ARE YOU GETTING WHAT YOU PAID FOR? A CASE STUDY IN FORENSIC GEOCHEMISTRY

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Introduction

Isotopes are atoms of the same element that differ in atomic mass due to different number of neutrons in the nucleus. Some isotopes are stable isotopes and others are unstable, or radioactive, isotopes. Stable isotopes maintain constant concentrations in the environment over time. Unstable isotopes continue to decay into daughter elements. Stable isotopes of oxygen, hydrogen, carbon, sulfur, and nitrogen are the most commonly used in environmental and ecological research.

Forensic geochemistry is a relatively new discipline that uses chemical and isotopic markers to solve problems of forensic interest. These include fingerprinting oil spills, food adulteration and forgery in arts, drug abuse in sports etc. Carbon isotope ratios were used in the famous Tour de France case where the gold medalist was charged with steroid use. Carbon isotope ratios can be used to check adulteration of natural honey with corn syrup, reportedly a common process. Hydrogen isotopes enable one to test if a bottle of orange juice is pure juice from Florida or it is made from extract mixed with water from Michigan.

In this preliminary study we explore the possibility of using stable oxygen and hydrogen isotopes to verify the claims made by select vendors of bottled water in Egypt. In other words, we investigate, based on isotope ratios if the claimed source such as "water from deep well", "water from mountain springs" etc. can be sustained. This may therefore qualify to be a study in "water adulteration". This is an important issue not only in tourist hot beds such as Egypt but in many parts of the world where use of bottled water is becoming increasingly popular.

Our approach makes use of the observation that processes of evaporation and rain out causes the isotopic ratio to be specific in a given place, dictated by mean surface temperature, latitude, altitude and distance from the oceans which are the main source of water vapor in the atmosphere (Dansgaard, 1964). This is illustrated in Figure (1). As illustrated in the figure, the rain gets stripped more and more of the heavier isotopes (^{18}O compared to ^{16}O and ^{2}H (Deuterium) compared to ^{1}H (Hydrogen). Similarly, at the same latitude, rain at higher altitudes will have more of the lighter isotope compared to the heavier one. If one were to collect a water sample, say, from the top of Alps and also from a well at the base of the Alps, they will be isotopically distinct.

Additionally, the oxygen and hydrogen define a linear line and serves as the foci of all natural waters (Figure 5). Values from this locus will shift if the water body were to undergo secondary effects such as evaporation.

In the specific case of Egypt, one of the extensively used ground water reservoirs is the Nubian Sandstone Aquifer System (NSAS). One finds them at great depths (300 m to 2000 m). This was formed thousands or even millions of years ago and has a distinct range of isotopic values, shown by the blue circle in Figure (5). On the other hand, surficial waters such as that from the Nile River, lakes or shallow wells are far removed as shown by the red circle.

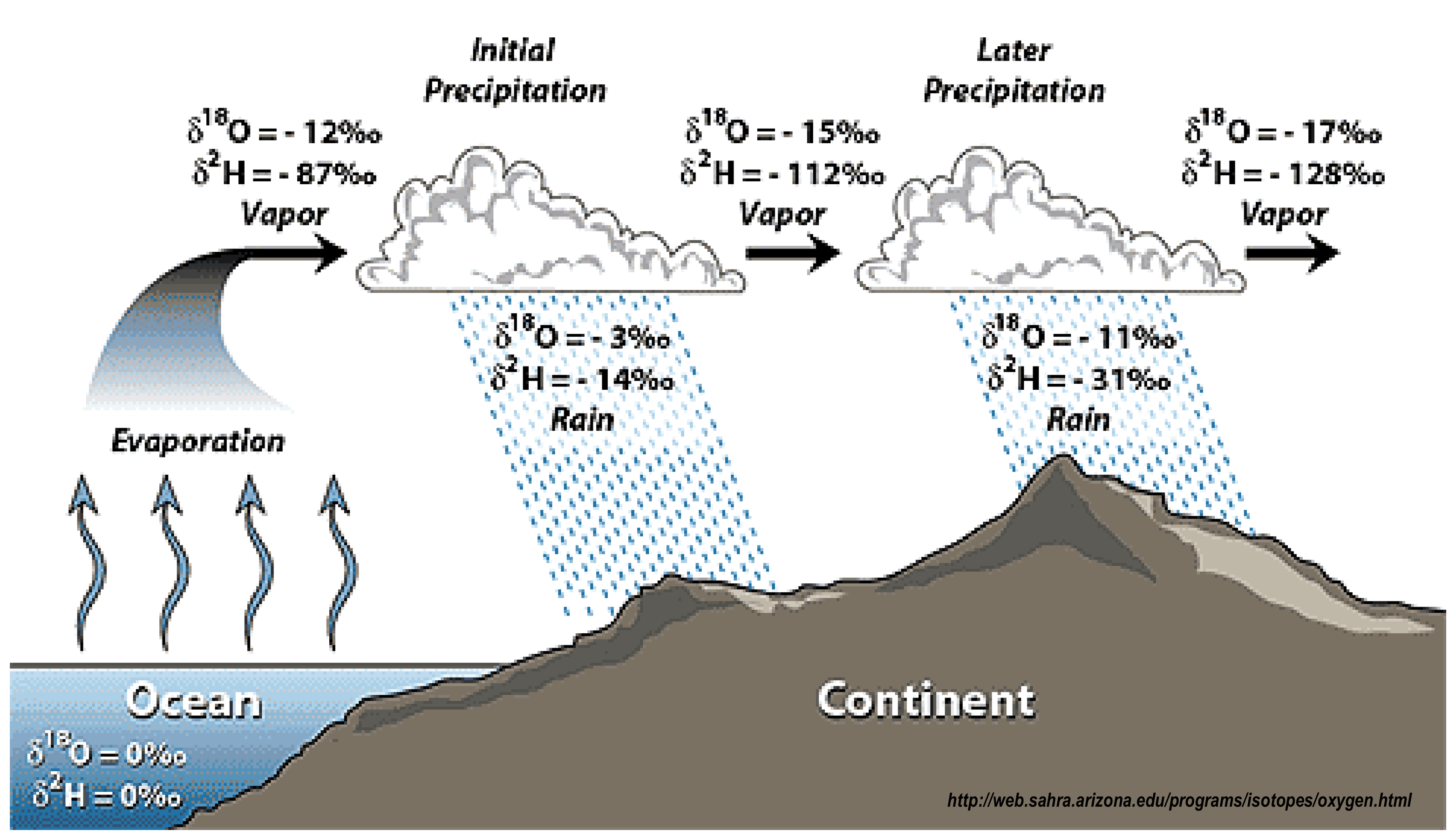

Figure 1. Rainout effect on δ^2H and $\delta^{18}O$ values

Location map of the sample sources

Figure 2. The source locations of the collected samples

Methods

Seventeen samples of bottled water were obtained during December 2013 and January 2014 from the Egyptian market (figure 3). Water samples were stored in small vials until the time of analysis. Available record of our sample set indicate that our sample set includes bottled water with sources from three countries other than Egypt. Brand names have been withheld because of the sensitive nature of the study.

Oxygen and hydrogen isotope ratios were determined using the new generation Laser Absorption Spectroscopy in the Stable Isotope Laboratory of the Department of Geosciences at Western Michigan University (figure 4).

The isotopic ratio are reported in per mil as δ^2H or $\delta^{18}O$, where

$$\delta^{18}O‰ = \frac{(^{18}O/16O)_{sample} - (^{18}O/16O)_{standard}}{(^{18}O/16O)_{standard}} \times 1000 \quad \text{and}$$

$$\delta^{2}H‰ = \frac{(^{2}H/^{1}H)_{sample} - (^{2}H/^{1}H)_{standard}}{(^{2}H/^{1}H)_{standard}} \times 1000$$

Figure 3. Bottled water market in Egypt

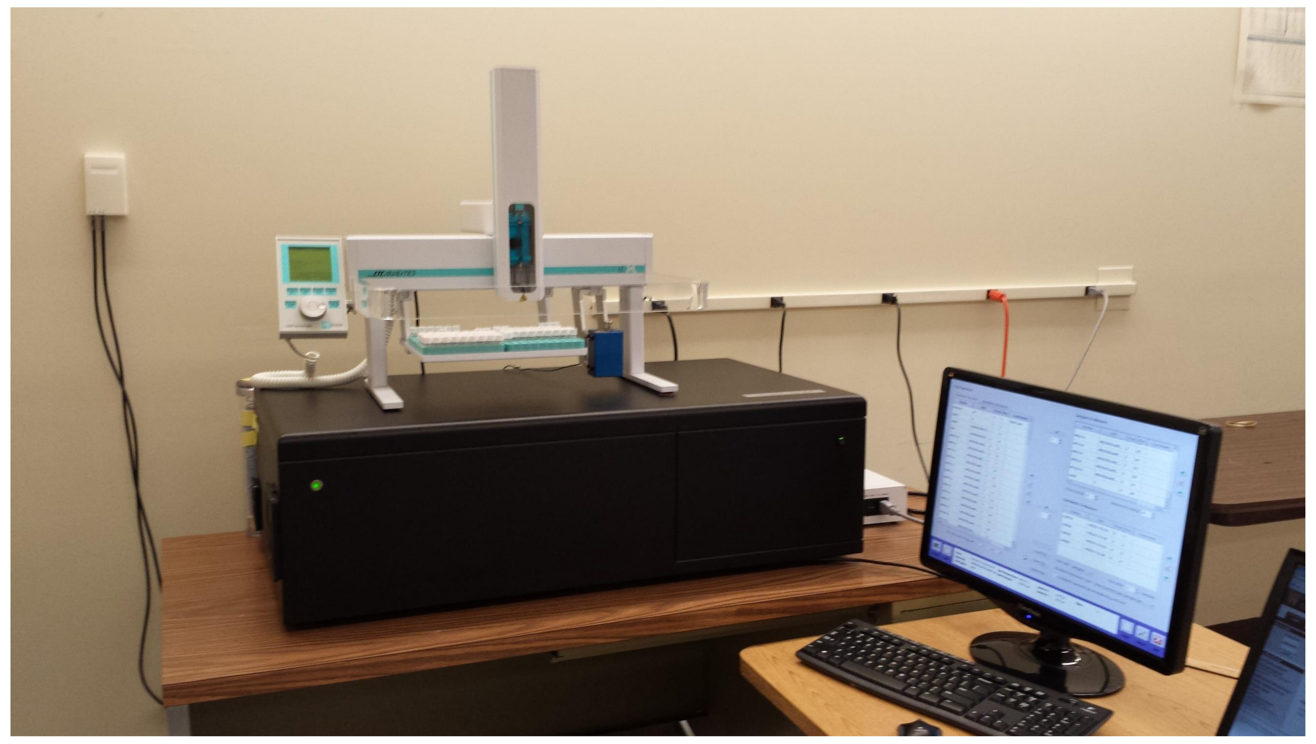

Figure 4. Triple Isotopic Water Analyzer

Discussion

Measured stable isotope ratios of our bottled water samples are shown in table 1 and figure 5. As summarized in the table and figure isotope ratios confirm the claimed origin of many of the samples (colored blue in table) . At the same time there are samples indicated in the table as "failed test" that seem suspect (colored red in table). More detailed study using a large number of samples is planned for the future.

Results

Table 1. The isotope results of the collected samples.

Sample	Claimed Source	δD	$\delta^{18}O$	Comments	Verdict
1	Amerta Indah Otsuka, Jakarta. Indonesia	----	----	Artificially Sweetened with sugars	Not analyzed due to added additives
2	Borsec city, Transylvania. *Romania*	-73.72	-11.51		Passed test, (Boglarka et al, 2013)
3	San Pellegrino Terme (Bergamo), *Italy*	-56.36	-8.87		Passed test, (Raco et al, 2013)
4	Saint-Galmier, *France*	-60.02	-8.28		Passed test
5	Spring, Scarperia (Florence), *Italy*	-47.43	-7.71		Passed test, (Raco et al, 2013)
6	1000 m deep well at SIWA Oasis, NSAS, *Egypt*	-81.69	-10.69	Typically Nubian Sandstone Aquifer System	Passed test, (Mohammed et al, 2013)
7	French Alps. Cachat Spring, *France*	-73.69	-10.31		Passed test, (Bowen et al, 2005)
8	Underground well - Bulbaas Desert, *Egypt*	-0.43	-0.38	Shallow aquifer well	Failed test, (Mohammed et al, 2013)
9	Deep well Located in Elnatroun Valley, *Egypt*	-1.39	-1.25	Shallow aquifer well	Failed test, (Mohammed et al, 2013)
10	Deep well, Kafr Al Arbein, Banha, Kalioubia, *Egypt*	23.85	2.57	Typically River Nile Water (tap water)	Failed test, (Mohammed et al, 2013)
11	Deep well, Meet Hebish El Bahria, Tanta, *Egypt*	12.16	1.18	Shallow aquifer well	Failed test, (Mohammed et al, 2013)
12	Deep well source, km 76 Cairo-Alexandria road, *Egypt*	3.63	-0.85	Shallow aquifer well	Failed test, (Mohammed et al, 2013)
13	Deep well in Kaliub City, *Egypt*	21.94	2.44	Typically River Nile Water (tap water)	Failed test, (Mohammed et al, 2013)
14	Deep well of 1000 meters from SIW Oasis, NSAS, *Egypt*	-80.18	-10.91	Typical Nubian Sandstone Aquifer System	Passed test, (Mohammed et al, 2013)
15	Deep well source, Kafr Al Arbein, *Egypt*	23.08	2.55	Typically River Nile Water (tap water)	Failed test
16	Deep well source, Sadat City, Cairo, *Egypt*	1.01	-1.01	Shallow aquifer well	Failed test, (Mohammed et al, 2013)
17	Source deep well in Wadi Elnatron, *Egypt*	-3.33	-1.39	Shallow aquifer well	Failed test, (Mohammed et al, 2013)
18	Deep well source in the west desert. Assuit, *Egypt*	5.28	-0.24	Shallow aquifer well	Failed test, (Mohammed et al, 2013)

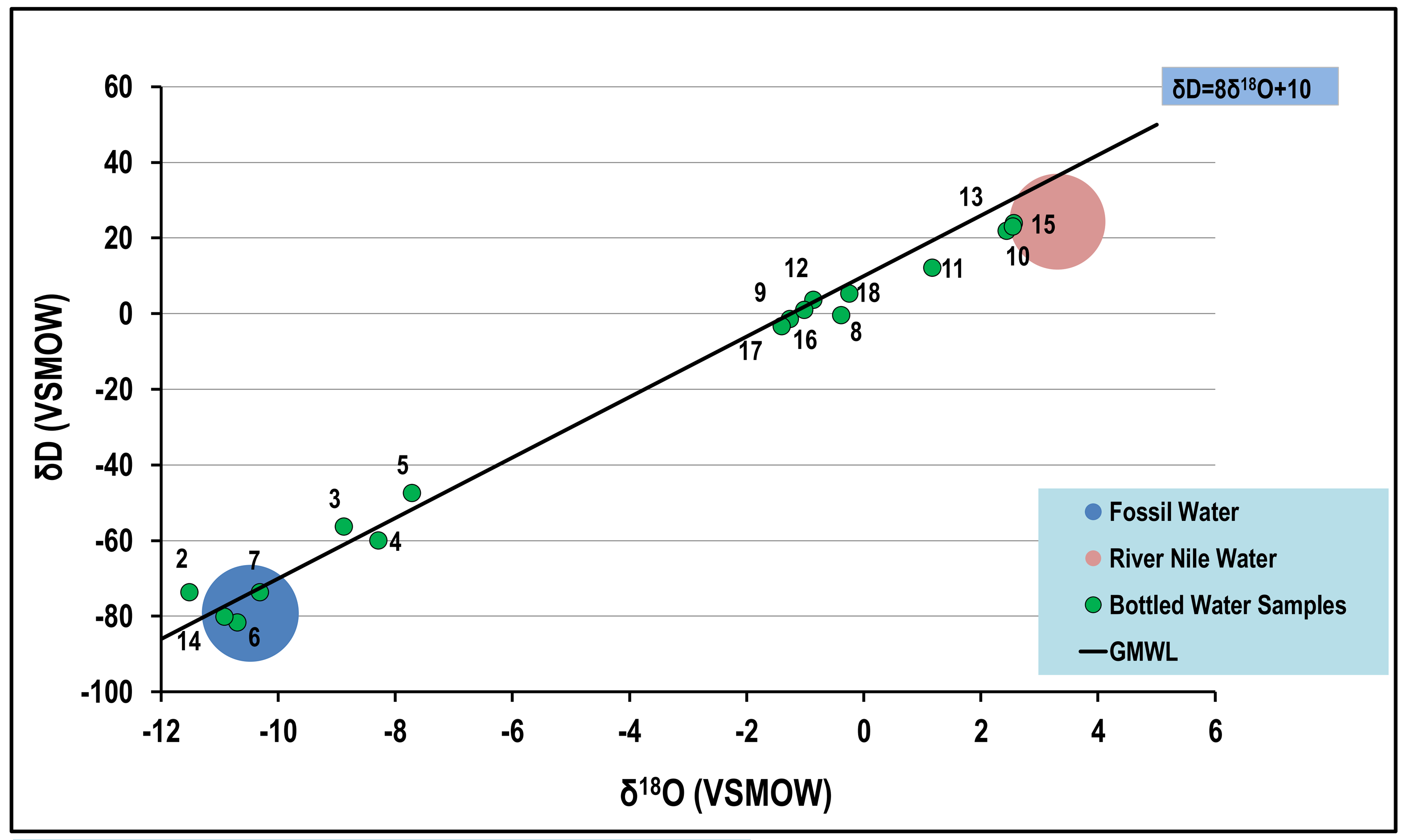

Figure 5. Oxygen and Hydrogen isotope values for studied samples.

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