The Stable Isotope Hydrology of Sable Island, NS, Canada

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Abstract

We investigated the stable isotope hydrology of Sable Island, NS, Canada over a four year period from September, 2017 until August, 2021. The δ 2 H and δ 18 O values of integrated monthly precipitation were weakly seasonal and ranged from -66 to -17 per mil and from -9.7 to -3.1 per mil, respectively. Fitting these monthly precipitation data resulted in a Local Meteoric Water Line (LMWL) defined by: δ 2 H = 7.28 ± 0.22×δ 18 O + 7.95 ± 1.38 per mil. Amount weighted annual precipitation had δ 2 H and δ 18 O values of -37 ± 12 per mil and -6.1 ± 1.6 per mil, respectively. Deep groundwater had more negative δ 2 H and δ 18 O values than mean annual precipitation, suggesting recharge occurs mainly in the winter, while shallow groundwater had δ 2 H and δ 18 O values more consistent with mean annual precipitation or mixing of freshwater with local seawater. Surface waters had more positive values and showed evidence of isolation from the groundwater system. The stable isotopic compositions of plant(leaf) water, on the other hand, indicate plants use groundwater as their source. Fog had δ 2 H and δ 18 O values that were significantly more positive than those of local precipitation, yet had similar 17 O-excess values. Our results establish an important framework for ongoing isotopic studies of feral horses and other wildlife on Sable Island.

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Key Points:

- Water on Sable Island exists as distinct isotopic pools allowing evaluation of source use by the resident horses and other fauna and flora.
- Winter precipitation on Sable island is important for groundwater recharge.
- Advective fog has similar ^{17}O-excess values as other precipitation (rain and snow), indicating that mass independent isotope fractionations do not occur during fog formation.
- Plants on Sable Island source their water from groundwater but standing pools and ponds may be locally isolated from goundwater.

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Abstract

We investigated the stable isotope hydrology of Sable Island, NS, Canada over a four year period from September, 2017 until August, 2021. The δ^2H and δ^{18}O values of integrated monthly precipitation were weakly seasonal and ranged from -66 to -17 per mil and from -9.7 to -3.1 per mil, respectively. Fitting these monthly precipitation data resulted in a Local Meteoric Water Line (LMWL) defined by: $\delta^2\mathrm{H} = 7.28 \pm 0.22 \times \delta^{18}\mathrm{O} + 7.95 \pm 1.38$ per mil. Amount weighted annual precipitation had δ^2H and δ^{18}O values of -37 $\pm$ 12 per mil and -6.1 $\pm$ 1.6 per mil, respectively. Deep groundwater had more negative δ^2H and δ^{18}O values than mean annual precipitation, suggesting recharge occurs mainly in the winter, while shallow groundwater had δ^2H and δ^{18}O values more consistent with mean annual precipitation or mixing of freshwater with local seawater. Surface waters had more positive values and showed evidence of isolation from the groundwater system. The stable isotopic compositions of plant(leaf) water, on the other hand, indicate plants use groundwater as their source. Fog had δ^2H and δ^{18}O values that were significantly more positive than those of local precipitation, yet had similar ^{17}O-excess values. Our results establish an important framework for ongoing isotopic studies of feral horses and other wildlife on Sable Island.

1 Introduction

Measurements of the stable isotopic compositions of hydrogen and oxygen in environmental waters have long been recognized as an important tool for tracing water origins and evaluating the hydrology of regions at local and continental scales (Craig, 1961; Dansgaard, 1964; Clark & Fritz, 1997). This approach is based on the fundamental principles of isotopic tracing involving knowledge of source water isotopic endmembers and the isotopic composition of waters associated with mixing and/or measured or predicted isotopic effects of evapotranspiration (Gonfiantini, 1986). The establishment of a Local Meteoric Water Line (LMWL), or the absolute relationship between δ^2H and δ^{18}O in precipitation at study sites will typically differ from the Global Meteoric Water line (GMWL) of Craig (1961), due to varying regional climatic and geographic parameters. These differences are a consequence of differential fractionation of hydrogen and oxygen isotopes in response to relative humidity during primary evaporation along with temperature and secondary evaporation effects (Craig & Gordon, 1965; Gonfiantini et al., 2018). Because of these processes, the measured δ^2H and δ^{18}O values of precipitation at different locations will produce different meteoric water lines. Relationships between δ^2H and δ^{18}O in surface and groundwater as well as plant leaf water can differ from the LMWL but the intercept of such relationships and the LMWL can reveal the ultimate source of water driving these pools.

Applications related to isotope hydrology are vast and have clearly informed a number of studies on abiotic and biotic processes. Among biological investigations, the field of hydroecology has been a fundamental addition to studies formally evaluating sources of water to foodwebs (Baxter et al., 2005; Meier-Augenstein, 2011). The use of isotopic measurements of water to establish key ecological information such as plant water uptake (Edwin et al., 2014) and water sources used by animals (Wolf et al., 2002; Vander Zanden et al., 2016) are now well established. More recently, measurements of δ^{17}O in environmental waters have been used together with δ^{18}O to provide additional information on sources of water and mechanisms of transport related to differential involvement of kinetic *vs.* equilibrium fractionation (Tian et al., 2021). As an example of this, fog and dew may be differentiated from precipitation using the relationship between their δ^{17}O and δ^{18}O values (Kaseke et al., 2017).

In this paper, we examine baseline isotopic information of precipitation, fog, surface waters, plantwater, and groundwater on Sable Island, a narrow sandbar in the open north Atlantic Ocean approximately 150 km east of Nova Scotia, Canada. Our motivation was to provide a framework to examine the integrity of the freshwater supply on the island and, ultimately, to assist us in understanding water use by vegetation and the iconic wild horses that persist on Sable Island (Plante et al., 2007; Freedman et al., 2011; McLoughlin et al., 2016). From a stable isotope ecology perspective, this isolated environment offers an ideal opportunity to study the routing of the stable isotopes of hydrogen and oxygen from water to animal tissues. Here, we present the first component of this work and focus on isotopically describing different water sources that form the primary reservoir of water that may be integrated by horses specifically, but also by other flora and fauna on the island.

2 Methods

2.1 Study Site

Sable Island is the only unsubmerged part of the Sable Island Bank, a series of sandbanks and shoals that border the Atlantic continental shelf and extend from Baffin Bay to the Gulf of Maine (Fig. 1). Historically, Sable Island was a notorious shipping hazard. The island is often subject to extreme weather for a large part of the year including high winds, breaking seas, and thick fog. This, coupled with strong ocean currents and its close proximity to shipping lanes, has resulted in the accumulation of hundreds of shipwrecks, the last of which was in 1999 (Stalter & Lamont, 2006). In modern times, however, it is most widely known for its population of feral horses (*Equus ferus caballus*), whose ancestors were introduced to the island in the mid 18th century (Freedman et al., 2011). Because of their long tenure on the island, these Sable Island Horses are considered genetically distinct (Plante et al., 2007) and the entire Sable Island ecosystem, including its horses, is protected as Sable Island National Park Reserve by Parks Canada. Because of this unique and isolated environment, Sable Island has been the focus of many scientific studies. These have mainly focused on the peculiar ecology of the feral horse population, but other investigations have ranged from traditional hydrology (Hennigar & Kennedy, 2016; Hennigar, 1976) to plant ecology (Tissier et al., 2013; Richardson et al., 2009).

Sable Island's climate is classified in the updated Köppen-Geiger climate classification as Dfb (cold with a warm summer, but lacking a dry season) (Eamer et al., 2021). Temperatures range from about 0 °C in the winter to highs of about 25 °C in the summer months (Stalter & Lamont, 2006). Sable Island receives approximately 1460 mm of precipitation, mainly rain, annually (Environment and Climate Change Canada, 2021). This relatively large amount of rainfall along with high infiltration and no run-off results in an island-wide discontinuous unconfined freshwater aquifer, essentially a fresh water lens, diffusing into the sea at the lateral margins of the island (Hennigar & Kennedy, 2016). Vegetation consists mostly of marram grass (*Ammophila arenaria*) however as many as 224 species of vascular plants have been identified, both native and introduced (Stalter & Lamont, 2006).

2.2 Water and Plant Collections

As part of an ongoing project, we collected monthly integrated precipitation using a Palmex integrator (Gröning et al., 2012) at the Parks Canada Station on Sable Island operated by the Meteorological Survey of Canada for four years, from September 2017 to August 2021. In addition to the precipitation samples, we collected monthly groundwater samples from the deep freshwater well (screened at 5 meters) that supplies the main station on the western spit of the island (Fig 1-inset) during the same time period. We also collected opportunistic pond, lake, and shallow well water samples from various locations on the island. Fog samples were collected using a fog collector constructed after Fischer and Still (2007), but using the same model of Palmex integrator for the sample collection reservoir. Precipitation amounts and other

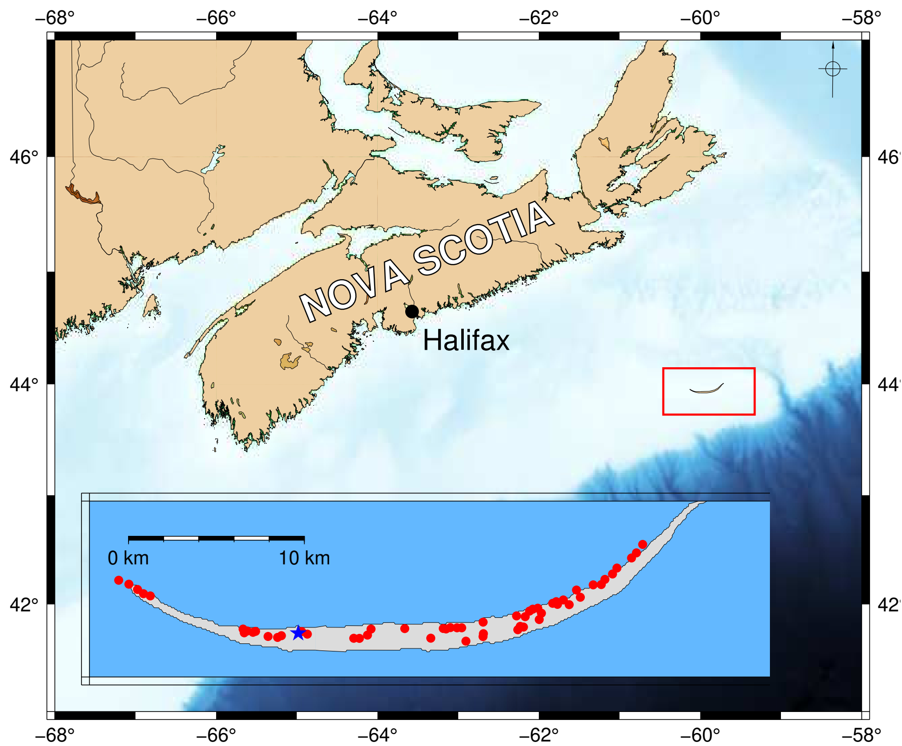

Figure 1. Location of Sable Island, NS, Canada, showing the locations of marram grass samples (red circles). The blue star indicates the location of the main Parks Canada Station where precipitation samples and deep groundwater were collected.

meteorological data were obtained from Environment and Climate Change Canada (Environment and Climate Change Canada, 2021).

In addition to the water samples, we collected samples of marram grass into double ziplock plastic bags (Fig 1-inset). Plant water was cryogenically extracted following the procedures of Koeniger et al. (2011) at the Global Institute for Water Security Laboratory at the University of Saskatchewan. This system was composed of independent extraction-collection units made up of two Exetainer vials (Labco Ltd, Lampeter, UK) connected by a stainless steel capillary (2.00 $\times$ 0.95 mm). The samples were heated to 200 °C for 15 min under a baseline vacuum pressure of 87.0 Pa. The volatile fraction in the plant sample was vaporized and collected in the second Exetainer vial, set in a liquid nitrogen cold trap. The samples were defrosted at room temperature in sealed conditions and the collected liquid was sampled for isotopic analysis. Extraction efficiency was determined gravimetrically and samples with an extraction efficiency of less than is 96% were rejected.

2.3 Stable Isotope Measurements

All precipitation, groundwater, and plant water samples were measured for their hydrogen and oxygen stable isotopic compositions at the NHRC Stable Isotope Laboratory in Saskatoon, SK, and are reported in the familiar delta notation on the VSMOW–SLAP reference scale. Precipitation and groundwater samples were measured by Off Axis Integrated Cavity Output Spectroscopy (OA-ICOS) using either a Los Gatos Research EP-45 triple isotope laser spectrometer or a Los Gatos Research DLT-100 dual isotope laser spectrometer. To minimize memory effects, samples and reference waters were injected 9 times and the last 5 measurements were averaged to obtain the final raw delta values.

To avoid spectral interferences caused by co-extracted organic compounds (Millar et al., 2021), plant water samples were measured by Isotope Ratio Mass Spectroscopy (IRMS) with an Elementar Isoprime mass spectrometer. For oxygen isotope analyses, we used the CO_2-H_2O equilibration technique of Epstein and Mayeda (1953) with an Elementar multi-flow peripheral device. Samples were allowed to equilibrate with CO_2 for at least 48 hours prior to measurement. For hydrogen isotope analyses, we reacted water with elemental Cr at 1030 °C followed by IRMS measurement of the produced H_2 (Morrison et al., 2001). To alleviate memory effects, samples were injected twice and the first measurement discarded.

For both laser and IRMS analyses, we used two calibrated reference waters, (CSNOW δ^2H = -204.7, δ^{18}O = -26.9 and LVIC (Lake Victoria) δ^2H = +10.0, δ^{18}O = +0.47 per mil, respectively) to normalize raw delta values to the VSMOW–SLAP scale. Precisions as determined by replicate analyses of samples and reference waters were ± 1 for δ^2H and ± 0.1 per mil for both δ^{17}O and δ^{18}O values. For δ^{17}O measurements, we calibrated our CSNOW and LVIC reference waters on the SMOW-SLAP scale following the procedures proposed by Schoenemann et al. (2013), whereby the VSMOW2 and V-SLAP2 reference waters supplied by the IAEA are assumed to have ^{17}O-excess values of 0. Following this procedure, our LVIC and CSNOW reference waters have δ^{17}O values of +0.1 and -14.1 per mil, respectively.

2.4 Statistical Analysis

We used the R programming language for all statistical calculations (R Core Team, 2015). The amount-weighted mean δ^2H and δ^{18}O values of precipitation can be calculated following Yurtsever and Gat (1981):

$$\delta_w = \frac{\sum_{i=1}^{n} P_i \delta_i}{\sum_{i=1}^{n} P_i} \tag{1}$$

where for each measurement, P is the precipitation amount and δ is its δ^2H or δ^{18}O value. Deuterium excess (D_{ex}) values were calculated following Dansgaard (1964):

$$\mathrm{D}_{ex} = \delta^2\mathrm{H} - 8\delta^{18}\mathrm{O} \tag{2}$$

Local meteoric water lines are most often calculated using ordinary least squares regression (OSLR) to model the relationship between δ^{18}O and δ^2H values assuming that each point carries equal weight (IAEA, 1992). Amount weighted models (either OLSR or Major Axis regressions) can also be used to model the LMWL (Hughes & Crawford, 2012; Crawford et al., 2014). While useful in certain circumstances, these alternate approaches are most applicable to locations where there are an abundance of small evaporative precipitation events that would otherwise skew the LMWL to shallower slopes and a less positive deuterium intercept.

3 Results and Discussion

3.1 Meteoric waters

The hydrogen and oxygen stable isotopic compositions of precipitation on Sable Island have δ^2H values that ranged from -66 to -15 per mil and δ^{18}O values that range from -9.7 to -1.9 per mil. Correlations between the hydrogen stable isotopic

model	slope	Intercept(‰)	r^2
OLSR	7.28 ± 0.22	7.95 ± 1.38	0.956
PW-OLSR	7.37 ± 0.26	8.44 ± 1.63	0.947
RMA	7.60 ± 0.33	9.84 ± 1.96	0.956

Table 1. Modelling of the local meteoric water line for Sable Island, NS. OLSR - Ordinary Standard Linear regression, PW-OSLR - Precipitation Weighted – Ordinary Standard Linear Regression, RMA - Reduced Mean Axis regression.

compositions and amount of precipitation (Fig. 2a) and between δ^{18}O values and temperature (Fig. 2b) were weak ($r^2 = 0.18$ and 0.22, respectively), typical for islands with a strong maritime influence (Bowen, 2008) where precipitation is likely a result of a first condensate of water vapour from marine evaporation. Although the fit is poor, the observed relationship between air temperature and δ^{18}O values of precipitation was approximately 0.12 per mil/ °C , significantly less than theoretical value of 0.66 per mil/ °C and observed values from continental locations (Dansgaard, 1964; Fricke & O'Neil, 1999). The hydrogen and oxygen stable isotopic compositions of precipitation were weakly seasonal, as were the amounts of precipitation (Fig. 2c), with amount weighted monthly summer precipitation having slightly more positive δ^2H and δ^{18}O values than those of winter (Fig. 2d). This is most likely a consequence of the slight temperature effect and the large annual temperature range (0-25 °C).

From these observations, the calculated mean annual amount weighted average δ^2H and δ^{18}O values of precipitation (MAP) on Sable Island are -37 ± 12 and -6.2 ± 1.5 per mil, respectively (Fig. 2d). These values were computed using all measurements from the four years of our study, but we were missing samples from July to November 2020, thereby possibly biasing the MAP to winter precipitation and more negative δ^2H and δ^{18}O values. As a comparison, we also calculated annual amount weighted means using interpolated values for the five months of missing data from the average values for the existing three years of data yielding δ^2H and δ^{18}O values of -37 ± 12 and -6.1 ± 1.6 per mil. These values are indistinguishable within error from those calculated using the incomplete data. This is not surprising considering the weak seasonality differences between the summer and winter δ^2H and δ^{18}O values.

Both ordinary least squares and major axis regression of the δ^2H and δ^{18}O values of integrated monthly precipitation resulted in a good fit to the data with major axis regression having a higher deuterium intercept and slightly steeper slope than OSLR models (Table 1). Weighting data points by precipitation amount resulted in a slightly poorer fit, suggesting that the amount of precipitation does not significantly affect the stable isotopic compositions of rainwater, as would be expected in a marine climate and as observed on Figure 2a. This is also observed in the temporal profiles of D-excess where there is no statistically significant periodicity (not shown); D_{ex}values across all seasons remain relatively constant and average +12.2 ± 2.7 per mil. Ultimately though, all regression models resulted in an almost identical fit within error (Fig. 3), reflecting the open ocean climate of Sable Island, where high rainfall and cool moist conditions result in minimal secondary evaporation of precipitation (Rozanski et al., 1993).

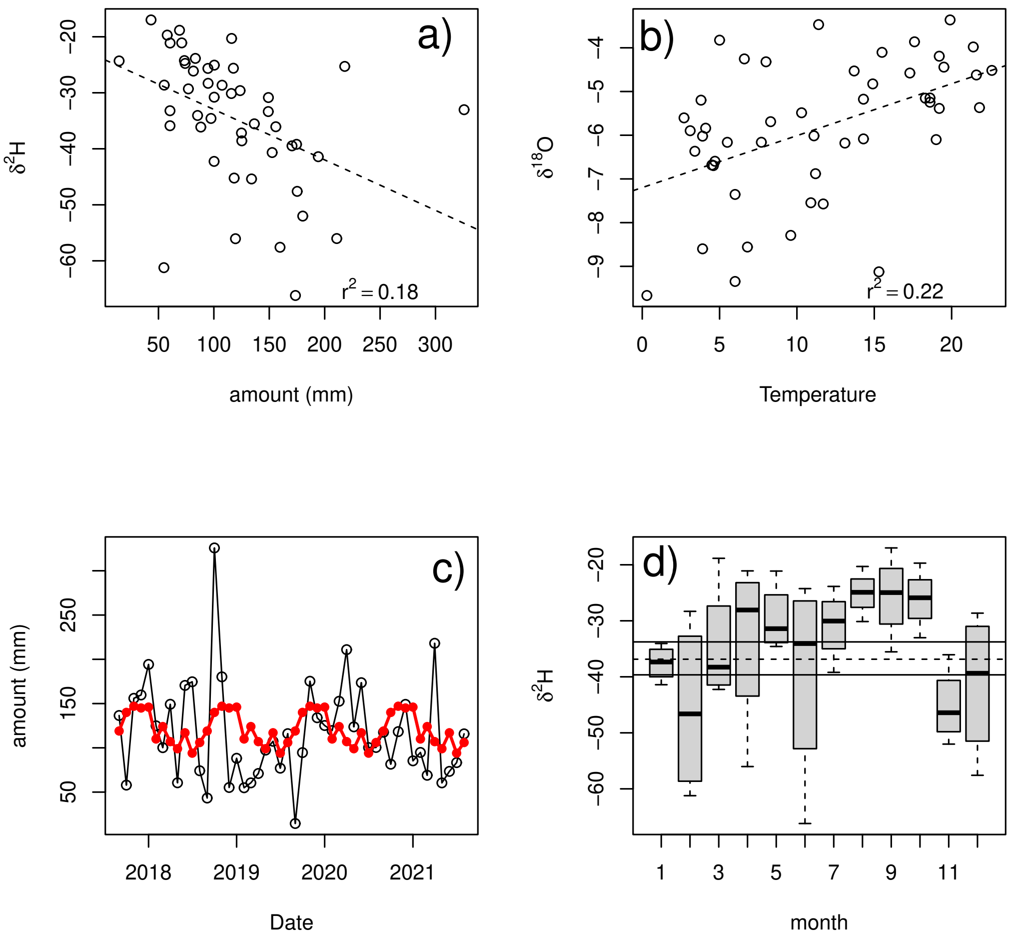

Figure 2. a.) Variation in δ^2H values with precipitation amount and monthly temperature on Sable Island, NS, Canada from September, 2017 to August, 2021. b.) Variation in δ^{18}O values of monthly precipitation with monthly mean temperature c.) Amounts of precipitation during the duration of this study. Shown in red are average precipitation amounts (Environment and Climate Change Canada, 2021). d.) Mean monthly δ^2H values with amount weighted summer and winter precipitation values (upper and lower solid lines, respectively) and the mean annual amount weighted value (dashed line).

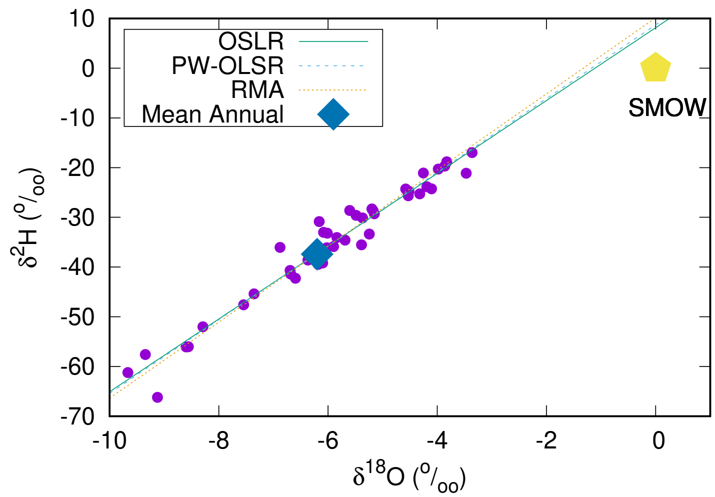

Figure 3. The relationship between δ^2H and δ^{18}O values of precipitation on Sable Island, NS, Canada from September, 2017 to August, 2021. Delta values are reported as per mil (‰) for both δ^2H and δ^{18}O . OLSR - Ordinary standard Linear regression, PW-OSLR - Precipitation Weighted – Ordinary Standard Linear Regression, RMA - Reduced Mean Axis regression, Mean Annual – amount weighted mean annual precipitation.

3.2 Seawater, surface, and groundwaters

Local seawater at Sable Island has relatively low δ^2H and δ^{18}O values of -13 and -2.6 per mil, respectively, considerably different from those of global average seawater values. This is consistent with the observations of LeGrande and Schmidt (2006) and reflects significant river input into the Arctic Ocean, North Sea, and Hudson Bay, the output of which contributes to the southward flowing Labrador current along the east coast of Canada, including Sable Island.

Shallow groundwater on Sable Island had a range of δ^2H and δ^{18}O values, from -44 to -12 (mean = -31 ± 7) per mil for hydrogen and -7.4 to -1.4 (mean = -5.7 ± 1.3) per mil for oxygen. The hydrogen and oxygen stable isotopic compositions of water from shallow groundwater wells all fall along the LMWL and are similar to the range of δ^2H and δ^{18}O values observed in local precipitation. It is also possible from a stable isotope perspective that these values are the result of mixing between local seawater to deep tap water at the main station (Fig. 4). Salinity of well waters were generally low, however, with most shallow wells having salinities of less than 1 ppt. This suggests that the variation in the δ^2H and δ^{18}O values likely reflects those of local precipitation rather than direct mixing. It is worth noting that a couple of the wells have salinities of up to 8-10 ppt Cl, indicating that incursion of seawater does occur into shallow groundwater in some instances.

These measurements support the model of Hennigar (1976) that groundwater on Sable Island consists of an elongated discontinuous freshwater lens that is recharged by infiltration of rainfall and diffuses out to the sea at the edges of the island. That direct mixing between groundwater and seawater may occur either by direct incursion or flooding of seawater during severe weather (Parker, 2018) is also consistent with our data.

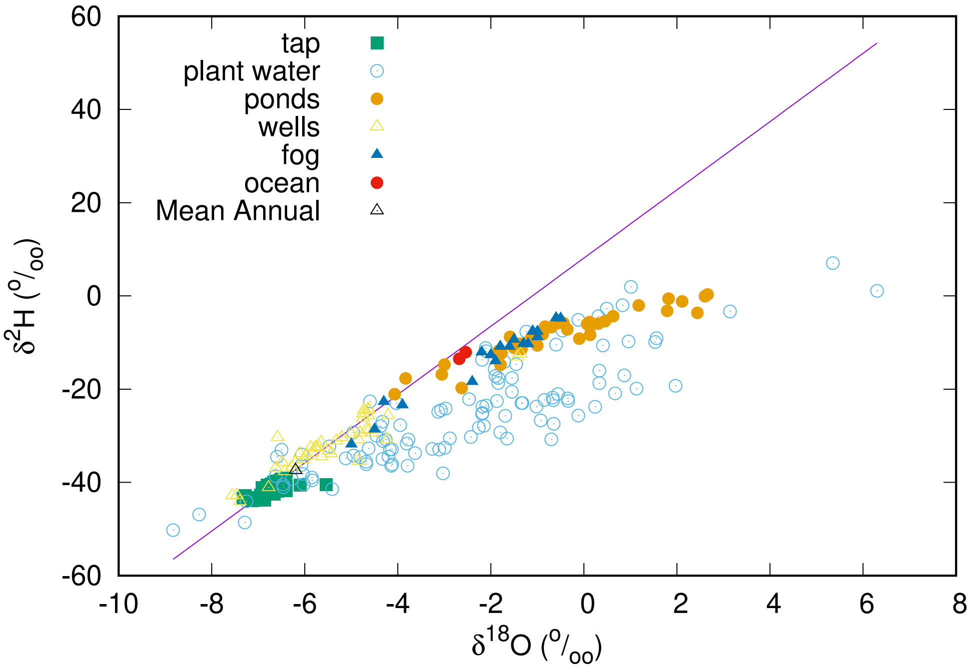

Figure 4. Hydrogen and oxygen stable isotopic compositions of deep groundwater, plant water, surface water, shallow groundwater, and fog from Sable Island, NS, Canada. Also shown are the Local Meteoric Water line (see Table 1) and the stable isotopic compositions of local seawater.

In contrast to shallow groundwater, groundwater from the deep well at the main station has a relatively constant hydrogen and oxygen stable isotopic composition with δ^2H and δ^{18}O values of -41 ± 1.3 and -6.7 ± 0.3 per mil respectively. These values are more negative than those of the mean annual precipitation or shallow groundwater on the island and most probably indicate that recharge of the freshwater lens occurs predominately in the winter. Indeed, calculated amount weighted mean winter precipitation δ^2H values average -40 per mil (Fig. 2d), identical within analytical error to those of deep groundwater.

The seasonality of groundwater recharge can be quantified based on the differences between groundwater stable isotopic compositions and those of amount-weighted summer, winter, and annual precipitation (Jasechko et al., 2014). In this derivation, the seasonal groundwater recharge bias can be expressed as:

$$\frac{(R/P)_{summer}}{(R/P)_{winter}} = \frac{\delta_{GW} - \delta_{summer}/\delta_{annual} - \delta_{summer}}{\delta_{GW} - \delta_{winter}/\delta_{annual} - \delta_{winter}} \tag{3}$$

where R/P is the recharge to precipitation ratio and GW, summer, winter, and annual are the average delta values of groundwater, and and the amount weighted average delta values of summer, winter, and annual precipitation, respectively. The resultant seasonal bias term, $\frac{(R/P)_{summer}}{(R/P)_{winter}}$, has values of less than one if summer recharge exceeds winter recharge and of greater than one if *vice versa*.

For Sable Island, where the delta values of mean winter precipitation are essentially identical to the groundwater values, the denominator of this calculation approaches zero, indicating that almost all of the groundwater is recharged by winter precipitation with little or no contribution from summer precipitation. The groundwater system on Sable Island has large discharge rates by which approximately 75% of the available reservoir is lost into the sea annually by diffusion (Hennigar, 1976). This, coupled with high evapotranspiration rates and lower precipitation amounts in the summer, may reduce recharge in the summer to zero or even to negative rates, if discharge exceeds input. Ponds and pools often disappear in the summer, indicating a lowering of the water table and thus higher groundwater discharge than recharge. We would also expect a seasonal variation in the stable isotopic compositions of main station groundwater if summer recharge was significant, but that was not observed.

The intersection of the freshwater lens water table with the topography of Sable Island results in standing pools, essentially surface exposures of the groundwater system (Hennigar, 1976). These pools are typically ephemeral and can dry out completely if the water table drops below the pond elevation. There is also observational evidence of standing or perched ponds that have elevations above the water table, likely from development of low permeability substrates (Hennigar & Kennedy, 2016).

The δ^2H and δ^{18}O values of these small ponds and pools can be compared to the LMWL and mean annual precipitation values (Fig. 4). The δ^2H and δ^{18}O values of the ponds range from -21 to 0 per mil and -4.1 to +2.6 per mil, respectively. The δ^2H and δ^{18}O values plot in as a linear cluster to the right of the LMWL, as a result of isotopic enrichment typical of surface waters. A linear fit to this trend results in the relationship $\delta^2\text{H} = 2.92 \times \delta^{18}\text{O} - 6.80$ with a goodness of fit (r^2) of 0.88.

This linear model intercepts the LMWL at δ^2H and δ^{18}O values of -17 and -3.4 per mil, values that are slightly more positive than those of the shallow wells and significantly more positive that those of deep groundwater. This is an unexpected result because considering that many of these pools are surface exposures of the local groundwater, we would expect this intersection to reflect δ^2H and δ^{18}O values typical of groundwater on the island. That they do not suggests that many of these small pools and ponds are indeed isolated from the groundwater system, adding to existing evidence that many of the pools on the island are standing or perched. These surface waters were sampled in the summer when the water table is presumably at its lowest adding to the probability of sampling these perched pools.

3.3 Plant Waters

Like surface waters, the hydrogen and oxygen stable isotopic compositions of waters extracted from marram grass form a broad linear array to the right of the LMWL (Fig. 4). The trend formed from the δ^2H and δ^{18}O values of plant water ($\delta^2\text{H} = 3.65\times\delta^{18}\text{O} - 15.6$, $r^2 = 0.744$) intersects the LMWL at more negative values than does the similar, but parallel, trend formed from ponds and pools. The intersection of this trend with the LMWL occurs at a δ^2H and δ^{18}O value of -37 and -6.2 permil respectively, identical to δ^2H and δ^{18}O values of MAP and similar to those of shalllow groundwater on the island.

These results follow the same pattern as those observed in controlled experiments by Millar et al. (2018) for plant water extracted from spring wheat (*Triticum aestivum L.*). In these experiments, the δ^2H and δ^{18}O values of extracted plant water plot along a trend with a shallow slope that intercepts the LMWL at values similar to the local irrigation water.

3.4 Fog

Fog is prevalent in the summer on Sable Island but we were only able to collect 20 samples during the summers of 2018–2021 because high winds continually damaged the fog collector. For the samples that were collected, fog had relatively positive δ^2H and δ^{18}O values that ranged from -32 to -4 per mil and -5.0 to -0.5 per mil, respectively (Fig. 4), and plot close to those of local seawater. With the exception of a few relatively negative values, these δ^{18}O values are consistent with those observed previously by Gonfiantini and Longinelli (1962) from the North Atlantic and most likely represent a first stage condensate from water vapour in equilibrium with local seawater. In agreement with a study of coastal fog described by Ingraham and Matthews (1990), the δ^2H and δ^{18}O values of fog plot slightly below the LMWL and have higher delta values and lower D_{ex}values (mean = 3 per mil) than local rainfall. These low D_{ex}values most likely are a result of equilibrium condensation of water vapour formed from evaporation at very high relative humidity, consistent with the formation of fog.

The exceptions are a few fog samples that show more negative δ^2H and δ^{18}O values and plot on the LMWL (Fig. 4, 5). These likely represent mixed samples where some rain was inadvertently collected by the fog collector on windy days. These samples also had the most positive D_{ex}values, further suggesting a component of rainwater.

Recently, it has been reported that non-rainfall events, such as dew, may display a slightly different δ^{17}O – δ^{18}O relationship from other meteoric waters as a result of non-equilibrium kinetic processes during formation although the sample size was small (Kaseke et al., 2017). While radiation-induced and possibly advective fog from the Nabib desert did not show any mass-independent fractionations between ^{17}O and ^{18}O, dew from the same location had measured ^{17}O-excess values of about -120 per meg (Kaseke et al., 2017), indicating that significant non equilibrium kinetic processes occur during dew formation. Both advective dew and fog form from similar processes involving the condensation of water vapour during contact with cold surfaces or air masses. For this reason, we measured δ^{17}O values of both fog and precipitation in order to determine if there were any differences of the magnitude seen in previous studies. We reasoned that if observed, these differences may ultimately allow us to estimate the contribution of fog to other water reservoirs on the island. Unfortunately, with laser based instruments, it is difficult to attain the precisions necessary for accurate ^{17}O-excess measurements ($\pm$ 10 per meg) without relatively long integration times, advanced statistical analysis and sufficient numbers of repeated measurements (Berman et al., 2013; Steig et al., 2014). However, even with the poor precisions offered by these instruments ($\sigma \approx \pm$ 100 per meg) a large difference in mean values of ^{17}O-excess , such as those previously seen between precipitation and dew, should be detectable by the methods used.

For Sable Island, both rainfall and fog had ^{17}O-excess values that ranged from -176 to +197 per meg and had mean values that were not statistically different (Welch T-test, p = 0.730). This suggests that the formation of advective fog does not involve significant non-equilibrium or kinetic processes and therefore ^{17}O-excess values may not be useful to determine the contribution of fog to the water budget or plant water of Sable Island. However, it is possible that the relatively positive δ^2H and δ^{18}O values and low D_{ex}values of fog may allow some isotopic tracing. For example, fog has similar stable isotopic compositions to those of ponds on the island but not to those of groundwater or plant water(Fig 4), indicating it is possible that fog drip may contribute to surface waters but not to groundwater.

4 Conclusions

This study presents the first dataset of the hydrogen and oxygen stable isotopic compositions of precipitation (rain and fog), seawater, groundwater, plant water, and surface water from Sable Island, NS, Canada. The δ^2H and δ^{18}O values of precipitation in this marine dominated environment define a local meteoric water line described by $\delta^2\text{H} = 7.32 \times \delta^{18}\text{O} + 8.13$, with annual amount-weighted mean δ^2H and δ^{18}O values of

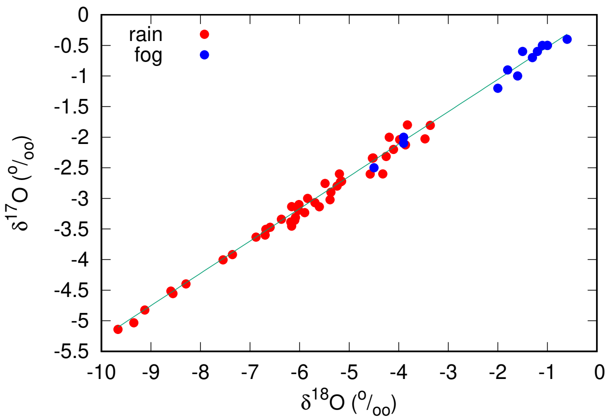

Figure 5. Relationship between δ^{18}O and δ^{17}O values in per mil (‰) for fog and rain samples on Sable Island, NS, Canada.

precipitation of -37 ± 12 and -6.2 ± 1.7 per mil, respectively. Seasonality in the stable isotopic composition of precipitation is small but evident, where summer amount-weighted precipitation have δ^{2}H and δ^{18}O values that are more positive than those in the winter.

Stable isotopic compositions of groundwater from shallow wells reflect those of precipitation but also may indicate that mixing between local seawater and groundwater occurs locally either as a diffusional edge or as direct mixing from seawater incursions during severe weather. Deep groundwater has hydrogen and oxygen stable isotopic compositions that are similar to those of winter precipitation suggesting that recharge of freshwater on the island occurs predominantly during the winter months with little contribution from summer precipitation.

The δ^{2}H and δ^{18}O values of pools and ponds were more positive and offset from those of precipitation indicating the usual evaporative enrichment of typical of surface waters. From stable isotopic considerations, it is evident that while plants are fed by local groundwater, many surface waters are likely isolated from the groundwater system. In addition, it is possible that water from fog may contribute to surface waters. In all, this is evidence of a precipitation-driven system with several distinct isotopic pools.

Importantly, the existence of these distinct isotopic pools, such as fog and groundwater, can allow the tracing of water to horses or other fauna on the island. These data will also be of benefit to determine the water/plant sources to horses and may also be used as a monitoring tool for water quality and quantity on the island. For example, lower winter precipitation amounts as a result of climate change (Smith et al., 2020) may reduce the amount of groundwater available to horses by lowering of the water table.

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6 Data Availability

All data used in this study will be publicly available the Government of Canada Open Data repository(ECCC, 2022) and through the GNIP program of the International Atomic Energy Agency (IAEA) (IAEA/WMO, 2018).

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