raw (unfiltered) measured isotope data and daily recorded temperature data in the Corner Brook weather station are plotted in Figure 4a. Further, the weighted monthly averages of both datasets are also plotted in Figure 4b. A prominent pattern from both the daily and monthly averages appears which confirms the overriding seasonality factor, consistent
with the concept that the isotopic composition of $\delta^{18}O$ and $\delta^2H$ is heavily dependent upon kinetic factors, and therefore, the impact of temperature (Vachon et al. 2010). It has been noted that fluctuations in air temperature are closely reflected by $\delta^{18}O$ and $\delta^2H$ signals (Delavau et al. 2011). It is, therefore, unsurprising that a clear distinction can be made between summer and winter seasons based on the $\delta^{18}O$ and $\delta^2H$ measurements in western Newfoundland (Corner Brook). Figure 4 shows that at the beginning of 2015 (January–March), $\delta^{18}O$ and $\delta^2H$ data show a more depleted pattern which is followed by a sharp increase in less depleted isotope values to April. This change in the isotopic values suggests a heavy influence of the temperature whereby solid precipitation (snow or hail) is usually more depleted in heavy isotopes, reflecting equilibrium conditions at much lower in-cloud temperatures (Peng et al. 2004; Rangarajan et al. 2017). A general trend of less-depleted $\delta^{18}O$ and $\delta^2H$ from April to October further reflects the shift from solid precipitation (snow or hail) to liquid (rain). Again, this suggests influence by temperature effects on isotopic re-equilibration of water droplets as they fall through the warmer (and therefore, more isotopically enriched) moisture in the air (Vuille et al. 2005; Kurita et al. 2012). A sharp decline of more depletion occurs to November, where more depleted $\delta^{18}O$ and $\delta^2H$ are observed from November to December (Fig. 4). Additionally, changes in the temperature lines are mirrored by the isotope lines. A clear distinction between highly depleted $\delta^{18}O$ and $\delta^2H$ and less depleted $\delta^{18}O$ and $\delta^2H$ can be made between winter and summer seasons (Peng et al. 2004; Mark and McKenzie 2007; Rangarajan et al. 2017).

The slope and deuterium excess values obtained from the equation of the LMWL serve as a useful index to evaluate the extent to which seasonality, among other factors, influences the isotopic fractionation (Rozanski et al. 1993; Edwards et al. 2002; Gat 2010). The seasonality pattern of isotopic depletion in this study is reinforced when examining Figure 3b, which depicts two different LMWLs for both winter and summer. The winter LMWL equation is $\delta^2H = 7.9988(\delta^{18}O) + 20.837$ with $R^2 = 0.9718$, whereas the summer LMWL equation is $\delta^2H = 7.831(\delta^{18}O) + 9.5517$ with $R^2 = 0.9796$. This difference between the two LMWLs is expected since the deuterium excess in winter is higher than 10, indicating less re-evaporation of water (solid and liquid), whereas the summer deuterium excess is less than 10, indicating more re-evaporation of water (Kendall and Coplen 2001; Bowen 2010; González et al. 2016). Paired with daily temperature data, as plotted in Figure 4a, it can be seen that the colder winter-time temperatures experienced in Corner Brook are reflected by more depleted $\delta^{18}O$ and $\delta^2H$ than those of the warmer summer time. This is a clear expression of several known isotopic fractionation mechanisms, including depletion owing to lower in-cloud temperatures (and thereby the formation of snow instead of rain), as well as the changing air pressure system which affects the area in different seasons. It should be noted, however, that during the winter season there is increased complexity of driving forces of water isotope patterns, such as enhanced kinetic effects during phase changes at below-zero temperatures, which accounts for the imperfect reflection of temperature by $\delta^{18}O$ and $\delta^2H$ (Delavau et al. 2011).

**Coherency of Atlantic Canada isotopic data linked to the atmospheric circulation**

The $\delta^{18}O$ and $\delta^2H$ data in western Newfoundland suggest a broader link to Atlantic Canada through atmospheric circulation. To assess the overarching mechanism for the water isotope data in western Newfoundland, publicly available data from three Atlantic sites (Fig. 2; https://nucleus.iaea.org/wiser/index.php) are also plotted in Figure 5. Among the various initiatives to characterize the isotopic variability in precipitation within Canada, the Canadian Network for Isotopes in Precipitation and the Canadian Air and Precipitation Monitoring Network (CAPMoN) have been collecting precipitation data and performing analysis since 1961 (Jamieson and Wadleigh 1999; Birks and Gibson 2009). Several sites of interest within Atlantic Canada have publicly available water isotope data, including Truro in Nova Scotia (Canadian Network for Isotopes in Precipitation: January 1975 to December 1983), Goose Bay in Labrador (Global Network of Isotopes in Precipitation: May 1961 to June 1969; CAPMoN: March 1997 to November 2010) and Bay D’Espoir in Newfoundland (CAPMoN: February 1997 to November 2010) (IAEA/WMO 2015). These sites are geographically similar (Fig. 2) and all have climatic factors, namely latitude, distance from the coast and seasonal variations, similar to those of Corner Brook (Vasseur and Catto 2008). However, each differs in specific climate because of differing atmospheric circulations and movement of air mass in each area.

It is well established that the $\delta^{18}O$ and $\delta^2H$ are controlled by Rayleigh distillation of atmospheric vapour, which is mainly determined by changes in temperature of air mass because of the moisture carrying capacity of air is temperature dependent (Dansgaard 1964; Delavau et al. 2011; Klein et al. 2015). Many different geographic and climatic factors are correlated with changes in temperature and therefore rainfall isotopic composition (Delavau et al. 2011; Mark et al. 2017). Such factors include latitude, elevation, distance inland from the coast and humidity. Further, changes in moisture sources, transport
processes, rainout history and seasonality also strongly influence the composition of stable water isotopes (Delavau et al. 2011). Moisture sources to continental Canada include the Pacific, Arctic, Gulf of Mexico, Gulf of North Atlantic, Gulf of St Lawrence and potentially large lake systems such as the Great Lakes (Vasseur and Catto 2008; Delavau et al. 2011). It is noteworthy that the Atlantic Provinces, i.e. New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland and Labrador, typically record more enriched δ\(^{18}\)O and δ\(^{2}\)H values than throughout the rest of Canada, predominantly as a result of their proximity to the ocean (close to moisture source) and lower latitude location (Delavau et al. 2011).

Owing to geographic similarities (e.g. similar latitude, distance from the coast, etc.), it can be expected that δ\(^{18}\)O and δ\(^{2}\)H patterns in western Newfoundland would be similar to those of other localities of Atlantic Canada. It is clear from Figure 5 that data from both Truro and Bay D’Espoir appear higher on the GMWL than those of Corner Brook and Goose Bay. These differences can be attributed to influences by the Labrador Current (Han et al. 2008; Rashid et al. 2017, 2019) and the North Atlantic Oscillation (NAO) (Visbeck et al. 2001). The Labrador Current brings cold polar water from Baffin Bay and Hudson Bay, south of the Hudson Strait (Rashid et al. 2017), whereas the NAO is a cyclic variation of pressure systems that influences weather patterns in northern areas including Newfoundland and Labrador (Khatiwala et al. 1999; Vasseur and Catto 2008). When a strongly positive NAO phase is in effect, Labrador experiences much colder

Fig. 4. (a) Daily average surface atmospheric temperatures (bottom panel) and measured daily averaged precipitation isotopes for Corner Brook (western Newfoundland) in 2015.
temperatures, and slightly below average colder temperatures are experienced along with the northern parts and eastern coastlines of Newfoundland (Vasseur and Catto 2008). A strongly positive NAO phase can also produce strong northwesterly to northeasterly winds varying in latitude throughout Newfoundland and Labrador (Vasseur and Catto 2008). In any case, the areas of Labrador and western Newfoundland are under these direct influences, which do not reach further south to Nova Scotia or southern Newfoundland, recording more depleted isotope signals in the winter. In addition, Nova Scotia and southern Newfoundland are more heavily influenced by warm air masses stemming from the Gulf Stream in the summer, which seldom reaches as far north as Labrador (Vasseur and Catto 2008). Western Newfoundland does experience the impact of warm air mass to some extent; however, air masses lose most of their precipitation when moving over the Long-Range Mountains (owing to the elevation effect), which can result in slightly more depleted isotopic signatures in the Humber Valley and Corner Brook (Kirby and Beersing 2012). Continued measurement of $\delta^{18}O$ and $\delta^2H$ of precipitation in western Newfoundland would provide a longer-term perspective of the impact of regional climate change and atmospheric processes in the fractionation of liquid water isotopes.

Based on air-mass flow and circulation analysis, it should be expected that Bay D’Espoir and Truro (Fig. 2) would have very similar $\delta^{18}O$ and $\delta^2H$, slightly higher on the GMWL (Fig. 5) as these sites are swept by westerlies and the occasional invasion of warm air from the Gulf Stream. It is unsurprising that there is much similarity between Corner Brook and Goose Bay $\delta^{18}O$ and $\delta^2H$ as
both sites experience a dominant influence of precipitation-laden and cold winter. Principally the δ¹⁸O and δ²H of both locations are moderately lower on the GMWL (Fig. 5), but, notably, Corner Brook has a wider range of δ¹⁸O and δ²H. This is most likely due to the regular return of warmer temperatures and the fluctuation of atmospheric circulation in Corner Brook. Much colder weather is experienced in Goose Bay, especially in the winter, because it is essentially unaffected by the warm air-mass systems (from the south) that have some impact on the weather in Corner Brook during the summer.

In summary, it is reasonable that the δ¹⁸O and δ²H values from western Newfoundland (Corner Brook) fall above the GMWL compared with those of the Goose Bay; however, these values are lower than those of Bay D’Espoir and Truro. Divergence and overlaps in δ¹⁸O and δD values at different locations suggest the interplay of various factors, namely the seasonality, latitude, elevation, distance inland from the coast and humidity.

Conclusions

Using the cavity ring-down Picarro L2130-i Liquid Water Isotope Analyzer, δ¹⁸O and δ²H values of 134 samples were determined by collecting direct precipitation in 2015 at Grenfell Campus of Memorial University of Newfoundland, western Newfoundland (Corner Brook). The δ¹⁸O and δ²H data in this study were validated with precipitation δ¹⁸O and δ²H data from Truro in Nova Scotia, Bay
D’Espoir in Newfoundland and Goose Bay in Labrador. The similarities in $\delta^{18}$O and $\delta^2$H data of these four sites are reflected by the geographic and climatic factors such as latitude, distance from the coast and seasonal atmospheric fluctuations.

The $\delta^{18}$O varies from $-33.4$ to $-0.03\%e$ ($\pm 0.023\%e$) and $\delta^2$H ranges from $-253.4$ to $15.1\%e$ ($\pm 0.148\%e$), and these measurements reflect fluctuations in local air temperature and precipitation (i.e. both rain and snow). In the cold winter months (i.e. November to March), the precipitation was more depleted in both of the heavy isotopes (i.e. $^{18}$O and $^2$H) compared with those in the warmer summer (i.e. April to October). Therefore, this suggests that $\delta^{18}$O and $\delta^2$H data from this study can be used to assess the characteristics of seasonal trends in the region of western Newfoundland of Canada.

Results from this study provide important background data related to liquid water isotopes in western Newfoundland. The establishment of this baseline is fundamental to further isotope hydrological studies that could be completed in the area. Therefore, the continued measurement of $\delta^{18}$O and $\delta^2$H in atmospheric precipitation is necessary to give a better representation of long-term trends in the western Newfoundland region.

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Author contributions

BMM: formal analysis (lead), methodology (equal), writing – original draft (lead); HR: conceptualization (equal), funding acquisition (lead), investigation (equal), methodology (equal), supervision (lead), writing – review & editing (equal); D-RP: formal analysis (equal), methodology (supporting), supervision (supporting), validation (equal), writing – review & editing (equal).

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Data availability

Data can be found in ‘The Expedition Database’ of Natural Resources Canada at: http://ed.gdr.nrcan.gc.ca/index_e.php. Moreover, an additional link to the data is given at: https://www.researchgate.net/profile/Harunur_Rashid.

References

Araguás-Araguás, L., Froehlich, K. and Rozanski, K. 2000. Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. Hydrological Processes, 14, 1341–1355, https://doi.org/10.1002/1099-1085(20000615)14:8<1341::AID-HYP983>3.0.CO;2-Z.

Bailey, A., Noone, D., Berkelhammer, M., Steen-Larsen, H.C. and Sato, P. 2015. The stability and calibration of water vapor isotope ratio measurements during long-term deployments. Atmospheric Measurement Techniques Discussions, 8, 5425–5466, https://doi.org/10.5194/amt-8-5425-2015

Birks, S.J. and Gibson, J.J. 2009. Isotope hydrology research in Canada, 2003–2007. Canadian Water Resources Journal, 34, 163–176, https://doi.org/10.4296/cwrj3402163

Bony, S., Risi, C. and Vimeaux, F. 2008. Influence of convective processes on the isotopic composition ($\delta^{18}$O and $\delta^2$H) of precipitation and water vapor in the tropics: 2. Physical interpretation of the amount effect. Journal of Geophysical Research, 113, D19306, https://doi.org/10.1029/2008JD009942

Bowen, G.J. 2010. Isoscapes: Spatial pattern in isotopic biogeochemistry. Annual Review of the Earth and Planetary Sciences, 38, 161–187, https://doi.org/10.1146/annurev-earth-040809-152429

Burnett, A.W., Mullins, H.T. and Patterson, W.P. 2004. Relationship between atmospheric circulation and winter precipitation $\delta^{18}$O in central New York state. Geophysical Research Letters, 31, https://doi.org/10.1029/2004GL021089

Craig, H. 1961. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. Science, 133, 1833–1834, https://doi.org/10.1126/science.133.3467.1833

Dansgaard, W. 1964. Stable isotopes in precipitation. Tellus, 16, 436–468, https://doi.org/10.1111/j.2153-3490.1964.tb00181.x

Darling, W.G., Bath, A.H., Gibson, J.J. and Rozanski, K. 2006. Isotopes in water. In: Leng, M.J. (ed.) Isotopes in Palaeoenvironmental Research, 10. Springer, Dordrecht, 1–51.

Delavau, C., Stadnyk, T. and Birks, J. 2011. Model based spatial distribution of oxygen-18 isotopes in precipitation across Canada. Canadian Water Resources Journal, 36, 313–330, https://doi.org/10.4296/cwrj3604875

Edwards, T.W.D., Birks, S.J. and Gibson, J.J. 2002. Isotope tracers in global water and climate studies of the past and present. International Conference on the Study of Environmental Change Using Isotope Techniques, April 2001. International Atomic Energy Agency, Vienna, IAEA-CN-80/66, 1–9.

Environment Canada 2015. Canadian climate normals 1981–2010 station data: Corner Brook, https://climate.weather.gc.ca/climate_normals/results_1981_2010_e.html?stnId=6610&lang=en&province=NL&provSubmit =go&dCode=0 (last accessed 28 October 2015).

Fiorella, R.P., Poulsen, C.J. and Matheny, A.M. 2018. Seasonal patterns of water cycling in a deep, continental mountain valley inferred from stable water vapor isotopes. Journal of Geophysical Research: Atmospheres, 123, https://doi.org/10.1029/2017JD0238093

Gat, J.R. 2010. Isotope Hydrology: A Study of the Water Cycle. World Scientific, London, 9–10.
González, Y. et al. 2016. Detecting moisture transport pathways to the subtropical North Atlantic free troposphere using paired H2O-δD in situ measurements. *Atmospheric Chemistry and Physics*, 16, 4251–4269, https://doi.org/10.5194/acp-16-4251-2016

Good, S.P., Mallia, D.V., Lin, J.C. and Bowen, G.J. 2014. Stable isotope analysis of precipitation samples obtained via crowdsourcing reveals the spatiotemporal evolution of superstorm sandy. *PloS One*, 9, e91171, https://doi.org/10.1371/journal.pone.009117

Han, G.-Q., Lu, Z.-S., Wang, Z.-L., Helbig, J., Chen, N. and de Young, B. 2008. Seasonal variability of the Labrador Current and shelf circulation off Newfoundland. *Journal of Geophysical Research*, 113, https://doi.org/10.1029/2007JC004376

International Atomic Energy Agency (IAEA) 2015. Reference sheet for international measurement standards, http://nucleus.iaea.org/rpst/Documents/VSMOW2_SLPAP2.pdf (last accessed 2 August 2015).

International Atomic Energy Agency (IAEA)/World Meteorological Organization (WMO) 2015. Global Network of Isotopes in Precipitation. The GNIP Database, https://nucleus.iaea.org/wiser/index.php (last accessed 27 August 2015).

IPCC. 2013. *Climate Change 2013: The Physical Science Basis*. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, New York.

Jamieson, R. and Wadleigh, M. 1999. A study of the oxygen isotopic composition of precipitation sulphate in eastern Newfoundland. *Water, Air, and Soil Pollution*, 110, 405–420, https://doi.org/10.1023/A:1005002006009

Jasechko, S. 2019. Global isotope hydrogeology – review. *Reviews of Geophysics*, 57, 835–965, https://doi.org/10.1029/2018RG000627

Jouzel, J. and Merlivat, L. 1984. Deuterium and oxygen 18 in precipitation: modeling of the isotopic effects during snow formation. *Journal of Geophysical Research*, 89, 11749–11757, https://doi.org/10.1029/JD089iD07p11749

Jouzel, J., Froehlich, K. and Schotterer, U. 1997. Deuterium and oxygen-18 in present-day precipitation: Data and modelling. *Hydrological Sciences Journal*, 42, 747–763, https://doi.org/10.1080/0262666970492070

Kendall, C. and Coplen, T.B. 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrological Processes*, 15, 1363–1393, https://doi.org/10.1002/hyp.217

Khatiwala, S.P., Fairbanks, R.G. and Houghton, R.W. 1999. Freshwater sources to the coastal ocean off northeastern North America: Evidence from H218O/H18O. *Journal of Geophysical Research*, 104, 18241–18255, https://doi.org/10.1029/1999JC000155

Kirby, A and Beersing, A. 2012. The Humber River Watershed in a Changing Climate. College of the North Atlantic, 24.

Klein, E.S., Cherry, J.E., Young, J., Noone, D., Leffler, A.J. and Welker, J.M. 2015. Arctic cyclone water vapor isotopes support past sea ice retreat recorded in Greenland ice. *Scientific Reports*, 5, https://doi.org/10.1038/srep10295

Kurita, N., Newman, B.D., Araguás-Araguás, L. and Aggarwal, P. 2012. Evaluation of continuous water vapor δ18O and δD measurements by off-axis integrated cavity output spectroscopy. *Atmospheric Measurement Technology*, 5, 2069–2080, https://doi.org/10.5194/amt-5-2069-2012

Leslie, D.L., Welch, K.A. and Lyons, W.B. 2017. A temporal stable isotopic (δ18O, δD, d-excess) comparison in glacier meltwater streams, Taylor Valley, Antarctica. *Hydrological Processes*, 31, 3069–3083, https://doi.org/10.1002/hyp.11245

Mark, B.G. et al. 2017. Glacier loss and hydro-social risks in the Peruvian Andes. *Global and Planetary Change*, 159, 61–76, https://doi.org/10.1016/j.gloplacha.2017.10.003

Mark, B.G. and McKenzie, J.M. 2007. Tracing increasing tropical Andean Glacier Melt with stable isotopes in water. *Environmental Science and Technology*, 41, 6955–6960, https://doi.org/10.1021/es071099d

Merlivant, L and Jouzel, J. 1979. Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. *Journal of Geophysical Research*, 84, 5029–5033, https://doi.org/10.1029/JC084iC08p05029

Peng, H., Mayer, B., Harris, S. and Krouse, H.R. 2004. A 10-yr record of stable isotope ratios of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada. *Tellus B*, 56, 147–159, https://doi.org/10.3402/tel lusb.v56i2.16410

Picarro Technology: Cavity ring-down spectroscopy (CRDS) 2015, http://www.picarro.com/technology/cavity_ring_down_spectroscopy/brief_technical_description_of_crds (last accessed 28 October 2015).

Rangarajan, R., Laskar, A.H., Bhattacharya, S.K., Shen, C.C. and Liang, M.C. 2017. An insight into the western Pacific wintertime moisture sources using dual water vapor isotopes. *Journal of Hydrology*, 547, 111–123, https://doi.org/10.1016/j.jhydrol.2017.01.047

Rashid, H., Piper, D.J.W., Lazar, K.B., McDonald, K. and Saint-Ange, F. 2017. The holocene Labrador current: changing linkages to atmospheric and oceanographic forcing factors. *Paleoceanography*, 32, https://doi.org/10.1002/2016PA003051

Rashid, H., Piper, D.J.W., Drapeau, J., Marin, C. and Smith, M.E. 2019. Sedimentology and history of sediment sources to the NW Labrador Sea during the past glacial cycle. *Quaternary Science Reviews*, 221, https://doi.org/10.1016/j.quascirev.2019.105880

Romanini, D., Kuchanov, A.A. and Stoeckel, F. 1997. Diode laser cavity ring down spectroscopy. *Chemical Physical Letters*, 270, 538–545, https://doi.org/10.1016/S0009-6166(97)00406-5

Rorabacher, D.B. 1991. Statistical treatment for rejection of deviant values: critical values of Dixon’s ‘Q’ parameter and related subrange ratios at the 95% confidence level. *Analytical Chemistry*, 63, 139–146, https://doi.org/10.1021/ac00002a010

Rozanski, K., Araguás-Araguás, L. and Gonfiantini, R. 1993. Isotopic patterns in modern global precipitation. In: Swart, P.K., Lohmann, K.C., McKenzie, J. and Savin, S. (eds) *Climate Change in Continental Isotopic Records*. Geophysical Monograph, 78. American Geophysical Union, Washington, DC, 1–36.
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