



Stable isotope composition of Hellenic bottled waters

Dotsika E.^{a,*}, Poutoukis D.^b, Raco B.^c, Psomiadis D.^a

^a Stable Isotope Unit, Institute of Materials Science, National Centre for Scientific Research “Demokritos”, 153 10 Agia Paraskevi, Attica, Greece

^b General Secretariat for Research and Technology, 14-18 Mesogion Ave., 115 10 Athens, Greece

^c Institute of Geosciences and Earth Resources, Via G. Moruzzi 1, 56124 Pisa, Italy

ARTICLE INFO

Article history:

Received 23 March 2010

Accepted 5 July 2010

Available online 14 July 2010

Keywords:

Bottled waters

Stable isotope

Recharge altitude

Greece

ABSTRACT

Bottled waters are an increasingly significant product in the human diet. In this work, we present a dataset of stable isotope ratios for bottled waters sampled in Greece. A total of 25 domestic brands of bottled still waters, collected on the Greek market in 2009, were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. The measured stable isotope ratios range from -9.9‰ to -6.9‰ for $\delta^{18}\text{O}$ and from -67.50‰ to -46.5‰ for $\delta^2\text{H}$. Comparison of bottled water isotope ratios with natural spring water isotope ratios demonstrates that on average the isotopic composition of bottled water tends to be similar to the composition of naturally available local water sources, showing that bottled water isotope ratios preserve information about the water sources from which they were derived and suggesting that in many cases bottled water should not be considered as an isotopically distinct component of the human diet. This investigation also helped to determine the natural origin of bottled water, and to indicate differences between the natural and production processes. The production process may influence the isotopic composition of waters. No such modification was observed for sampled waters in this study. The isotopic methods applied can be used for the authentication of bottled waters and for use in the regulatory monitoring of water products.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In the past (Albu et al., 1997; Ferrier, 2001), bottled water was a food product that was mainly used for therapeutic purposes. Today, bottled water represents an increasingly important component of human dietary intake worldwide and is related with urban cultural strategies. In general, the chemical and isotopic contents of the water depend on the environment, natural and anthropogenic, from which it originates. The main natural influences in the chemical and isotopic composition of the water are the water–rock interaction, the transit time, the evaporation processes and the recharge elevation of the wells or springs captured for bottling (Craig, 1961; Fontes and Zuppi, 1976; Gat, 1996; Clark and Fritz, 1997; Mook, 2000). The main anthropogenic influences of the water chemistry are the pollution and the mixing of different types of water. The quality of the bottled water depends on all the above factors. In theory (Guillou and Reniero, 1999; Rossmann, 2001), bottled water is used as a safe food product and many consumers believe that the bottled water represents a reliable, quality-assured source of water because it originates from remote springs and unpolluted areas. However, commercial practice and analysis show that bottled waters are often the subject of fraud and product misrepresentation (Spangenberg and Vennemann, 2008) that may be physically or economically

damaging to consumers. Also, the uncontrolled commercial exploitation of water could damage unique or sensitive water resources especially in low-precipitation environments. Thus, monitoring and authentication are critical in certifying the quality of bottled waters and to ensure that bottled water production does not damage the water resources. Authentication of bottled water represents an important and increasing challenge to regulators that monitor and assure the quality, authenticity and region of origin of consumer goods. The isotope hydrologies represent one possible tool for the authentication of bottled water (Bowen et al., 2005; Brencic and Vreca, 2006, 2007).

The isotopic compositions of hydrogen and oxygen reflect natural processes in the hydrological cycle. The isotopic ratio $[(R^{2}\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$; reported as $\delta^2\text{H}$ or $\delta^{18}\text{O}$, where $\delta = ((R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}) * 1000]$ of fresh water varies greatly and systematically across the earth as a result of the spatially and temporally variable climatic patterns which govern the delivery of precipitated water to geographic regions. Strong trends in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ occur with increases in latitude, altitude, temperature and continentality (Craig, 1961; Fontes and Zuppi, 1976; Gat, 1996; Clark and Fritz, 1997; Mook, 2000) and these patterns are relatively well known and documented as maps of precipitation stable isotope ratios (Dotsika et al., 2010). Locally the isotopic composition of precipitation is primarily controlled by regional scale processes: it is greatly influenced by the provenance of wet air masses, the trajectories of the water vapour transport over the continents, their possible partial condensation in continental areas (Merlivat and Jouzel, 1979) and in

* Corresponding author. Tel.: +30 2106503305; fax: +30 2106519430.

E-mail addresses: edotsika@ims.demokritos.gr (D. E.), dpoutoukis@gsrt.gr (P. D.), b.raco@igg.cnr.it (R. B.), dapsom@ims.demokritos.gr (P. D.).

general the average rain-out history of the air masses (e.g., Rozanski et al., 1982; Gat et al., 2003; Longinelli and Selmo, 2003; International Atomic Energy Agency, IAEA, 2004a, b). A rather complicated pattern has been observed in the Mediterranean basin, due to intense air–sea interaction processes and the contribution of sea vapour to moisture-depleted continental air masses. The meteoric line for the eastern Mediterranean is estimated to be on average $\delta^2\text{H} = 8\delta^{18}\text{O} + 20$ (International Atomic Energy Agency, IAEA, 2001; Bowen and Revenaugh, 2003; Aouad et al., 2004) while for the western Mediterranean it is $\delta^2\text{H} = 8\delta^{18}\text{O} + 13.7$ (Celle-jeanton et al., 2004). This reflects the difference of origin, of vapour supply and of removal history of the air masses over the two areas, which is also observed in recent isotopic data of atmospheric vapour collected across the Mediterranean Sea (Gat et al., 2003). The meteoric line estimated for Greece is $\delta^2\text{H} = 8.7 \pm 0.44 \delta^{18}\text{O} + 19.5 \pm 3.1$ (Dotsika et al., 2010).

The amount of moisture deficit is the excess of potential evapotranspiration over rainfall when soil moisture storage is assumed to be nil. The calculations are made on a monthly basis and totaled for the year. Differences in d-excess arise as a consequence of varying temperature, relative humidity and wind speed at the sea surface, where global atmospheric moisture mainly originates, as well as from admixture of recycled continental vapour. A typical excess of deuterium, greater than that observed globally, characterises air masses on the leeside of continental areas, due to intense evaporation of seawater in conditions of moisture deficit (Gat and Carmi, 1970; Gat et al., 2003). This effect has been widely observed in coastal precipitation in the eastern Mediterranean basin (Gat and Carmi, 1970; Kattan, 1997; Longinelli and Selmo, 2003), whereas precipitation in the western Mediterranean is more influenced by Atlantic derived moisture (Cruz-San Julian et al., 1991). In fact, values higher than 15‰ for the deuterium excess are found in the eastern Mediterranean (Gat and Dansgaard, 1972; Bowen and Revenaugh, 2003), with a gradient of 6‰ from the Aegean to the coast of Israel (International Atomic Energy Agency, IAEA, 2001). A deuterium excess of 22‰ for the eastern Mediterranean area was proposed by Nir (1967) and Gat and Carmi (1970). The isotopic composition of precipitation and, consequently, spring water in Greece is determined both by its location within the Mediterranean basin and by a complex morphology dominated by the presence of the Pindos mountain range crossing Greece from NW to SE, and the existence of Ionian and Aegean seas around Greece.

In this study, the hydrogen and oxygen isotopic compositions of 25 bottled waters available on the Greek market in 2009 were determined. Moreover, 9 spring waters from specific locations were analysed isotopically, supplemental to existing data (Dotsika et al., 2010). A primary goal here is to present the first isotopic characterization of bottled waters sourced in Greece. The results were used to provide a general overview of the Greek bottled waters, representative geographically for the whole of Greece. Also we compare the results of bottled waters with spring water isotope ratios for reported sources, where these are available. We also examined whether it is possible to define the recharge altitude of the bottled water, and to determine the natural origin of waters from the hydrogen and oxygen isotopic compositions of bottled waters. The patterns revealed by this analysis offer a foundation for the application of stable $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopes in the authentication of Greek bottled waters.

2. Experimental procedures

A total of 25 bottled waters commercially available from supermarkets around Greece (Fig. 1a, Table 1) and 11 spring waters (sources of bottled water, Table 2) were sampled. Also, as a few samples come from springs located in Pindos ridge, 10 spring waters from different altitudes were sampled in order to calculate the mean recharge altitude of the springs. All bottled waters were contained in

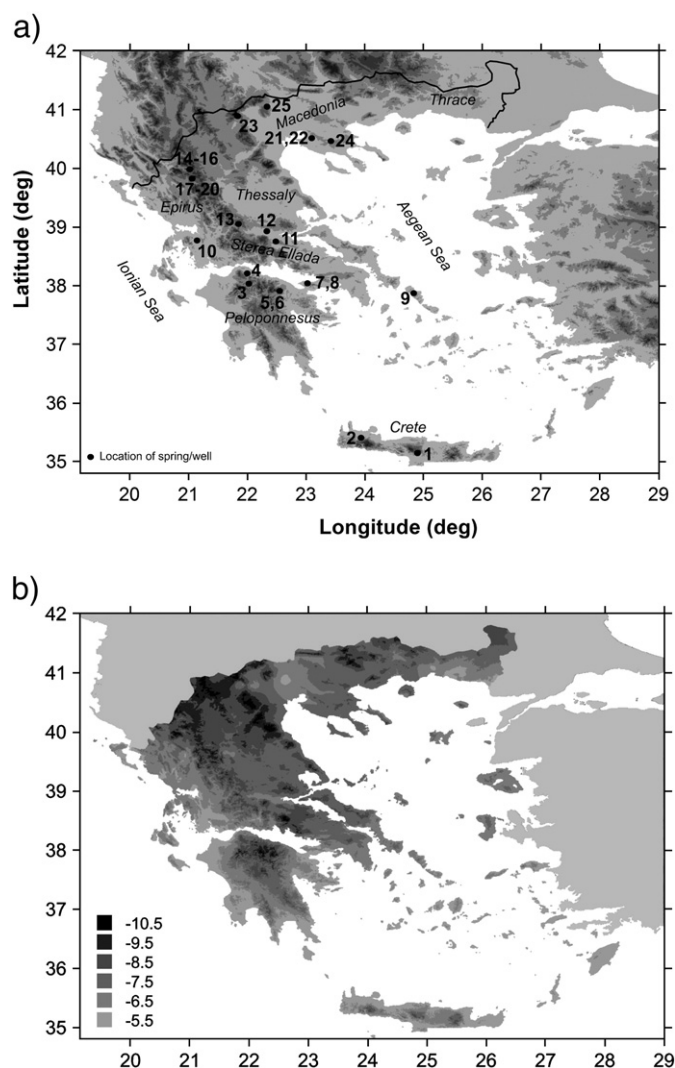


Fig. 1. a) Geographical distribution of springs/wells locations across Greece. b) Spatial distribution of $\delta^{18}\text{O}$ (‰) of springs across Greece (Dotsika et al., 2010).

clean plastic bottles, 0.5 L (except for samples 9, 13, 15, 17, 21 which were in bottles of 1.5 L). The isotopic composition of the spring waters from the respective regions of the bottled waters has been determined by Dotsika et al. (2010) (Fig. 1b). The spring isotopic map of Greece has been created based on a huge amount of spring data and is considered as highly reliable as it eliminates the error from local boreholes in the production premises.

The isotopic composition of hydrogen (^2H) and oxygen (^{18}O) was measured in Stable Isotope Unit, Institute of Materials Science, NCSR Demokritos (Athens, Greece) on a continuous flow Finnigan DELTA V plus (Thermo Electron Corporation, Bremen, Germany) stable isotope mass spectrometer according to the procedures described by Epstein and Mayeda (1953) and Coleman et al. (1982). The results are expressed in standard delta notation (δ) as per mil (‰) deviation from the standard VSMOW as: $\delta = ((R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}) * 1000$ where R_{sample} and $R_{\text{standard}} = ^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ ratios of sample and standard respectively. Measurement precision, based on the repeated analysis of internal standard waters, was 1.5 and 0.05‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively (1σ).

All measurements were carried out against laboratory standards that were periodically calibrated against international standards recommended by the IAEA.

Table 1General data and isotopic ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) composition of 25 Greek bottled waters.

No sample	Brand name	Spring (s)/well (w) name	Location	Region	WGS84 coordinates		Expiration date	$\delta^{18}\text{O}$ (‰, VSMOW)	$\delta^2\text{H}$ (‰, VSMOW)
					North	East			
1	Zaros	Psiloritis (s)	Heraklion	Crete	35°07'	24°54'	24/11/2010	−7.88	−50.33
2	Nera Kritis	Foot of White Mountains (s)	Varipetro Therisso Chania	Peloponnesus	35°24'	23°59'	26/11/2010	−8.70	−51.84
3	Avra	Avra (s)	Avra, Aegion		38°12'	22°03'	31/12/2010	−8.22	−49.87
4	Rioba	Anastassopoulou (s)	Rododafni, Aegion		38°17'	22°02'	01/2011	−7.98	−51.33
5	Krinea	Kaliani (s)	Kaliani, Korinthias		37°52'	22°27'	1/5/2011	−9.08	−61.50
6	Yas	Kaliani (s)	Kaliani, Korinthias		37°52'	22°27'	23/10/2010	−9.02	−60.10
7	Loutraki Provis	Loutraki (s)	Loutraki		38°01'	23°00'	10/12/2010	−7.66	−50.49
8	Loutraki Ivi	Gerania Mountains (s)	Loutraki	South Aegean	38°00'	23°05'	10/12/2010	−6.90	−46.46
9	Sariza	Sariza (s)	Andros Island		37°50'	24°53'	18/8/10	−8.06	−50.05
10	Korpi	Korpi (w)	Monastiraki, Vonitsa		38°51'	20°57'	11/2010	−7.49	−55.62
11	Ioli	Ioli (s)	Moschochori, Fthiotida		38°50'	22°27'	10/2010	−9.25	−61.70
12	Evdoro	Evrora (s)	Mexiatia, Ypati, Fthiotida	Epirus	38°52'	22°14'	29/9/2010	−9.77	−67.47
13	Velouchi	Kefalovriso Aghias Triadas (s)	Velouchi, Evritania		38°59'	21°49'	21/12/2010	−9.88	−67.16
14	Vikos	Vikos (s)	Ioannina		39°57'	20°42'	13/1/2011	−7.86	−52.19
15	Zagorochoria	Zagorochoria (s)	Ioannina		39°57'	20°42'	07/2011	−8.07	−54.08
16	Zagori	Zagori (s)	Kranoula, Ioannina		39°55'	20°45'	12/2010	−8.19	−51.92
17	Eviva	Sepeta (s)	Ioannina		39°45'	20°50'	01/2011	−8.19	−52.86
18	Marata	Sepeta (s)	Zagorochoria, Ioannina	Macedonia	39°45'	20°50'	22/01/2011	−7.90	−52.75
19	Physiko Nero AB	Sepeta (s)	Ioannina		39°45'	20°50'	29/12/2010	−8.16	−52.31
20	Mitsikeli	Sepeta (s)	Ioannina		39°45'	20°50'	13/01/2011	−8.07	−53.48
21	Ydor Sourotis	Anthemia (s)	Souroti, Thessaloniki		40°28'	23°02'	07/2010	−7.82	−51.19
22	Daly Drink Water	Anthemia (s)	Souroti, Thessaloniki		40°28'	23°02'	11/2010	−7.78	−52.27
23	Drossia	Drosia (s)	Drosia, Edessa		40°47'	21°52'	10/2010	−9.12	−61.20
24	Athos	S. Platani Poligirou (s)	Akonorachi, Poligiros, Chalkidiki		40°23'	23°27'	01/2011	−8.16	−54.60
25	Pigi Paikou	Axioupolis Paikou (s)	Axioupolis, Kilkis		41°06'	22°07'	15/11/201	−9.10	−62.53

3. Results and discussion

The isotopic compositions of these still waters are assumed as typical of groundwater in shallow aquifers regarding that no artificial addition of dissolved CO_2 , gaseous and organic flavours took place during production. This fact is justified by the type of the product (still waters) which assures that no additives like the abovementioned were used. Measured stable isotope ratios of our bottled still water samples (Fig. 2) range from -9.9‰ to -6.9‰ for $\delta^{18}\text{O}$ and from -67.50‰ to -46.5‰ for $\delta^2\text{H}$.

Isotopic data of all waters are shown in Fig. 2, also reporting the global meteoric water line (GMWL) and the East Mediterranean meteoric water line (EMMWL) (Craig, 1961) for reference and the local meteoric line estimated for Greece. In Greece, the correlation function for rainwater is: $\delta^2\text{H} = 8.7\delta^{18}\text{O} + 19.5$ (Dotsika et al., 2010). Generally, an isotope relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ with a slope of about 8 is normal for meteoric precipitation of all types (Craig,

1961), as well as for surface waters not subjected to excessive evaporation relative to input.

As shown by Dotsika et al. (2010), the correspondence between the isotopic composition of precipitation in Greece and that of the spring water located in whole of Greece is not very well correlated, and for this reason, the spring water line of Greece has been drawn in Fig. 3a. In general, spring waters are depleted in isotopic values in relation to rain water. This is probably due to the fact that rainwater sampling stations are often located at lower altitudes with respect to ground waters recharge areas (Dotsika et al., 2010). The relative equation for all spring waters (Local Spring Water Line:LSWL) in Greece is: $\delta^2\text{H} = 7.5 \pm 0.17 \delta^{18}\text{O} + 10 \pm 1.4$ (Dotsika et al., 2010). The

Table 2Isotopic ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) composition of spring waters (sources of bottled water).

No sample	Spring	Location	Region	$\delta^{18}\text{O}$ (‰, VSMOW)	$\delta^2\text{H}$ (‰, VSMOW)
1	Loutraki	Loutraki	Peloponnesus	−7.6	−44.7
2	Corinth	Corinthia		−9.14	−56.1
3	Corinth	Corinthia		−8.98	−57.3
4	Kefalovriso	Velouchi, Evritania	Stereia Ellada	−10.7	−70
5	Kefalovriso	Velouchi, Evritania		−9.8	−65
6	Kefalovriso	Velouchi, Evritania		−10.5	−69
7	Mexiatia	Ypati, Fthiotida		−9.5	−68.01
8	Vikos	Ioannina	Epirus	−7.9	−52.8
9	Sepeta	Ioannina		−7.8	−52.4
10	Sepeta	Zagorochoria, Ioannina		−7.2	−48.9
11	Drosia	Drosia, Edessa	Macedonia	−9.3	−64

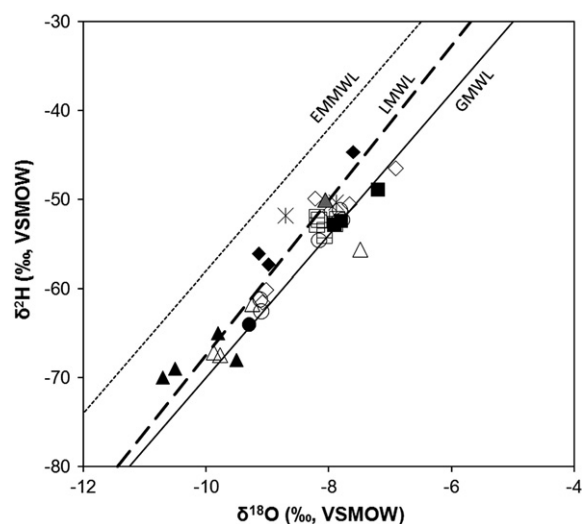


Fig. 2. $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ composition of bottled waters. Continuous line: Global Meteoric Water Line (GMWL); dashed-line: Local Meteoric Water Line (LMWL); short-dashed-line: Eastern Mediterranean Meteoric Water Line (EMMWL); circles: Central Macedonia; squares: Epirus; triangles: Sterea Ellada; grey triangles: South Aegean; diamonds: Peloponnesus; dashed-x: Crete. Filled symbols indicate spring waters from respective areas.

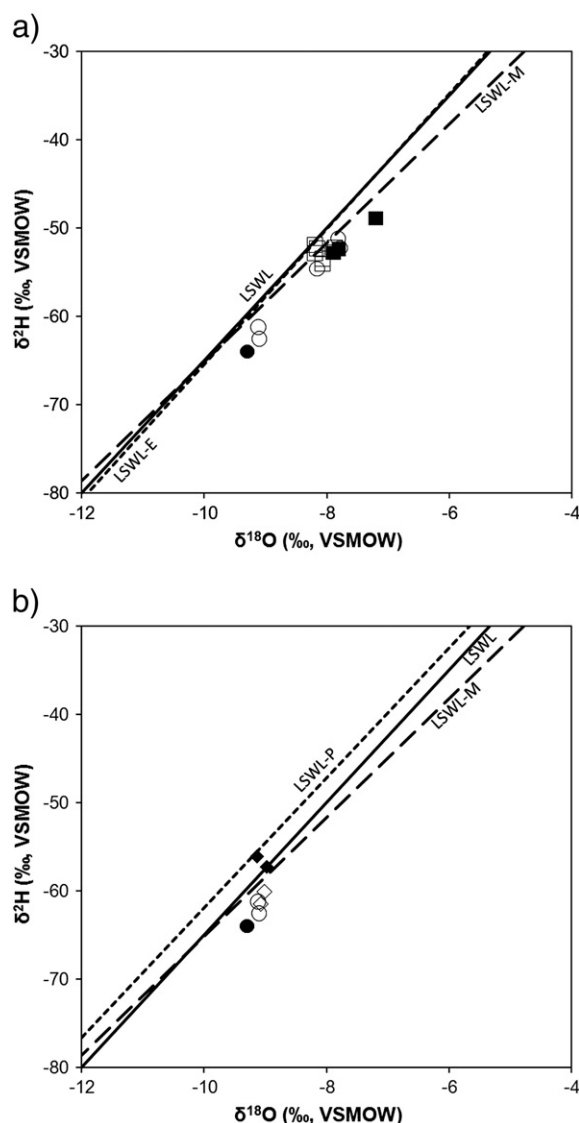


Fig. 3. a) $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ composition of bottled waters from Epirus and Macedonia. Continuous line: Local Spring Water Line (LSWL); dashed-line: Local Spring Water Line in Macedonia (LSWL-M); short-dashed-line: Local Spring Water Line in Epirus (LSWL-E). Symbols same as Fig. 2. b) $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ composition of bottled waters from the areas of Corinth and Central Macedonia. Continuous line: Local Spring Water Line (LSWL); dashed-line: Local Spring Water Line in Macedonia (LSWL-M); short-dashed-line: Local Spring Water Line in Peloponnese (LSWL-P); diamonds: Corinth; circles: Central Macedonia (Kilkis and Edessa). Filled symbols indicate spring waters from respective areas.

observed decrease in LSWL slope and intercept in relation to the rain water indicates that the ground water is possibly affected by evaporation processes. Possible cause for this enrichment is the partial evaporation of water before the infiltration, the infiltration of recycled irrigation water and evaporation of soil water. Local spring water lines have been plotted for all regions of Greece, based on a huge isotopic database of spring waters. The relative equations for spring waters in different parts of Greece present slopes between 7 and 7.6 for Epirus, Peloponnese and Thrace regions (Dotsika et al., 2010). A slope lower than 7 was reported for Crete, for Aegean Islands, for Macedonia, for Sterea Ellada and for Thessaly spring waters (Dotsika et al., 2010). Similar equations with slightly greater slopes of 7 and 7.5 were proposed for the northern part of Eastern Macedonia and for the Eastern Peloponnese, respectively (Leontiadis et al., 1984). A slope lower than 7 was reported for Central Macedonia (Christodoulou et al., 1993), for the southern part of

Eastern Macedonia and Thrace (Leontiadis et al., 1996), as well as for the northern part of Epirus (Leontiadis and Nikolaou, 1999).

The hydrogen and oxygen isotope ratios of our bottled water samples lie within a range of values typical of meteoric waters. Most samples cluster between the local meteoric water line (Fig. 2) and the global meteoric water line (GMWL; Craig, 1961). Only a few waters from Crete and Peloponnese plot above the local meteoric water line (exceeding the analytical error), presenting a deuterium excess value higher than that of the estimated mean annual precipitation. In general these observations imply that the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the bottled waters might reflect a relatively unaltered source water signature.

The most negative values for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were measured for samples 13 and 12 (Table 1 and Fig. 2). The recharge area of Velouchi and Evdoro is positioned in the Velouchi and Iti Mountains in Sterea Ellada, respectively. Velouchi and Iti are the higher massifs in Sterea Ellada region, with peak altitude around 2315 m and 2150 m respectively and characterized by numerous springs.

According to the local topography, the isotopic composition for these waters reflects the high altitude recharge area. The isotopic values of Mexiatai (Velouchi) and Evdoro spring waters are identical to these of the respective bottled waters. Thus, as the isotopic values are not changed during the production process, Velouchi and Evdoro data indicate that their parent water is recharged in the same altitude area. The small isotopic differences are within the precision of the applied analytical methods. The relationship between the bottled water isotope ratios and the isotope ratios of precipitation at the source locations does not reflect natural, hydrological modification of the precipitation-derived isotopic value prior to extraction of the water for bottling or discrepancies between the reported and true sources of bottled water.

Negative values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were also measured for samples 5, 6, 23 and 25 which come from the mountainous vicinity of Corinth (NE Peloponnese) and Macedonia (Edessa and Kilkis) (Fig. 3b). The negative values of Krinea–Yas water (south Greece) are similar to those of Drossia and Paiko springs (north Greece). The first couple of water sources (Krinea–Yas) are known to recharge in the Kaliani region (Krinea spring). The recharge area of the Krinea spring is in the aquifer of the Ziria Mountain, near Corinth. Ziria Mountain is one of the highest massifs in Greece, with five peaks exceeding 2000 masl. Drossia and Paiko springs are bottled in continental Greece from Drossia spring near the city of Edessa and in Axioupoli, Kilkis respectively. Drossia water originates from 2525 m altitude in Voras Mountain while Axioupoli–Paiko spring is charged from 1650 m. Therefore, it seems that irrespective of the fact that the springs are located in south or north Greece, the altitude and continental effect influences the isotopic contents of the water. Measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (Table 1) of these springs are in accordance with published values (Dotsika et al., 2010).

The bottled waters Loutraki (Loutraki Ivi and Loutraki Provis) from Loutraki city, close to the sea, present the most positive isotopic values (Table 1 and Fig. 2). These values can be attributed to the low altitude of their recharge area.

The largest group in the set of data is represented by isotopic data in a median area between the most negative and positive isotopic values (Table 1 and Fig. 3a). They are sample waters from Epirus and various parts of Greece (Thessaloniki, Crete, Andros, Chalkidiki, Aegion and Korpi–Akarnanika Mountain). These last, except Korpi water, have similar low altitude, <1000 m, recharge areas. The isotopic composition of these waters is very similar to that of precipitation data (Dotsika et al., 2010) as shown in Fig. 2, indicating that their $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were probably not changed during the production process. Korpi water is the only exception that plots much below the LMWL. This discrepancy is probably due to the fact that it is the only borehole sample and the enrichment may be the impact of evaporation processes during extraction or production

procedures. Its isotopic composition was measured in duplicate analysis from different bottles.

Most of the bottled waters come from Pindos ridge, Mikro Papigo of 980 m altitude. All bottled waters from Pindos plot around the local meteoric water line indicating that the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the bottled waters in general reflect a moderately unchanged source water signature.

The correlation also between the Epirus bottled water isotope ratios and the isotope ratios of precipitation at the source locations (LMWL in Fig. 3a) (Dotsika et al., 2010) supports this observation. However, as it is noticed that all Pindos bottled waters and Central Macedonia bottled waters are below the local meteoric water line in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram, the local Epirus and Macedonia spring water lines ($\delta^2\text{H} = 7.67 \pm 0.29$ $\delta^{18}\text{O} + 11.3 \pm 2.3$; $\delta^2\text{H} = 6.73 \pm 0.43$ $\delta^{18}\text{O} + 2.2 \pm 4$) (LSWL; Dotsika et al., 2010) are reported for reference (Fig. 3a). All bottled waters from Pindos and Macedonia lie underneath the typical range of values for the region's spring waters, suggesting that the isotopic contents of Pindos and Macedonia bottled waters reflect a slightly changed source water signature. This change, as it is reported for waters after the extraction in comparison to source waters, is considered as a sign of isotopic modification after extraction of the water for bottling.

4. Recharge altitude

The oxygen isotopic composition of spring waters in Greece is inversely correlated with sampling altitude (Dotsika et al., 2010). The isotopic gradient is estimated between -0.06 and $-0.28\text{‰}/100\text{ m}$ for Macedonia, between -0.07 and $-0.16\text{‰}/100\text{ m}$ for Epirus and $-0.22\text{‰}/100\text{ m}$ for Crete. In addition, for Peloponnesus the gradient is between -0.34 and $-0.27\text{‰}/100\text{ m}$ and for Sterea Ellada the proposed values are from -0.15‰ to $-0.20\text{‰}/100\text{ m}$ (Dotsika et al., 2010). These data are similar with most literature data (Leontiadis, 1981; Leontiadis, 1987; Leontiadis et al., 1992) indicating the presence of small hydrological basins of springs as shown by the low spring water supply. In these literature papers, the authors had calculated the mean recharge altitude of the springs, considering the surface and the annual precipitation between two consecutive contour lines of the recharge area. Particularly, for the areas of Macedonia where the bottled waters (Kozani, Thessaloniki) are situated, the values from -0.27 to $-0.28\text{‰}/100\text{ m}$ (Leontiadis et al., 1992) are suggested, for Sterea Ellada the proposed values are from $-0.22\text{‰}/100\text{ m}$ (Leontiadis, 1987) and for Sparta (S. Peloponnesus) $-0.51\text{‰}/100\text{ m}$ (Leontiadis, 1981). The difference of the gradient value from literature in comparison to the gradient value proposed in Dotsika et al. (2010) is due to the fact that the values were estimated for the entire region (e.g. Macedonia) and not only for a specific area (e.g. Sparta instead of the entire Peloponnesus).

Since most of the bottled waters come from Pindos ridge, Mikro Papigo of 980 m altitude, spring waters were sampled from this area. Oxygen isotope values of spring waters in the area of Pindos, where the capturing of the water for bottling takes place, are inversely correlated with sample altitude, as shown in Fig. 4. The isotopic gradient is estimated by the regression line ($\delta^{18}\text{O} = a + b \cdot \text{elevation}$) which was fitted on the available data from the Epirus area. The regression line for Epirus springs, Mikro Papigo area, shows an isotopic gradient $\delta^{18}\text{O}/100\text{ m}$ equal to $-0.18 \pm 0.01\text{‰}$ (95% confidence interval). This value is close to that from literature (-0.15) (Dotsika et al., 2010) which was estimated for the entire Epirus and not only for the area of springs where the bottling takes place.

According to the above, the isotopic difference which is observed in Epirus waters (-7.9 to -8.2) indicates a recharge altitude difference of approx. 150 m. The isotopic difference for the waters from Loutraki, Corinth and Aegion areas is 2‰ , suggesting a recharge altitude difference of approx. 900 m. The isotopic difference for the

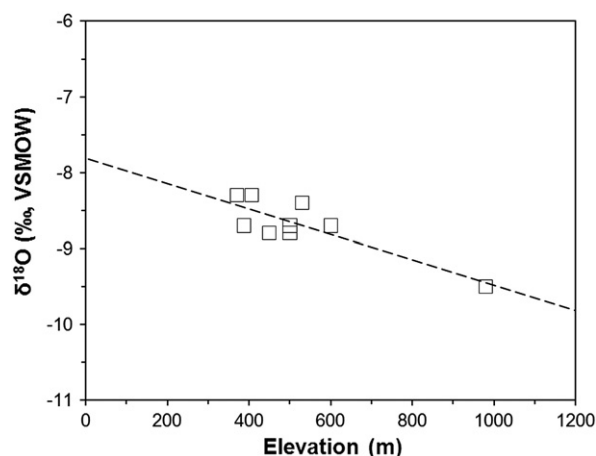


Fig. 4. $\delta^{18}\text{O}$ vs. elevation of spring waters from the area of Pindos ridge.

water from Thessaloniki, Edessa, Kilikis and Chalkidiki areas is 1.3‰ , suggesting a recharge altitude difference between 470 and 500 m.

5. Conclusions

The stable hydrogen and oxygen isotopic compositions of bottled waters available in the Greek market were analysed. The ranges of values are large but within the reported natural variations for Greek waters. The isotopic compositions of bottled waters have no direct health implications. They can, however, prove very important as a quality control tool for market regulators. It can also help in determination of the origin of bottled water and determination of the natural conditions of the parent water.

The bottled waters from Greece specify the range and patterns of stable hydrogen and oxygen isotopic variability in commercially marketed water. In general, it was possible to confirm the bottled waters similarity with their natural sources as deduced from information on the labels as well as with further information by some of their water sources. The isotope ratio data for these waters assure to be applicable as a tool for authenticating and understanding the source of bottled water products.

Isotopic composition of water is used as tracer of primary water sources and reflects the geographic origin of water recharge, including recharge altitude. The isotopic fingerprint of the primary source water could be slightly modified from natural causes (prior to bottling) such as evaporation. However, this does not seem to apply in Greek bottle waters, as their isotopic compositions do not reflect natural, hydrological modification of the precipitation-derived isotopic value prior to extraction of the water for bottling or discrepancies between the reported and true sources of bottled water. A fully detailed sampling of the parent water used for the production of particular bottled water is also required.

Acknowledgements

The authors would like to thank the Chief Editor for his crucial contribution as well as the two unknown reviewers for their fruitful remarks and recommendations. They would also like to express their gratitude to A. Demetriades, Associate Editor of this Special Issue, for his guidance throughout the preparation and submission of this paper.

References

- Albu, M., Banks, D., Nash, H., 1997. History of mineral and thermal waters. In: Albu, M., Banks, D., Nash, H. (Eds.), *Mineral and Thermal Groundwater Resources*. Chapman and Hall, pp. 3–20.

- Aouad, A., Travi, Y., Blavoux, B., Job, J.-O., Najem, W., 2004. Isotope study of snow and rain on Mount Lebanon: preliminary results. *Hydrolog. Sci. J.* 49 (3), 429–441.
- Bowen, G.J., Revenaugh, J., 2003. Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.* 39 (10) art. no 1299.
- Bowen, G.J., Winter, D.A., Spero, H.J., Zierenberg, R.A., Reeder, M.D., Cerling, T.E., Ehrlinger, J.R., 2005. Stable hydrogen and oxygen isotope ratios of bottled waters of the world. *Rapid Commun. Mass Spectrom.* 19, 3442–3450.
- Brencic, M., Vreca, P., 2006. Identification of sources and production processes of bottled waters by stable hydrogen and oxygen isotope ratios. *Rapid Commun. Mass Spectrom.* 20, 3205–3212.
- Brencic, M., Vreca, P., 2007. Isotopic composition of dissolved inorganic carbon in bottled waters on the Slovene market. *Food Chem.* 101, 1533–1542.
- Celle-Jeanton, H., Gonfiantini, R., Travi, Y., Sol, B., 2004. Oxygen-18 variations of rainwater during precipitation: application of the Rayleigh model to selected rainfalls in Southern France. *J. Hydrol.* 289 (1–4), 165–177.
- Christodoulou, T., Leontiadis, I.L., Morfis, A., Payne, B.R., Tzimouras, S., 1993. Isotope hydrology study of the Axios river plain in northern Greece. *J. Hydrology* 146, 391–404.
- Clark, I., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, 328pp.
- Coleman, M.L., Shepard, T.J., Durham, J.J., Rouse, J.E., Moore, G.R., 1982. Reduction of water with zinc for hydrogen analysis. *Anal. Chem.* 54, 993–995.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Cruz-San Julian, J., Araguas, L., Rozanski, K., Benavente, J., Cardenal, J., Hidalgo, M.C., Garcia-Lopez, S., Martinez-Garrido, J.C., Moral, F., Olias, M., 1991. Sources of precipitation over South-Eastern Spain and groundwater recharge. An isotopic study. *Tellus* 44B, 226–236.
- Dotsika, E., Lykoudis, S., Poutoukis, D., 2010. Spatial distribution of the isotopic composition of precipitation and spring water in Greece. *Glob. Planet. Change* 71, 141–149.
- Epstein, S., Mayeda, T., 1953. Variation of ^{18}O content of water from natural sources. *Geochim. Cosmochim. Acta* 4, 213–224.
- Ferrier, C., 2001. Bottled water: understanding a social phenomenon. *Ambio* 30, 118–119.
- Fontes, J., Zuppi, G., 1976. Isotopes and water chemistry in sulphide-bearing springs of central Italy. *Proc. Adv. Gr. Meeting on Interpretation in Environmental Isotope and Hydrochemical data in Groundwater Hydrology*. IAEA, Vienna, pp. 143–158.
- Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth Planet. Sci.* 24, 225–262.
- Gat, J.R., Carmi, I., 1970. Evolution of the isotopic composition of the atmospheric water in the Mediterranean Sea area. *J. Geophys. Res.* 75, 3039–3048.
- Gat, J.R., Dansgaard, W., 1972. Stable isotope survey of the freshwater occurrences in Israel and the Jordan rift valley. *J. Hydrol.* 16, 177–211.
- Gat, J.R., Klein, B., Kushnir, Y., Roether, W., Wernli, H., Yam, R., Shemesh, A., 2003. Isotope composition of air moisture over the Mediterranean Sea: an index of the air–sea interaction. *Tellus* 55B, 959–965.
- Guillou, C., Reniero, F., 1999. Isotopic methods for control of food products and beverages. IAEA TECDOC 247, 39–53.
- International Atomic Energy Agency (IAEA), 2001. GNIP Maps and Animations, International Atomic Energy Agency, Vienna.
- International Atomic Energy Agency (IAEA), 2004a. Isotope hydrology information system: the ISOHIS database v.12/2005. Int. Atomic Energy Agency, Vienna. Available at <http://isohis.iaea.org>.
- International Atomic Energy Agency (IAEA), 2004b. Global Network of Isotopes in Precipitation: The GNIP Database v.12/2005, Int. Atomic Energy Agency, Vienna. Available at <http://isohis.iaea.org>.
- Kattan, Z., 1997. Chemical and environmental isotope study of precipitation in Syria. *J. Arid Environ.* 35 (4), 601–615.
- Leontiadis, I.L., 1981. Isotope hydrology study of Molai area in Laconia. Nucl. Res. Cent. “Demokritos”, Internal Report, Demo 81/4, Athens.
- Leontiadis, I.L., 1987. Environmental isotopic techniques as a mean for the investigation of eventual leakages in the dam of Mornos (Greece). Nucl. Res. Cent. “Demokritos”, Internal Report, Demo 87/5, Athens.
- Leontiadis, I.L., Nikolau, E., 1999. Environmental isotopes in determining groundwater flow systems, northern part of Epirus, Greece. *Hydrogeology J.* 7, 219–226.
- Leontiadis, I.L., Payne, B.R., Letsios, A., Papagianni, N., Kakarelis, D., Chadjiagorakis, D., 1984. Isotope hydrology study of Kato Nevrokopi of Drama. *Proc. Symp. on Isotope hydrology 1983*. IAEA, Vienna, pp. 193–206.
- Leontiadis, I.L., Stamos, A., Manakos, A., 1992. Isotope hydrology study of the wider area of Kozani, Greece. *Proc. 6th Int. Symposium on water tracing*, Karlsruhe, pp. 233–240.
- Leontiadis, I.L., Vergis, S., Christodoulou, T., 1996. Isotope hydrology study of areas in Eastern Macedonia and Thrace, Northern Greece. *J. Hydrology* 182, 1–17.
- Longinelli, A., Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. *J. Hydrol.* 270, 75–88.
- Merlivat, L., Jouzel, J., 1979. Global climatic interpretation of the deuterium-oxygen 16 relationship for precipitation. *J. Geophys. Res.* 84 (C8), 5029–5033.
- Mook, W.G., 2000. Environmental isotopes in the hydrological cycle. Principles and applications. Introduction: Theory, Methods, Review. IAEA, Vol. 1. 280 pp.
- Nir, A., 1967. Development of isotope methods applied to groundwater hydrology. *Proc. Symp. On Isotope Techniques in the Hydrologic Cycle*, A.G.U. Monograph Series No. 11, p. 109.
- Rossmann, A., 2001. Determination of stable isotope ratios in food analysis. *Food Rev. Int.* 17, 347–381.
- Rozanski, K., Sonntag, G., Munnich, K.O., 1982. Factors controlling stable isotope composition of European precipitation. *Tellus* 34, 142–150.
- Spangenberg, J.E., Vennemann, T.W., 2008. The stable hydrogen and oxygen isotope variation of water stored in polyethylene terephthalate (PET) bottles. *Rapid Commun. Mass Spectrom.* 22, 672–676.