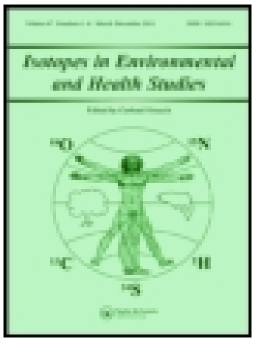

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Isotopic composition of bottled water in Saudi Arabia

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ABSTRACT

The $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios of 18 water brands representing the most popular bottled water brands in the Saudi market were measured using a system based on the latest advancements in tunable off-axis integrated cavity output diode laser spectroscopy (OA-ICOS) in the near-infrared spectral region. Utilizing $\delta^{18}O$ and the $\delta^{2}H$ values of locally produced water samples, a meteoric water line ($\delta^{2}H = 7.84\ \delta^{18}O + 2.11$) was extracted and found to be consistent with the slope of the global meteoric water line (GMWL) and the geographic location of Saudi Arabia.

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1. Introduction

During the past few decades, a significant increase in the consumption of bottled water has been recorded worldwide [1,2]. It is projected that the demand for bottled water will continue to grow due to many factors, namely rapid global population growth, fresh water reservoir pollution, and climate change [3]. Knowledge of the origin of bottled water and its processing is important. The analysis of stable isotopes of hydrogen and oxygen may help in assessing the origin and source of bottled water [4–14]. The ratio $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of water is traditionally measured using the mass spectrometry technique. Nevertheless, a general challenge with this technique is its unsuitability with condensable vapours such as water, resulting in susceptibility to erroneous measurements and inaccuracies [15,16]. This work, however, uses an emerging alternative technique based on light absorption in the infrared region measuring $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios of water with high accuracy. During the last decade, and hand in hand with the recent advancements in diode laser spectroscopy, H and O isotope ratio analysis of water vapour based on tunable diode laser absorption spectroscopy has emerged as a powerful tool to determine these isotope ratios of water vapour by accurately determining absorption line strengths in the active near-infrared region [15–17].

Saudi Arabia is one of the driest regions in the world, with typical hot arid climate and no perennial rivers or lakes. There are four distinct sources of fresh water in Saudi Arabia, namely non-renewable underground water from the deep fossil aquifers, desalinated water, surface water and renewable underground water from shallow alluvial aquifers. Henceforth, fresh water resources in Saudi Arabia are scarce, and with the country's rapid population growth, the demand for bottled water is increasing. Due to the high

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salinity of Saudi water compared to standard fresh water, reverse osmosis is usually necessary to purify water, including bottled water. This physical process may slightly affect the natural isotopic composition of bottled water. During the last three decades, many studies were conducted to assess the quality of bottled water in Saudi Arabia [18–23]. These studies were performed to assess the metal concentrations [18], the microbiological quality [19], the level of dissolved solids [20], and the chemical composition [21–23] in Saudi bottled water.

This study is dedicated to investigate the isotopic composition of most popular bottled water brands in the Saudi market. In fact, and to the best of our knowledge, the only study on stable isotope ratios of H and O of water in Saudi Arabia was undertaken in 2001 by Alyamani [24] where the isotopic composition of rainfall and ground water recharge in the western province of Saudi Arabia were investigated. It was concluded that the stable water isotope distribution of the rainfall over the western province is sensitive to latitude, vapour sources and rainfall amount [24]. This paper is the first study to investigate hydrogen and oxygen isotope ratios in bottled water brands most popular in the Saudi market. The brands chosen are considered to be representative of Saudi bottled water as they cover most of the areas in which bottled water is produced in the country.

2. Materials and methods

In an effort to study the stable H and O isotope composition of water samples, a total of 17 brands of most popular and domestically produced bottled waters and one imported brand from Finland (all non-carbonated) of different sources, i.e. underground and processed water, were studied. All bottled water samples were procured from different local food stores throughout Saudi Arabia, in addition to one tap water sample for comparison. All water samples were collected in April 2015 and were purchased and used within two weeks of production with a validity date of one year from the production date, as per the Saudi Ministry of Health certification and regulations. The holding capacities of the procured bottled water containers varied between 0.25 and 1.0 L. All water samples were placed in 0.45 mL tight air sealed vials made of nylon (Whatman Inc.), each vial having a filter at the bottom of the male part of the vial. We employed a commercially available off-axis integrated cavity output spectroscopy (OA-ICOS) laser absorption spectrometer (Los Gatos Research Triple Isotope Water Analyzer) for simultaneous direct measurement of the $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios in liquid water. The OA-ICOS instrument utilizes the near-infrared IR absorption spectra of the water vapour molecules using tunable diode laser absorption spectroscopy with a laser-coupled off-axis to an optical cavity to provide highly accurate measurements of $\delta^{18}O$ and $\delta^{2}H$ in injected samples [4–6]. Water samples were introduced without sample conversion into the OA-ICOS system using a PAL HTC-xt autoinjector into a heating block at 85 °C, where the water samples were evaporated directly to water vapour for isotope analysis. The injection of the liquid water into the injector block was performed using a Hamilton 1.2 µL syringe. Simultaneous evaluations of $\delta^{18}O$ and $\delta^{2}H$ were completed at a rate of 100 s per measurement for each individual injection. Each sample was injected 8 times with the first 2 preparatory injections being ignored for conditioning and optimization, in addition to eliminating common inter-sample memory of the instrument. The uncertainties in the $\delta^{18}O$ and the $\delta^{2}H$ measurements are 0.2 and 0.8 ‰, respectively. The samples were measured versus the laboratory standard ($\delta^2H = -427.5$ ‰, $\delta^{18}O = -55.5$ ‰) and calibrated to the international standard Vienna Standard Mean Ocean Water (V-SMOW).

3. Results and discussion

Figure 1(a,b) presents the geographical distribution of the bottled water origin with average $\delta^{18}O$ and δ^2H values of each location and Table 1 summarizes the average $\delta^{18}O$ and δ^2H values of the 18 brands used in this study and the average value of the tap water sample for comparison. Figure 1(a) shows that $\delta^{18}O$ varies from +0.9 ‰ for bottled water originating from Mecca spring waters to −6.0 ‰ for bottled water brands from sources originating from the underground of the Buraydah region. The range of these values is consistent with the range obtained from the maps of global and regional water isotope distribution for Saudi Arabia [25]. It can be observed that the $\delta^{18}O$ values of the water samples are generally more negative as moving in the northeastern direction due to the depletion of heavy isotopes. This variation might be attributed to climatic and topographic variations across Saudi Arabia. The topography of the west is dominated by a mountain ridge, and the central part is mainly a rocky plateau while the eastern part is a coastal plain. It is also observed that the variation in $\delta^{18}O$ values does not perfectly correlate with specific geographical locations. For example, in Mecca in the west, $\delta^{18}O$ ranges from +0.9 to −2.1 ‰ and in Buraydah, in the central part, from −2.2 to −6.0 ‰, while in Dammam in the eastern part $\delta^{18}O$ varies between −2.9 and −5.5 ‰. The variation within the same geographical location might be due to different sources of the bottled water. For example, the Hada and Safa brands originate from spring water in Mecca, while Zamzam brand water is desalinated, consequently the $\delta^{18}O$ values of Hada (+0.0 ‰) and Safa (+0.9 ‰) samples are relatively close but are different from the Zamzam brand with −2.1 ‰. Moreover, the Arwa, Aquafina and Nestle brands are from the same location and source; henceforth, their $\delta^{18}O$ values are close and range from −2.3 ‰ for Aquafina brand to −3.4 ‰ for Arwa brand. In the same context, the bottled water brands from the Dammam area, namely Farm and Panda, are from the same underground source and are observed to have close $\delta^{18}O$ values, while desalinated bottled water brands of Yanabee and Pure Aqua from the Dammam area have close $\delta^{18}O$ values of −3.3 and −2.9 ‰, respectively.

Thus, it is difficult to use oxygen isotope ratios to recognize the origin of bottled water produced in Saudi Arabia. But the $\delta^{18}O$ value might be useful to confirm the origin of imported water produced from locations at latitudes far north from Saudi Arabia. The $\delta^{18}O$ value of imported bottled water from Finland (NORD brand) was measured to be −11.2 ‰ (Table 1), which is significantly different from any value measured for local bottled water. The value measured for the NORD brand is consistent with the fact that depletion of heavy isotopes, ^2H and ^{18}O, is obtained for water originating from northern Europe.

Just as the $\delta^{18}O$ patterns, the δ^2H varies significantly (Figure 1(b)) from +6.1 ‰ for bottled water from the spring source in Mecca to −44.4 ‰ for bottled water brands from underground sources from the Buraydah region. Also, and similar to the trend observed with $\delta^{18}O$, the δ^2H values of bottled water vary within a specific location due to source variations. For example, the desalinated bottled water Yanabee brand from the Dammam area has a δ^2H value of −26.3 ‰ compared to the underground source of the bottled water Panda brand from the same area with −42.0 ‰.

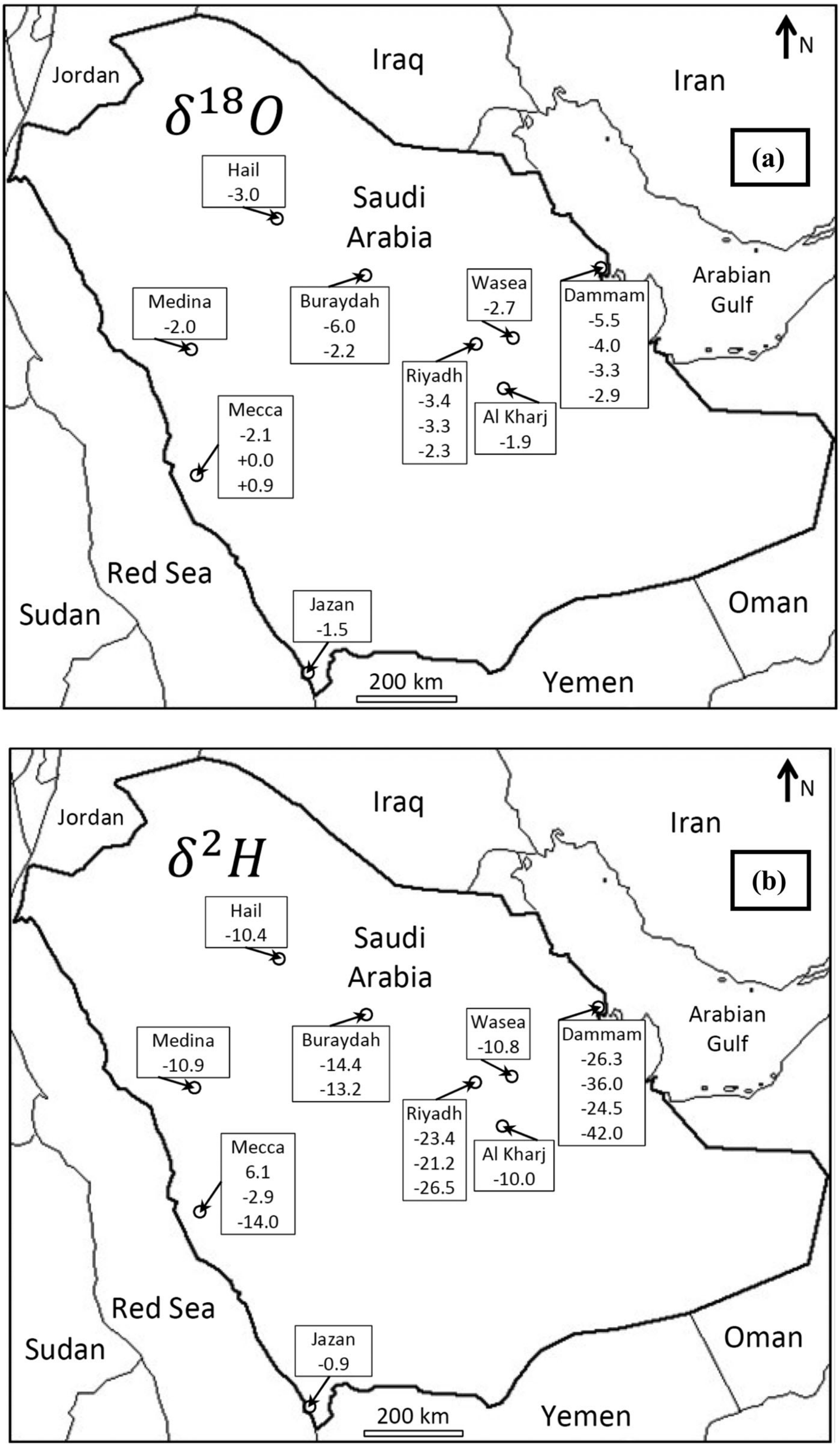

Figure 1. Average $\delta^{18}O$ (a) and $\delta^{2}H$ (b) values [in‰] of bottled water brands as a function of geographical distribution of their origins in Saudi Arabia.

Table 1. Summary of the average δ^2H and $\delta^{18}O$ values of the 18 brands and one tap water used in this study along with the source and location of each brand.

#	Brand name	Location	Source	$\delta^{18}O$ (‰)	δ^2H (‰)
1	Hada	Mecca	Spring	0.0	−2.9
2	Safa	Mecca	Spring	0.9	6.1
3	Fayha	Al Kharj	Desalinated	−1.9	−10.0
4	Hana	Buraydah	Underground	−6.0	−44.4
5	Nova	Wasea	Desalinated	−2.7	−10.8
6	Yanabee	Dammam	Desalinated	−3.3	−26.3
7	Arwa	Riyadh	Desalinated	−3.4	−23.4
8	Abar	Hail	Desalinated	−3.0	−10.4
9	Mozan	Jazan	Underground	−1.5	−0.9
10	Aquafina	Riyadh	Desalinated	−2.3	−21.2
11	Farm	Dammam	Underground	−4.0	−36.0
12	Pure Aqua	Dammam	Desalinated	−2.9	−24.5
13	Nestle	Riyadh	Desalinated	−3.3	−26.5
14	Alqassim	Buraydah	Desalinated	−2.2	−13.2
15	Zamzam	Mecca	Desalinated	−2.1	−14.0
16	Hala	Medina	Desalinated	−2.0	−10.9
17	Panda	Dammam	Underground	−5.5	−42.0
18	Tap	Dammam	Desalinated	−2.8	−27.0
19	Nord	Finland	Spring	−11.2	−80.5

It is generally observed that the desalination process yields a slightly higher variation in δ^2H of about 16.5 ‰ from −10.0 to −26.5 ‰ than in $\delta^{18}O$ with only about 1.5 ‰ from −1.9 to −3.4 ‰. However, the variation both in stable isotope of H and O in desalinated

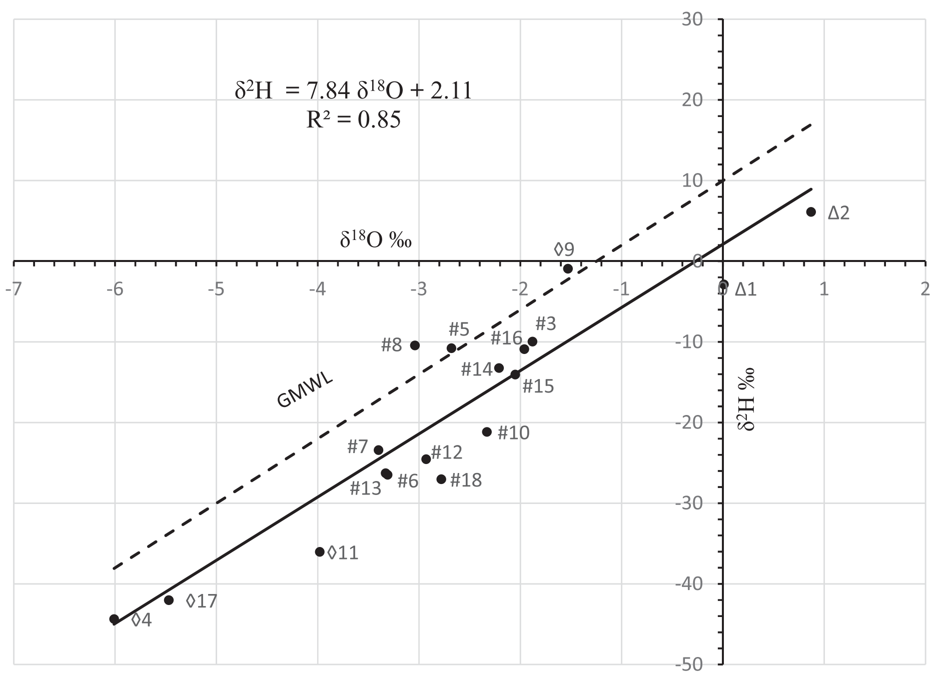

Figure 2. Average δ^2H and $\delta^{18}O$ values from water brands from Saudi Arabia listed in Table 1 with the correlation line (solid line) of slope 7.84. According to sample sources, spring samples are denoted by Δ, and underground samples are denoted by ◊, while the desalinated samples are shown as #. The global meteoric water line (GMWL) is inserted.

water is consistent to the correlation line (see Figure 2) and thus in the range of the slope ~8.

Overall, the range of these values is consistent with the range obtained from the maps of global and regional water isotope distribution for Saudi Arabia [25]. This variation in δ^2H values might be also attributed to climatic and topographic variations across Saudi Arabia. Similar to the $\delta^{18}O$ patterns, the δ^2H values follow the same trend of depletion of deuterium (^2H) towards the northeastern direction. However, the δ^2H variation does not correlate well with the specific geographical locations.

As expected, $\delta^{18}O$ and δ^2H of all bottled water samples correlate linearly as shown in Figure 2. The slope of the isotope relationship is 7.84, which is very close to the slope 8 of the GMWL. It should be noted that a meteoric water line with a slope close to 8 is basically related to meteoric precipitation of all kinds and, hence, for surface waters not exposed to extreme evaporation relative to rainfall. The observed scattering of the data points along the fitted line may indicate isotope effects due to possible physical processes before bottling such as evaporation especially in very warm and dry climate like Saudi Arabia.

4. Conclusions

In summary, the stable hydrogen and oxygen isotope composition of 18 water brands is measured for the purpose of investigating source and nature of local bottled water samples in the Saudi market. The $^{18}O/^{16}O$ and $^2H/^1H$ ratios of bottled water are accomplished using a system based on the latest advancement in tunable OS-ICOS in the near-infrared spectral region of 1.39 µm. A linear relationship of $\delta^2H = 7.84\ \delta^{18}O + 2.11$ is obtained between δ^2H and $\delta^{18}O$ values of bottled water with a slope very close to the slope 8 of the GMWL. A general trend of depletion of ^2H and ^{18}O is noted when moving in the northeastern direction. It is observed that oxygen and hydrogen isotope ratios can vary within a specific geographical location in Saudi Arabia according to the water source and physical processes during desalination. However, the scattering of the δ^2H and $\delta^{18}O$ values is small enough to be useful to confirm the origin of imported water produced from locations at latitudes far north from Saudi Arabia.

Disclosure statement

No potential conflict of interest was reported by the authors.

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