

Spatial variability of ^2H and ^{18}O composition of meteoric freshwater lakes in Scotland

Jurian Hoogewerff¹, Helen F. Kemp², Melanie J. Leng³, Wolfram Meier-Augenstein^{2,4,✉}

¹*Faculty of Science & Technology, University of Canberra, Bruce, ACT, Australia;*
jurian.hoogewerff@canberra.edu.au

²*Stable Isotope Laboratory, James Hutton Institute, Dundee, UK;*
helen.kemp@oealabs.com

³*NERC Isotope Geosciences Facilities, , British Geological Survey, Keyworth, UK, and*
Centre for Environmental Geochemistry, School of Biosciences, University of
Nottingham, Loughborough, UK; mjl@bgs.ac.uk

^{4,✉}*School of Pharmacy and Life Sciences, Robert Gordon University, The Sir Ian Wood*
Building, Garthdee Road, Aberdeen AB10 7GJ, UK; w.meier-augenstein@rgu.ac.uk

Spatial variability of ^2H and ^{18}O composition of meteoric freshwater is not always dominated by the latitude effect

Abstract

Coastal regions, and in particular islands where precipitation from clouds formed out at sea occurs for the first time, are prime candidates for regions where ^2H and ^{18}O composition of precipitation will deviate significantly from the global mean geographic and physiographic trends of vapour-transport patterns. The results reported here are the outcome of a study that aimed to test this hypothesis by ‘isotopographically’ mapping the characteristic $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signatures of Scottish freshwaters. The resulting isotope abundance landscapes or ‘isoscapes’ will underpin studies aiming to authenticate origin of Scottish produce but may also offer a baseline against which environmental changes could be assessed. Between April 2011 and May 2012 freshwater samples were collected from 127 different freshwater lochs and reservoirs across Scotland and analysis results were compared to precipitation data provided by the British Geological Survey. Here we present the results of the ^2H and ^{18}O analyses of these water samples as well as the first detailed Scotland freshwater isoscapes with a grid resolution of about 5×5 km (0.05 degrees).

Keywords: coastal regions; continental effect; evaporated rain; freshwater; island; isoscapes; Hebrides; hydrogen-2; latitude effect; oxygen-18; precipitation; Scotland; stable isotopes; Western Isles

Introduction

Since the seminal work by Dansgaard [1, 2] and the inception of the Global Network of Isotopes in Precipitation (GNIP) by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) in the 1960s our understanding of how factors such as altitude, latitude and temperature influence changes in isotopic composition of precipitation has increased quite considerably. Yet despite these early beginnings and the wealth of data collated by the GNIP stations, it was the seminal work by Bowen and Wilkinson in 2002 that unlocked the information present therein by creating a spatial framework to model and visualise the geographic distribution of ^{18}O abundance values ($\delta^{18}\text{O}$ values) in precipitation [3]. In their article, Bowen and Wilkinson applied a two-step regression technique to deconvolve the effects of latitude and altitude on $\delta^{18}\text{O}$ values of global precipitation. The resulting equation combined a second-order polynomial for absolute values of GNIP station latitude ($|\text{LAT}|$) with a linear residual for altitude (ALT).

$$\delta^{18}\text{O}_{\text{precip.}} = -0.0051(|\text{LAT}|)^2 + 0.1805(|\text{LAT}|) - 0.002(\text{ALT}) - 5.247 \quad (1)$$

During a study into the potential use of ^2H and ^{18}O signatures as indication of provenance and authenticity of Scottish Single Malt whiskies [4] two of the authors (HFK and WMA) measured $\delta^{18}\text{O}$ values of -4.06 ‰ and -4.73 ‰ for water samples from precipitation fed freshwater lakes on the Isle of Islay, Scotland, UK. Even accounting for potential effects of time-averaging on the ^2H and ^{18}O composition of larger bodies of water, these values were significantly different to the modelled $\delta^{18}\text{O}$ value of -8.4 ‰ as calculated by the Online Isotopes in Precipitation Calculator (OIPC) [5]. The measured $\delta^{18}\text{O}$ values of -4.06 ‰ and -4.73 ‰ were also significantly different to $\delta^{18}\text{O}$ values of about -6.5 to -6.0 ‰ one would have expected to see based

on a published $\delta^{18}\text{O}$ contour map of groundwater and surface waters in the British Isles [6]. A similar observation was made for a freshwater sample from Orkney (main island). Here, measured and OIPC calculated $\delta^{18}\text{O}$ values were -5.0‰ and -6.9‰ respectively, while the $\delta^{18}\text{O}$ contour map by Darling, Bath and Talbot (2003) suggested a $\delta^{18}\text{O}$ value of -6.0‰ . While artefacts due to sampling or sample storage of waters collected as part of the whisky study could of course not be completely discounted as potential explanation for these differences, we formed the hypothesis that these differences between measured and expected $\delta^{18}\text{O}$ values were a reflection of the sampling locations where ^2H and ^{18}O composition of precipitation was dominated by the continental effect due to the locations proximity to the North Atlantic and associated weather patterns.

Scottish water is the only mandatory requirement for production and bottling of Scottish whisky. Scottish distilleries source the water they use from lochs, reservoirs or their outflows. Therefore, any method aiming to use ^2H and ^{18}O analysis as one way to prove or disprove geographic origin requires sound knowledge of the spatial variability of ^2H and ^{18}O composition of freshwater across Scotland. It was therefore deemed necessary to collect freshwater samples across Scotland including additional samples from Islay and Orkney.

The opportunity to revisit the sampling locations on Islay and Orkney and to test this hypothesis arose when, part of a wider research project of Scottish freshwaters, the Stable Isotope Laboratory at the James Hutton Institute (JHI) in Dundee (UK) was given the opportunity to survey predominantly rain water fed freshwater lochs and reservoirs for their ^2H and ^{18}O composition over a two year period during which a total of 127 samples were collected, 29 of them on the Hebrides alone. Scotland's water provides a vital resource for sustaining biodiversity, agriculture, food production as well

as for human consumption. Therefore the aim of this survey was to compile a ^2H and ^{18}O inventory of Scottish freshwater bodies that could be turned into well resolved stable isotope contour maps or isoscapes which in turn could serve as both baseline for studies in food authenticity or traceability and as a springboard for future surveys into the impact of climate change.

As mentioned above we also expected the results of this survey to support or disprove our hypothesis for the relatively high $\delta^{18}\text{O}$ values observed for freshwaters on the Scottish Islands to be a consequence of the continental effect rather than artefacts. As a rule of thumb, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation become lower with increasing distance to the equator, i.e. the higher the latitude the lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation will be. This latitude effect is illustrated quite nicely by the global $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isoscapes of precipitation published at http://wateriso.utah.edu/waterisotopes/pages/data_access/figures.html. However, earlier work by Darling, Bath and Talbot [6] had already given an indication that across the British Isles the continental effect (i.e. proximity to the sea) may outweigh the latitude effect. The Western coastal regions of Ireland and the British Isles receive between 700 and 1200 mm of rain per year (30 year average) [7] owing to the fact that rain clouds formed out in the North Atlantic make their first landfall in Ireland and the Western Isles. This is particularly the case for the Hebrides, the West coast of Scotland but also applies to the Orkneys and, to a lesser degree to the Shetland Isles.

Here, we report and discuss the results of this survey of surface freshwater collected from lochs and reservoirs in Scotland and the Scottish Isles. In the context of this freshwater survey we also report and discuss results of a survey of precipitation samples collected in Scotland and analysed by the British Geological Survey (BGS)

which served as a point of reference against which the results of the freshwater survey were compared.

Materials and Methods

Collection and analysis of freshwater samples (JHI)

From April 2011 to May 2012, freshwater samples were collected with the support of the Scottish Environment Protection Agency (SEPA) from 127 freshwater lochs and reservoirs across Scotland. Lochs and reservoirs were chosen that, based on information provided by SEPA, had a residence time of >2.0 years. Due to the potential for evaporation around the margins and on the surface of the Lochs and reservoirs [8], samples were collected at least 5 m away from the shore at a depth of at least 0.5 m to avoid artefacts in isotopic composition. On site, samples were pushed through syringe filter disks of $0.8\ \mu\text{m}$ pore size into 22 mL glass vials until vials were filled to the point of overflowing. Vials were capped using crimp seals fitted with white PTFE/silicon septa. In the laboratory, samples were inspected for any loss of water on account of breakage or leaking crimp seals and nine samples were discarded. Subsamples of the remaining 118 samples were prepared by filling 2 mL amber glass vials with water ultimately pushed through syringe filter disks of $0.22\ \mu\text{m}$ pore size. Vials filled to the point of overflowing were capped by crimp sealing and stored in a fridge at $+2^\circ$ to $+4^\circ$ C until analysis.

Sterile filtered water samples were analysed for their ^2H and ^{18}O stable isotopic composition by direct injection on a Delta^{plus}XP isotope ratio mass spectrometer system (Thermo-Fisher, Bremen, Germany) coupled to a High Temperature Conversion Elemental Analyser (Thermo-Fisher, Bremen, Germany). Samples were analysed in

replicates of $N = 5$ and sample volume injected was $0.1 \mu\text{L}$. Measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were scale normalised to VSMOW by 2-point end-member correction derived from contemporaneously analysed samples of VSMOW and SLAP, and quality controlled using contemporaneously analysed injections of GISP. Typical errors of measurement for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were ± 0.64 and ± 0.19 ‰ respectively.

Collection and analysis of precipitation samples (BGS)

The rainwater samples were collected using a funnel method with silicon oil to prevent evaporation. At the British Geological Survey, oxygen isotope ($\delta^{18}\text{O}$) measurements were made using the CO_2 equilibration method with an Isoprime 100 mass spectrometer plus Aquaprep device (sample volume $100 \mu\text{l}$, with random repeats). Hydrogen isotope ($\delta^2\text{H}$) measurements were made using an online Cr reduction method with a EuroPyrOH-3110 system coupled to a Micromass Isoprime mass spectrometer (sample volume 2ml , replicates $\times 3$). Isotope measurements used internal standards calibrated against the international standards VSMOW2 and VSLAP2. Errors are typically $< \pm 0.05$ ‰ for $\delta^{18}\text{O}$ and ± 1.0 ‰ for $\delta^2\text{H}$.

Data analysis

Rather than using a strictly spatial interpolation based on latitude and altitude [3] we followed a similar approach as van der Veer *et al.* [9] for European mineral waters by first correlating the calibrated results with gridded climate data using the WorldClim dataset with $\sim 1\text{km}$ resolution [10]. In addition, we determined the distance between each sampling site and the nearest coast and the nearest coast in the general westerly wind direction (270°) for the whole of Scotland [11]. We tested both multiple linear

regression approaches and Random Forrest regression using the R statistical environment [12] with multiple spatial analysis packages (sp, rgeos, raster) and home written code (JH, pers. commun.; unreferenced). The Random Forrest regression on a combination of: mean temperature in coldest quarter [9], annual mean temperature [9], coastal distance in the wind direction (JH, pers. code; unreferenced) and longitude provided the most explanation of variance ($\delta^2\text{H}$: 82 % and $\delta^{18}\text{O}$: 78 %) of the data. Linear regression on the same parameters provided an adjusted R^2 for $\delta^2\text{H}$ of 78 % and $\delta^{18}\text{O}$ of 74 % with mean temperature in the coldest quarter being the most dominant explainer of variance for both isotope systems. The correlation matrix for all the parameters is presented as Table 1. The residuals between the predicted and observed values were used to make residual variation maps using the spatial kriging interpolation function in "sp" R package. The Random Forrest models were used in a first step to predict $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for all Scottish WorldClim grid cells and subsequently the kriging models added to account for the remaining ~20 % (spatial) variation of the data. The final data was imported in Surfer (v13) and resampled at a 0.05 x 0.05 degree (~ 5 x 5km) scale and the resulting $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isoscapes are presented in Figures 1a and 1b. Importantly, due to uneven spatial distribution of the sampling points it must be appreciated that the isoscapes are model interpretations and locations between actual measured points are interpolations and not necessarily true values. It is important to be aware of these two latter points for any applications of these maps in a forensic context.

MS Excel 2007 was used to create correlation plots, carry out regression analyses and calculate solutions to regression lines presented in Figures 2 to 5.

Results and Discussion

Survey of Standing Freshwater Bodies in Scotland

Scale normalised $\delta^{18}\text{O}_{\text{VSMOW}}$ values of 118 Scottish freshwaters samples collected all over Scotland and the Scottish Isles extended over a range from -9.70 to -2.36 ‰. Corresponding $\delta^2\text{H}_{\text{VSMOW}}$ values ranged from -65.6 to -20.4 ‰. Colour gradients in Figure 1 represent differences in isotopic composition and clearly show that westernmost locations exhibit $\delta^{18}\text{O}_{\text{VSMOW}}$ values higher than -4.8 ‰ (Figure 1b). In spite of their location $> 56^\circ$ Northern Latitude, water samples collected from lochs on the Hebridean islands Harris, Lewis South Uist and North Uist (cf. data sheet provided in Supplemental Materials) showed more than 80 % of $\delta^{18}\text{O}_{\text{VSMOW}}$ values was higher than $\delta^{18}\text{O}_{\text{VSMOW}}$ values reported in the GNIP database for South European coastal locations such as Brest (-4.31 ‰; $48.36^\circ / -4.57^\circ$) or Gibraltar (-4.80 ‰; $36.13^\circ / -5.35^\circ$). Analyses of samples from revisited sample locations on the Isle of Islay as well as additional sample locations there yielded $\delta^{18}\text{O}$ values that ranged from -4.74 to -3.24 ‰ thus confirming the observations made as part of the aforementioned whisky authenticity project [4]. Similarly, analysis of a sample from Kirbister Loch on Orkney that had also been sampled as part of the whisky project yielded a $\delta^{18}\text{O}_{\text{VSMOW}}$ value of -4.59 ‰ as compared to the then observed $\delta^{18}\text{O}_{\text{VSMOW}}$ value of -5.00 ‰.

Plotting ^2H or ^{18}O abundance values of Scottish freshwater versus altitude showed weak correlation between the two variables (Figure 2). Coefficients of determination R^2 for solutions of linear regression and logarithmic regression analysis were 0.38 and 0.42 respectively. Plotting ^2H or ^{18}O abundance values of Scottish freshwater versus degree latitude values showed no correlation between isotopic composition and degree Northern latitude (Figures 3a and 3b). Coefficients of

determination R^2 for solutions of linear regression and second order polynomial regression analysis were 0.091 and 0.115 respectively.

However, when plotting ^2H or ^{18}O abundance values versus degree longitude values a different picture emerges. A plot of data from all sampling locations already shows some degree of correlation between ^{18}O abundance and degree longitude although values from locations on the Shetland Isles ($\sim+60^\circ$ latitude) appear to buck this trend (Figure 4a). This interpretation was confirmed by re-plotting this data set but this time excluding data from the three Shetland Isles' sampling locations (Figure 4b). Coefficients of determination R^2 for solutions of linear regression and second order polynomial regression analysis were 0.62 and 0.65 and, hence, correlation coefficients R were 0.79 and 0.81 respectively. This strongly suggests the predominant driver for ^2H and ^{18}O composition of freshwater in Scotland and the Scottish Isles is longitude and thus the continental effect, which in this case is synonymous with proximity to the Atlantic Ocean, prevailing Westerly winds and resulting movement of air masses and rain clouds from the Atlantic. This interpretation receives some support from a comparison of measured $\delta^{18}\text{O}$ values for sample locations Scotland and France which are in close and unsheltered proximity to the Atlantic Ocean with OIPC modelled $\delta^{18}\text{O}$ values (Table 2). For these locations, differences between measured and OIPC modelled $\delta^{18}\text{O}$ values range from 0.89 to 3.82 ‰. By contrast, for the comparatively sheltered location on the West Coast of Norway the difference between GNIP measured and OIPC modelled $\delta^{18}\text{O}$ value was only 0.15 ‰. Noteworthy are also the within 0.71 ‰ similarity between $\delta^{18}\text{O}$ values for precipitation in Brest and Lochan na Crege Duibhe and freshwater of Loch An Eilan Liath, or the identical within error $\delta^{18}\text{O}$ values for Loch Osgaig and Valentia Island (Ireland) despite the more than 6° difference in Northern Latitude. The Scottish sample locations presented in Table 2 were selected

because they were the closest match to locations for which data were available in the GNIP data base in terms of latitude, longitude and coastal location.

Greater similarities between $\delta^{18}\text{O}$ values of Scottish water, GNIP data and OIPC modelled $\delta^{18}\text{O}$ values were found when comparing sample location of comparable inland locations sheltered from the open seas (Table 3). For these locations modelled $\delta^{18}\text{O}$ values are consistent with measured $\delta^{18}\text{O}$ values though for one Scottish Highland location the OIPC modelled $\delta^{18}\text{O}$ value underestimated the measured $\delta^{18}\text{O}$ values by 3.3 ‰.

Comparing Standing Freshwater with Precipitation

While some may argue time averaged ^2H and ^{18}O abundance values of freshwater bodies with residence times of >2 years might not be a good proxy for isotopic composition of meteoric water, i.e. annual average $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation. Regrettably, we were not in a position to compare freshwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values with corresponding annual average values of precipitation for the survey period 2011/12 or any of the preceding two years. Searching the GNIP data base for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation in 2011 or any of the preceding two years returned no data for sample locations between 55.0° and 60.9° Northern Latitude and -7.45° and -0.88° Western Longitude. The nearest GNIP sample location for which $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were available was Wallingford in England at 51.60° Northern Latitude and -1.10° Western Longitude.

Quite fortuitously, the British Geological Survey (BGS) had data from analysing samples of a survey of precipitation at 21 locations in Scotland collected in the period of January to February 2002 and again in the period of January to March of 2005. Precipitation records by the UK Met Office show for years 2005 to 2011, rainfall in

Scotland as a whole or in Scottish regions such as the Highlands from January to May typically amounted to 40 % of the total annual rainfall total (Table 4; note, hydrological summaries for the UK published by the UK Met Office referenced in Table 4 only provide precipitation amount for certain time frames; the Jan to May record was the closest match to the time frame of precipitation sampling). Given five months represent 41.67 % of a whole year, the BGS precipitation samples ought to be a fairly representative in terms of rainfall accumulation in mm rainfall during the period of their collection. While there is not a 100 % coincidence in sampling locations between the BGS and the JHI data, longitude and latitude of the 21 BGS sampling locations were still quite close to corresponding JHI sampling locations (Supplemental Material and Table 5). Data provided by the BGS were thus deemed suitable to serve in a comparative capacity as points of reference, a kind of benchmark to compare against and thus gauge measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the JHI survey samples. Based on available information regarding recharge rates, it is obvious samples from standing bodies of freshwater we surveyed would yield time averaged ^2H and ^{18}O abundance values of the last two years prior to 2011 at least. For the avoidance of doubt, therefore no claim is made for $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values of these precipitation samples to represent annual averages for years 2002 or 2005. However, work by van der Veer *et al.* has shown the coldest months dominate the annual mean isotope values of precipitation in Europe and thus provide a good approximation of annual average values [9]. The spreadsheet supplied as Supplementary Material lists all GPRS grid references, location names, date of collection (where known) and results of stable isotope analyses of both precipitation samples collected and analysed by BGS (formatted in Italics) and freshwater body survey samples collected and analysed by JHI. A representative sample from either data set is presented in Table 5.

Comparing solutions of linear regression analyses of $\delta^{18}\text{O} / \delta^2\text{H}$ correlation plot of both the JHI freshwater survey and the BGS precipitation survey shows results of the two surveys to be in very good agreement (Figure 5). With a slope of 6.97 for the freshwater regression line and slopes of 6.73 or 6.28 for the two precipitation regression lines respectively (Figure 5), the slopes of any of these Scottish Water Lines are shallower than that of 8.0 of the Global Meteoric Water Line (GMWL) [13]. However, the slope of the freshwater line is steeper than the slopes of either precipitation line. The findings for these two regional precipitation lines are however in good agreement with the slope of 6.798 reported for the regression line for monthly precipitation samples from Valentia Island on the West Coast of Ireland [14]. A slope of <8 is usually interpreted as representing evaporation trend of residual water after evaporation; the shallower the slope, the greater the evaporative trend. However, by taking samples well below the water surface great care was taken during sample collection of standing freshwater bodies to at least minimize if not exclude any mass discriminatory influences surface evaporation may have had on sample isotopic composition of the freshwater samples. While a cumulative effect of evaporation owing to convection of water layers over a prolonged period of time cannot be excluded, it seems strange for bodies of water fed almost entirely by precipitation to show consistently lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values than the precipitation feeding them (Table 5 and Figure 5). A possible first explanation could be the contribution of snow melt water. Very low $\delta^{18}\text{O}$ values have been documented for a remote mountain lake in Scotland [15]. It is noteworthy that the difference in $\delta^2\text{H}$ (and $\delta^{18}\text{O}$) values between freshwater and precipitation is stronger for locations in the West of Scotland and becomes less pronounced for more Easterly locations (Table 5).

The finding of Scottish freshwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in mainland Scotland locations between approximately -4.7° and -2.7° Western Longitude and 56.2° and 58.2° Northern Latitude being very similar to those of precipitation in corresponding locations (Table 5) within 2 ‰ and 0.2 ‰ respectively, as well as being similar to isotopic abundance values calculated using the OIPC (Table 3) suggests whichever singular effect or combination of effects dominates isotopic composition of freshwater bodies and precipitation on the West Coast of Scotland is replaced by latitude and altitude driven effects for more inland locations. With a slope of almost 7, the freshwater regression line is much closer to the slope of 8 of the GMWL and therefore presumably already a reflection of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of Scotland's freshwater bodies representing time averaged ^2H and ^{18}O abundance values of Scotland's precipitation (Figure 5). A possible interpretation of measured freshwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values being significantly lower than precipitation $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for the Western half of Scotland (Table 5) might be for the isotopic composition of water in these reservoirs to be less a result of evaporative loss from the water surface but representing an integrated time average of the precipitation feeding the freshwater bodies over the years. As a consequence of seasonal changes in temperature and humidity, isotopic composition of precipitation will be subject to seasonal if not monthly variability. Run-off from snow melt, as mentioned above, could be a strong influence that would cause averaged isotopic abundance values of these freshwater bodies to be lower than those of precipitation. A longitudinal survey of precipitation and freshwater at a remote Scottish mountain loch reported $\delta^{18}\text{O}$ values for snow as low as -10 ‰ and on one occasion even -16.7 ‰ [15]. The authors of that study concluded precipitation amount to be of particular importance since it controls catchment and lake residence times, and

determines the degree of phase lag and amplitude change between $\delta^{18}\text{O}$ (freshwater body) and $\delta^{18}\text{O}$ (precipitation).

From a precipitation perspective, a potential explanation for higher $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values observed for the precipitation samples may be water loss incurred during rainfall by partial evaporation of rain drops while they are falling from the clouds to the ground [16]. This evaporative process can occur when rain falls through air of relatively low humidity resulting in the rain reaching the surface being isotopically heavy. Conversely, and in the Scottish climate more likely, with increasing humidity levels falling rain droplets will increasingly interact with vapour molecules and exchange will occur. In particular at coastal locations of low altitude, $\delta^{18}\text{O}$ values of precipitation are less likely to be influenced by the amount of precipitation. This is exactly what a study of precipitation in the British Isles has found for a low altitude sampling site on the East Coast of Scotland near Montrose [17]. In these locations raindrops are more likely to encounter vapour parcels in the initial stages of moisture depletion because rainout occurs as a function of progressive cooling e.g. due to convective uplift of a vapour parcel [17]. In other words, because of the positive direction of the isotopic fractionation between liquid and vapour, this process also results in the liquid rain drops becoming richer in the heavier isotopes [18]. The two processes of evaporation and exchange are therefore further drivers in addition to the continental effect for the observed enrichment in heavy isotopes in precipitation in the West of Scotland. For West coast precipitation to be fed by rain relatively ^2H and ^{18}O rich would also fit with the finding of small d-values ($d = \delta^2\text{H} - 8\delta^{18}\text{O}$ [1]) around zero for the water lines of all three data sets (see Figure 5). d-values are predominantly controlled or influenced by levels of atmospheric humidity during vapour formation or condensation with low d-values being consistent with the general pattern of

precipitation in the northern hemisphere [7]. This potential explanation receives further support from modelled d-values across Scotland shown in Figure 6. Along the Western islands and West coast regions d-values are consistently close to zero, ranging from +1 to +3 ‰. By comparison, in more inland and/or higher altitude regions of Scotland between approximately -4.7° and -2.9° Western Longitude and 56.6° and 57.5° Northern Latitude, d-values are of the order of +6 to +8, even $>+10$ ‰ in places, i.e. values close to the d-value of the GMWL. The combined Random Forrester and kriging modelling show a general trend of d-values increasing from coast into the Highlands. However, it should be noted individual measurements show larger variations in d-values which is probably indicative of varying atmospheric conditions for the specific precipitation samples.

Conclusions

Results from the standing freshwater survey confirmed observations made during an earlier study [4], namely, for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of freshwater bodies in the West of Scotland's and Scottish Isles to be higher than one would expect based on data from the nearest GNIP stations (Valentia, Wallingford and Keyworth) or on currently available modelled OIPC data. Clearly, more regularly monitored sampling points than the current three GNIP sites in Ireland and the UK are required for extrapolated regression models and isoscapes to provide a more realistic data set underpinning any modelled representation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in meteoric water of Scotland if not Ireland and the entire British Isles.

The strong correlation seen between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of Scottish freshwaters and longitude contrasts the weak correlation seen between these values and either

altitude or latitude. We therefore conclude the influence of a strong continental effect due the prevailing wind direction and resulting movement of air masses and rain clouds, potentially in combination with the effect of evaporative and/or exchange driven enrichment in the falling droplets offer a conceivable explanation for the findings of higher than expected $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of Scottish precipitation and freshwater bodies in Scotland especially on the Western Isles and on West Coast locations [14].

We also conclude existing algorithms for calculating expected regional $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation may need to be reassessed and possibly amended by a term accounting for continental effects.

Irrespective as to the exact nature of the underlying effect or combination of effects for the difference between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of Scottish freshwater and those of precipitation, especially along the West Coast and on the Western Isles, we conclude $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of Scotland's freshwater bodies may be a useful proxy for isotopic composition of Scotland's precipitation when it comes to cost effective longitudinal monitoring on a like-for-like basis to study e.g. what, if any effects climate change may have on Scotland's water budget. Of course, time and cost involved in sampling and analysing water from >100 locations on a regular basis in Scotland alone would still be prohibitive. However, annual sampling of freshwater bodies would still be a more cost effective way to generate data sets and isoscapes albeit based on time averaged $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values than sampling and analysis of precipitation from >100 locations on a monthly basis. Hence, future work will focus on using the data set discussed here to determine the minimum number and optimal location of samples required to create isoscapes providing a realistic picture so any longitudinal changes can be detected, monitored and interpreted in a meaningful way.

Acknowledgements

The survey of Scotland's freshwater lochs and reservoirs was supported through funding received by The James Hutton Institute from the Scottish Government's Rural and Environment Science and Analytical Services Division (RESAS). HFK and WMA also gratefully acknowledge the help and time graciously given by Lynda Davidson, Danny Frew and their colleagues at the Scottish Environment Protection Agency (SEPA) with access to access controlled freshwater bodies as well as with collection of freshwater samples. The authors would have liked to thank two reviewers for helpful and constructive comments but, given the lack of such, cannot bring themselves to do so.

References

- [1] Dansgaard W, Stable Isotopes in Precipitation. *Tellus*. 1964; 16: 436-468.
- [2] Dansgaard W, The O-18-Abundance in Fresh Water. *Geochim Cosmochim Acta*. 1954; 6: 241-260.
- [3] Bowen GJ, Wilkinson B, Spatial distribution of delta O-18 in meteoric precipitation. *Geology*. 2002; 30: 315-318.
- [4] Meier-Augenstein W, Kemp HF, Hardie SML, Detection of counterfeit scotch whisky by H-2 and O-18 stable isotope analysis. *Food Chem*. 2012; 133: 1070-1074.
- [5] The Online Isotopes in Precipitation Calculator (OIPC), version 3.1 [Internet]. Salt Lake City (UT): Gabriel Bowen. Available from: <http://www.waterisotopes.org>
- [6] Darling WG, Bath AH, Talbot JC, The O & H stable isotopic composition of fresh waters in the British Isles. 2. Surface waters and groundwater. *Hydrol Earth Syst Sci*. 2003; 7: 183-195.
- [7] Darling WG, Talbot JC, The O & H stable isotopic composition of fresh waters in the British Isles. 1. Rainfall. *Hydrol Earth Syst Sci*. 2003; 7: 163-181.
- [8] Xiao W, Wen XF, Wang W, et al., Spatial distribution and temporal variability of stable water isotopes in a large and shallow lake. *Isotopes Environ Health Stud*. 2016; 52: 443-454.
- [9] van der Veer G, Voerkelius S, Lorentz G, et al., Spatial interpolation of the deuterium and oxygen-18 composition of global precipitation using temperature as ancillary variable. *J Geochem Explor*. 2009; 101: 175-184.
- [10] Fick SE, Hijmans RJ, WorldClim 2: new 1-km spatial resolution climate surfaces for global land areas. *International Journal of Climatology*. 2017; 37: 4302-4315.
- [11] Wester Scotland: climate [Internet]. Exeter (Devon, UK): Met Office. Available from: <https://www.metoffice.gov.uk/climate/uk/regional-climates/ws>
- [12] R: A language and environment for statistical computing [Internet]. Vienna (Austria): R Foundation for Statistical Computing. Available from: <http://www.R-project.org>
- [13] Craig H, Isotopic variation in meteoric waters. *Science*. 1961; 133: 1702-1703.
- [14] Observed Isotope Effects in Precipitation. In: Gat JR, Mook WG, Meijer HAJ, editors. *Environmental Isotopes in the Hydrological Cycle - Principles and Applications*. Vienna: International Atomic Energy Agency; 2001; pp. 197-207.

- [15] Tyler JJ, Leng MJ, Arrowsmith C, Seasonality and the isotope hydrology of Lochnagar, a Scottish mountain lake: implications for palaeoclimate research. *Holocene*. 2007; 17: 717-727.
- [16] Vlasova LS, Ferronsky VI, Water transport over Western Europe and its correlation with climate variations based on data on precipitation isotopic composition. *Water Resources*. 2008; 35: 502-521.
- [17] Tyler JJ, Jones M, Arrowsmith C, et al., Spatial patterns in the oxygen isotope composition of daily rainfall in the British Isles. *Climate Dynamics*. 2016; 47: 1971-1987.
- [18] Sharp ZD. *Principles of Stable Isotope Geochemistry*. Upper Saddle River, NJ 07458: Pearson Prentice Hall; 2007.