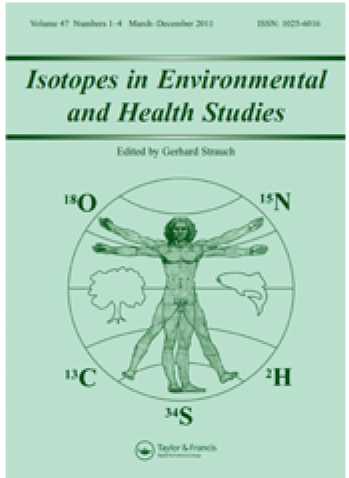

Stable hydrogen and oxygen isotope abundance of major bottled water brands sold in the United Kingdom

Journal:	*Isotopes in Environmental & Health Studies*
Manuscript ID	GIEH-2021-0044.R1
Manuscript Type:	Short Communication
Date Submitted by the Author:	24-Sep-2021
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Keywords:	stable isotopes, bottled water, oxygen-18, hydrogen-2, groundwater < isotope hydrology, United Kingdom, water cycle < isotope hydrology, isotope geochemistry < Isotope geology, water resources, drinking water

Stable hydrogen and oxygen isotope abundance of major bottled water brands sold in the United Kingdom

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Bottled water in the UK has a ~20 % share of the soft drinks market with a sales value of >£1.5 billion. Bottled water is susceptible to fraud and it is important to characterise the chemical signature of aquifers used by the bottled water industry. Measuring $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios in bottled water is one important step in fraud prevention and aquifer characterisation as these ratios in groundwater tend to be stable or change very slowly through time. Here we characterise the isotopic signature of 30 brands of bottled water sold in the UK. The average $\delta^{18}O$ of bottled waters is –7.4 and –48.4 for $\delta^{2}H$. This isotopic composition is closely related to that of the annual rainfall and follows latitudinal and longitudinal gradients which combine to explain 77 % of the $\delta^{18}O$ variance.

Keywords: bottled water; geochemistry; hydrogen-2; isotope geology; isotope hydrology; oxygen-18; United Kingdom

1. Introduction

Bottled water (defined as single-use packaged water) has become increasingly important in the human diet with rises in consumption driven by complex factors, including the perceived higher purity of bottled water, rapid population growth, pollution of natural resources, and climate change [1,2]. During the last decade, bottled water consumption has increased by 175 % in many low and middle income countries, while in developed countries there has been an increase of 26 % over the same period [3]. This raises significant concerns about the environmental effects of the bottled water industry [4]. In addition, a major challenge associated with bottled water consumption is their authentication [5] which is required due to the potential for product misrepresentation and fraud in the form of mislabelling source location. Oxygen and hydrogen stable isotopes have also been used as useful tracers in detecting the authenticity and origin of other beverages and food products, including wines [6], ciders

[7] or roasted coffee [8].

Stable isotopes in bottled water can be used for fraud prevention [9], as the water reflects the environment from which it originates [10]. Most bottled water isotopic variation occurs as a result of differences in source location [11], with the main spatial patterns occurring as a result of latitudinal temperature gradients. There have been many studies of isotopes in drinking water [10,12–15] which have identified spatial correlations between the isotopic ratios of bottled water, tap water and precipitation. Studies have found that the stable isotope composition of bottled water is similar to that of locally available water sources and precipitation [16,17].

The aim of this study is to investigate the isotopic composition of some of the most popular brands of bottled water for sale in the United Kingdom (UK) and, to our knowledge, this is the first study of this type in this country. In the UK, bottled water has a share of 20.6 % of soft drink sales with a total volume of sales in 2019 of 2.811 billion litres and a value of 1.6 billion British pounds [18]. There are three types of bottled waters sold in the UK market: natural mineral water, spring water and bottled drinking water. Governmental regulations are different for the four nations of the UK. The Department for Environment, Food and Rural Affairs regulates bottled waters in England, the Food Standards Scotland is responsible for regulations in Scotland, and the Food Standards Agency is responsible for the regulation of this sector in Wales and Northern Ireland. In broad terms, they all require bottled waters to be free from disease-causing bacteria and parasites and meet limits for chemical, microbial and radioactive substances. Natural mineral waters and spring waters must come from an underground source, be bottled at the source, and be protected from pollution. Natural mineral waters have the additional requirements that the chemical composition must be labelled, be stable over a lengthy period of time, and must not change from source to bottle.

2. Materials and methods

The acquisition of bottled water samples was completed by purchasing those manufactured and commercially available in the UK between June 2018 and April 2021. A total of 30 different bottled water brands were purchased with volumes ranging from 330 ml to 2 L. The brands purchased in this study are identified as the most popular bottled water brands sourced in the UK [19]. Purchases were made from local shops in NE England with three bottles for each brand being acquired separately. The purchase of bottled water samples was not limited to still water, with both still and sparkling samples being collected from the same brand (where possible). The origin of each sample (Figure 1, Table 1) was obtained from the brand labelling where the bottles clearly state the contents were bottled at source. All waters were packaged in polyethylene terephthalate (PET) bottles, except for Waitrose Royal Deeside and M&S Mountain Water Speyside which used glass bottles. Geographical coordinates for each location were obtained from Google Earth, and the water source is assumed to be within 15 km of the location indicated on the bottle. Samples remained unopened and in their original bottles from the time of purchase until analysis and were stored in a cool, dark environment. Secondary data containing the stable isotope composition of precipitation across the UK was obtained from the GNIP database [20]. We constructed the meteoric water line for the UK based on the GNIP stations at Altnabreac (1981-1982, 13 samples), Armagh Observatory (2012–2019, 87 samples), Fleam Dyke (1980–1983, 48 samples), Inchnadamph (2003–2005, 22 samples; [21]), Keyworth (1985–1996, 118 samples) and Wallingford (1979–2015, 409 samples). Secondary bottled water $\delta^{18}O$ and $\delta^{2}H$ values were obtained from Bowen et al. [16] for two brands to increase the stable isotope dataset. In order to compare the consistency of isotopic composition of bottled water through time, we have also analysed bottled water from

Blackford, Scotland, which was also included in [16].

The waters were analysed on a Los Gatos Research off-axis integrated cavity output laser absorption spectrometer (TWIA-45EP) to simultaneously determine $^2H/^1H$ and $^{18}O/^{16}O$ stable isotope ratios in liquid water [22]. Based on the expected isotopic range of our samples, we used standards provided by Los Gatos Research, Inc. (San Jose, CA, USA) which were calibrated to the VSMOW2-SLAP2 scale. The standards have the following δ^2H and $\delta^{18}O$ values, respectively (expressed relative to VSMOW): lgr1e: −165.7 and −21.28 ‰, lgr2e: −123.8 and −16.71 ‰, lgr3e: −79.6 and −11.04 ‰, and lgr5e: −9.9 and −2.99 ‰. In addition, for each set of measurements, the standard lgr4e (−51.00 and −7.69 ‰) was run as internal control as it was the most similar to the expected isotopic range of our samples. Each measurement included two preparatory injections (to help mitigate any memory effects prior to measured injections) followed by six measured injections. The isotopic value of each sample or standard was determined based on the mean of the last four injections, with the first two injections ignored in order to remove any residual memory effects left after the preparatory injections. For each batch of samples, a full set of standards were run at the beginning and end of the batch, and a standard was measured after every fifth sample. Quality control and data processing was performed via the LWIA Post Analysis software (version 4.5.0), developed by Los Gatos Research. The analytical precision for the reported values is better than 0.2 ‰ for $\delta^{18}O$ and 0.8 ‰ for δ^2H.

3. Results and discussion

The average value of all bottled waters is –7.5 ± 0.9 ‰ for $\delta^{18}O$ and –48.4 ± 6.8 ‰ for δ^2H. Three of the waters were available in both still and sparkling form, and it is apparent that the process of adding CO_2 to bottled waters does not have a significant impact on the isotopic signature of sparkling waters (Table 1). The lowest isotopic values were found at Glenlivet Estate in Scotland ($\delta^{18}O$ = –9.6 ± 0.18 ‰ and δ^2H = -61 ± 0.52 ‰) and the highest in SW Wales ($\delta^{18}O$ = –5.5 ± 0.1 ‰ and δ^2H = -32.1 ± 0.2 ‰) (Table 1). The stable isotope ratios of water bottled in Blackford, Scotland were reported in 2005 as –8.2 ± 0.07 ‰ for $\delta^{18}O$ and –56 ± 0.6 ‰ for δ^2H [16], which is similar to our findings here (Table 1). This suggests that the isotopic signature of this water source remains constant over a long time as is required by UK's bottled water regulations.

The water bottling sites span a latitudinal range of 5.7°, from Brecon Beacons, Wales in the south to Glenlivet Estate, Scotland in the north, and extend over 4.7° longitude, from Ballymena in the west to Morpeth in the east (Figure 1). In order to evaluate the role of the geographical position in controlling the isotopic ratios of bottled waters, we performed linear regressions of $\delta^{18}O$ *vs* latitude and longitude. There is a significant correlation between latitude and $\delta^{18}O$ (p-value = 0.0003), with latitude explaining 58 % of $\delta^{18}O$ variance (Figure 2). The correlation of $\delta^{18}O$ with longitude is much weaker than with latitude (r^2 = 0.16, p-value <0.005). However, using a multiple regression, the latitude and longitude combined explain 77 % of $\delta^{18}O$ variance ($\delta^{18}O$ = 13.997 + (–0.418) · Latitude + (–0.354) · Longitude). The spatial pattern of isotopic composition of bottled water therefore follows latitudinal and longitudinal gradients similar to those observed in precipitation and groundwater in the UK [23]. The latitudinal control is primarily due to changes in mean annual temperature and degree of rainout, while the longitudinal effect is due to the Rayleigh fractionation of airmasses affecting the area [24], which are dominated by southwesterly flow, and their interaction with local topography. Since we do not have information about the recharge rate, the age of groundwaters used in bottled waters in this study, and detailed hydrogeological characterisation of each well, a comparison with variables such as temperature, precipitation amount or altitude is not feasible here.

The plot of δ^{18}O *vs* δ^{2}H for bottled waters has a slope of 7.4, which is similar to the slope of 7.2 for the UK meteoric water line, and is close to the slope of 8 for the global meteoric water line (Figure 3). We can therefore infer that the bottled groundwaters are relatively young and reflect the isotopic composition of modern precipitation. The δ^{18}O *vs* δ^{2}H slope in precipitation can vary significantly both on a seasonal basis and also from year to year.

4. Conclusions

We characterised the isotopic composition of 30 brands of water sourced and bottled in the UK. The isotopic composition of bottled water is similar to that of rainfall, which suggests limited kinetic fractionation in the aquifers used for commercial operations. Latitude and longitude have an important influence on the isotopic signature of groundwaters and together they explain 77 % of δ^{18}O variance.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure and table captions

Figure 1. Source locations for bottled waters used in this study.

Figure 2. The influence of latitude and longitude on the δ^{18}O signature of UK bottled waters.

Figure 3. Bottled water line (blue) compared with the UK meteoric water line (black) and the global meteoric water line (dotted). The two red circles are bottled waters values published in [16] from Trofarth Farm and Bethania.

Table 1. Mean δ^{18}O and δ^{2}H values for each bottled water brand. The isotopic values from Trofarth Farm and Bethania are from [16].

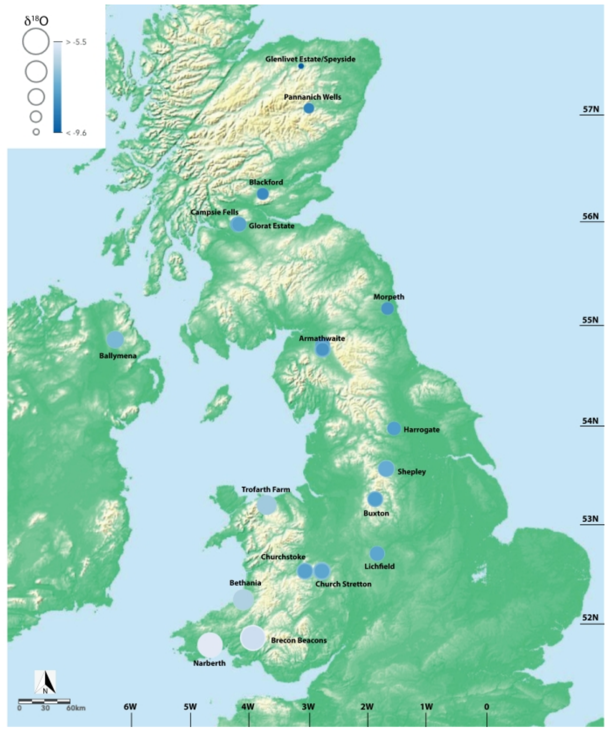

Figure 1. Source locations for bottled waters used in this study.

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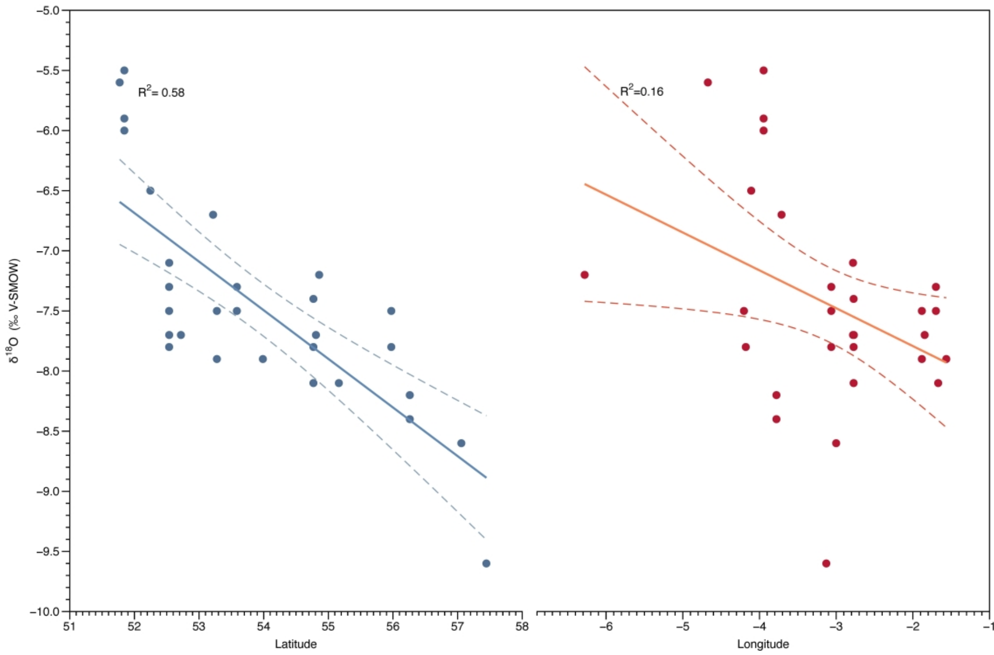

Figure 2. The influence of latitude and longitude on the $\delta^{18}O$ signature of UK bottled waters.

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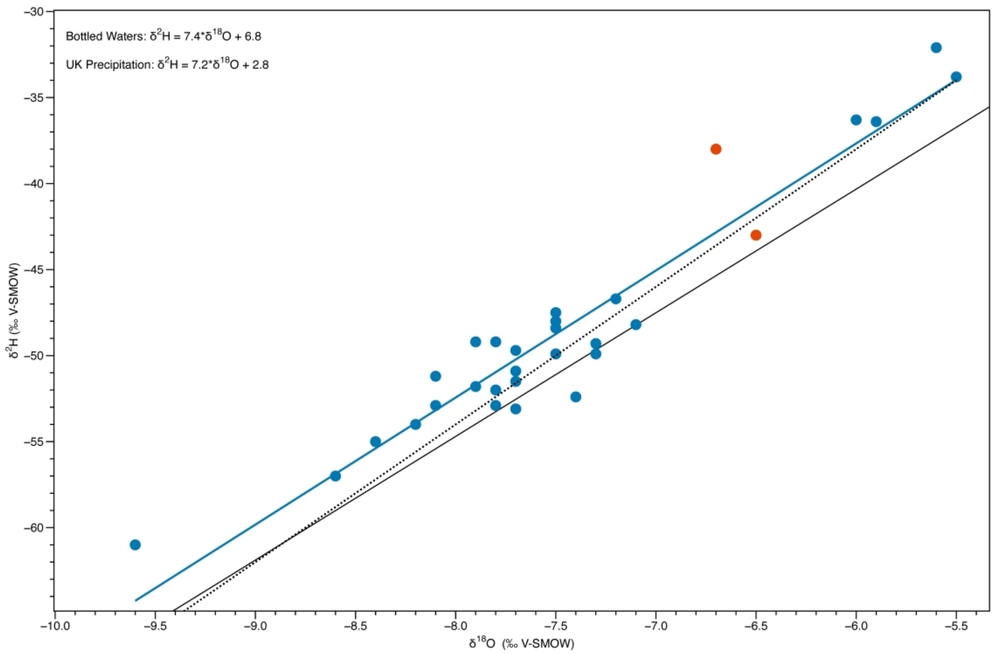

Figure 3. Bottled water line (blue) compared with the UK meteoric water line (black) and the global meteoric water line (dotted). The two red circles are bottled waters values published in [16] from Trofarth Farm and Bethania.

357x234mm (600 x 600 DPI)

Brand	$\delta^{18}O$ (‰ VSMOW)	St. dev.	$\delta^{2}H$ (‰ VSMOW)	St. dev.2	Source	Latitude	Longitude	Type
Buxton	-7.9	0.05	-49.2	0.15	Buxton	53.27611	-1.88269	natural mineral
Nestle Pure Life	-7.5	0.09	-48.4	0.01	Buxton	53.27611	-1.88269	spring
Harrogate	-7.9	0.05	-51.8	0.03	Harrogate	53.98752	-1.56378	spring
H2GO	-7.3	0.11	-49.9	0.08	Churchstoke	52.53732	-3.06382	natural mineral
Belu	-7.8	0.37	-52.0	0.27	Churchstoke	52.53732	-3.06382	natural mineral
Coop Still Water Churchstoke	-7.5	0.43	-49.9	0.07	Churchstoke	52.53732	-3.06382	natural mineral
Coop Still Water Chruch Stretton	-7.7	0.29	-49.7	0.19	Church Stretton	52.538535	-2.780155	natural mineral
Actiph	-7.1	0.35	-48.2	0.16	Church Stretton	52.538535	-2.780155	spring
Morrisons Yorkshire Vale	-7.3	0.07	-49.3	0.63	Shepley	53.58572	-1.69939	spring
Morrisons Yorkshire Vale (Sparkling)	-7.5	0.27	-48.0	0.15	Shepley	53.58572	-1.69939	spring
ASDA Still	-7.4	0.14	-52.4	0.07	Armathwaite	54.76941	-2.77232	natural mineral
Tesco Ashbeck	-7.8	0.07	-52.9	0.11	Armathwaite	54.76941	-2.77232	natural mineral
Gill Beck	-8.1	0.11	-51.2	0.26	Armathwaite	54.76941	-2.77232	spring
Waitrose Essentials	-7.7	0.39	-53.1	0.37	Armathwaite	54.808933	-2.769192	natural mineral
Glaceau Smartwater	-8.1	0.09	-52.9	0.03	Morpeth	55.16291	-1.66982	spring
Sainsburys Still	-7.5	0.06	-47.5	0.22	Campsie Fells	55.97415	-4.20242	drinking
Highland Spring	-8.4	0.04	-55.0	0.09	Blackford	56.26061	-3.77901	spring
Highland Spring (Sparkling)	-8.2	0.30	-54.0	1.02	Blackford	56.26061	-3.77901	spring
ALDI Still	-7.7	0.10	-51.5	0.43	Lichfield	52.71995	-1.84596	spring
ALDI Aqueo (Sparkling)	-7.7	0.49	-50.9	1.14	Lichfield	52.71995	-1.84596	spring
Boots Brecon Carreg	-6.0	0.06	-36.3	0.19	Brecon Beacons	51.84418	-3.94599	natural mineral
Greggs Still	-5.9	0.03	-36.4	0.02	Brecon Beacons	51.84418	-3.94599	natural mineral
Wilkos Mountain Falls	-5.5	0.08	-33.8	0.10	Brecon Beacons	51.84418	-3.94599	spring
JUST Water	-7.2	0.07	-46.7	0.24	Ballymena	54.85856	-6.27936	spring
Princes Gate	-5.6	0.01	-32.1	0.16	Narberth	51.77257	-4.67273	natural mineral
M&S Mountain Water	-9.6	0.18	-61.0	0.52	Glenlivet Estate/Speyside	57.444736	-3.128582	drinking
M&S Mountain Water	-7.8	0.42	-49.2	0.26	Glorat Estate	55.974	-4.1785	drinking
Waitrose Royal Deeside	-8.6	0.28	-57.0	0.27	Pannanich Wells	57.057799	-3.000099	natural mineral
Decante	-6.7		-38.0		Trofarth Farm	53.21754	-3.71218	natural mineral

Ty Nant	-6.5	-43.0	Bethania	52.24719	-4.10756	natural mineral